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**RESUMEN.** Charles Frédéric Kuhlmann (1803-1881), químico francés, realizó investigación en una extensa variedad de áreas y convirtió muchos de sus resultados en una realidad industrial que lo llevó a fundar un poderoso imperio químico que se mantiene hasta hoy en día. Realizó trabajos sobre catálisis con esponja de platino, cristalización, tinturas vegetales y minerales, metalurgia, fertilidad del suelo, nitrificación, azúcares de varios orígenes, fluoruros y ácido fluorhídrico, eterificación fermentación alcohólica, florescencia de muros, etc.

**ABSTRACT.** Charles Frédéric Kuhlmann (1803-1881), French chemist who carried research in a wide variety of subjects and transformed many of his results into industrial reality that led him to fund a powerful chemical empire that is still active. He did work on catalysis with sponge of platinum, crystallization, vegetable and mineral dyes, metallurgy, soil fertility, nitrification, sugars of different sources, fluoride and hydrogen fluoride, etherification, alcoholic fermentation, wall efflorescence, etc.

### LIFE AND CAREER<sup>1-3</sup>

Charles Frédéric Kuhlmann was born on May 22, 1803 in Colmar (Alsace), the sixth of the ten children of Georges Chrétien Kuhlmann, a geometer-geographer, who died when Frédéric was only eight years old. Frédéric started his basic education at the school of his town and completed them as a boarder at the Lycée Royale de Nancy where he distinguished as a brilliant student. After studies at the University of Strasbourg he moved to Paris to become a préparateur at the laboratories of Louis Nicolas Vauquelin (1763-1829). During his three year stay in this position Frédéric became an expert in the chemistry and synthesis of dyes. In 1823 his native town, in collaboration with the Société des Sciences, de l'Agriculture et des Arts de Lille, decided to establish a chair on chemistry applied to industry, in parallel to the free public one about physics, given by the mathematician Charles Delezenne (1776-1866). Delezenne requested the advice of Vauquelin for a proper candidate who promptly suggested Frédéric for the post. This event represented the beginning of a fast academic and professional career for Frédéric; his brilliant classes, deep knowledge, and personality promptly gained the confidence of the local businessmen. In 1825, with the financial support of the brothers Descat, manufacturers of dyed, printed, and dressed fabrics, he established an industry in Loos for the fabrication of chemicals, initially sulfuric acid, using the lead chamber procedure. This act was the beginning of the powerful industrial concern Établissements Kuhlmann or Manufacture des Produits Chimiques du Nord (1852), which in the nineteenth and twentieth century would become one of the most powerful industrial groups of France (Péchiney-Ugine-Kuhlmann). Production of sulfuric acid by the lead chamber method was followed by the manufacture of HCl, sodium carbonate by the Leblanc process (1829), sulfuric acid by the contact method using platinum as catalyst (1833), nitric acid from ammonia using platinum as a catalyst (1838), fertilizers, particularly superphosphates, dyes, beet sugar, etc.<sup>1-3</sup>



Kuhlmann occupied the chemistry chair until 1854 when he decided to abandon his academic activities and dedicate fully to manufacturing. Benjamin Corenwinder (1820-1884), one of his most brilliant assistants, replaced him at the chair. Eventually Louis Pasteur (1822-1895) occupied the chair within the framework of the recently established Faculty of Science of Lille.<sup>1-3</sup>

In 1831 Frédéric married Romaine Woussen with whom he had one son, Jules (1841-1881) and five daughters. Frédéric passed away on January 27, 1881, shortly before his only son and collaborator.

Kuhlmann received many honors and awards for his contributions to science and professional life. He was elected member of the Chamber of Commerce of Lille and its president from 1840 to 1848, general councilor of the department of the North, representing the Lille Nord-Est canton; he was one of the founding members of the Société Industriel du Nord de France, of the bank Crédit du Nord, and the Institut Industriel du Nord de France (afterwards, École Centrale de Lille); he was appointed officier of the Légion d'Honneur (1854) and promoted to commander in 1867; he was corresponding member of the Institute de France (section of rural economy, 1847), member of the Société des Sciences, de l'Agriculture et des Arts de Lille (1824), director of the Mint during the kingdom of Louis-Philippe, administrator of the Chemin de Fer du Nord, member of the Conseil de Salubrité, chevalier of the Ordre de Léopold (Belgium), Ordre de la Tour et de la Epée and Ordre de Christ (Portugal), Ordre de Saint Stanislas and Ordre de Sainte-Anne (Russia), Order of the Lion and the Sun (Persia), etc..<sup>1-3</sup>

## SCIENTIFIC WORK

Kuhlmann published about 80 paper and books<sup>4,5</sup> about the different subjects of his activities, mainly, chemistry, metallurgy, dyes, bleaching, fertilizers, catalytic processes, building materials, heating and lighting with gas, alcoholic fermentation, etc. He also published a 781 page-long book containing all his works, divided into memoirs, agronomy, sugar industry, bleaching, dyeing, pure chemistry, construction, hygiene, as well as speeches pronounced at public events.<sup>5</sup> In addition to the memoirs described below, he also did work on the production of artificial ultramarine,<sup>6</sup> manufacture of bread,<sup>7,8</sup> alcoholic fermentation,<sup>9</sup> sugar production from sugar beet and farina,<sup>10-14</sup> fabrication of animal black,<sup>15</sup> nitrification and soil fertilization,<sup>16,17</sup> oxygenation,<sup>18-22</sup> fixation of colors on cloths,<sup>23</sup> production of sulfuric acid in lead chambers,<sup>24,25</sup> etc.

### Vegetable dyes

#### Madder

According to Kuhlman, madder (*Rubia tinctorum*) was the most valuable of all known vegetable dyes; alone it was the basis of the fabrication of Turkey red, the most important French dyeing product.<sup>26</sup> Kuhlmann had become interested in this dye during his stay at the laboratory of Vauquelin, trying to isolate the dyeing principle present in the roots of madder. In his first experiments he extracted the roots with cold and boiling water; the filtrated cold extract was found to be acid, sweet, and tawny, and to contain very little of the red dye. It was then neutralized with baryta water and the resulting white flocculent precipitate filtrated, washed with alcohol, and dissolved with dilute HCl. Treatment of the solution with several reagents showed that it was a mixture of calcium phosphate and a barium salt, probably the malate. The sweet liquor was evaporated to a syrupy consistency, followed by extraction with alcohol. Analysis of this matter showed it was a mixture of gum and probably grape sugar, which fermented very easily. The hot water extract contained a large amount of the red dye. After filtration it was treated with sulfuric acid and the resulting orange precipitate was washed with water slightly acidulated with sulfuric acid. The solid material was completely soluble in concentrated alcohol forming an orange solution and leaving a brown nitrogenous residue. Examination of the red alcoholic extract showed that it could be kept without change for a long time but eventually it decomposed precipitating the red dye in the form of brown flakes. The red dye was very soluble in water but upon concentration it changed and precipitated. Its dissolution in water was greatly helped by alkalis, without affecting the color. Treatment of the aqueous solution with acid caused precipitation of the dye.<sup>26</sup>

Kuhlmann's procedure for isolating the red matter was based on its low solubility in acid water: The hot aqueous extract of the roots was filtrated and the liquid phase treated with sulfuric acid to precipitate the dye. This procedure was repeated as many times as necessary to exhaust the infusion. It could be accelerated if the original decoction was done with a dilute solution of KOH instead of pure water. The dye precipitated by cooling the aqueous acid solution. All the joined precipitates were then washed with cold water.<sup>26</sup>

Kuhlmann also tried to separate the substance that gave the roots a bitter taste and aromatic odor. For this purpose, he boiled a certain amount of the roots with water acidulated with sulfuric acid, concentrated the decoction and then neutralized it with limewater. The resulting solid was separated by filtration, dried over a water bath, and extracted with boiling alcohol. The alcoholic liquor was dried and then extracted with acidulated water. The resulting solution had a strong smell similar to that of henbane (*Hyoscyamus albus*, L.) and promptly began depositing a black resinous matter, while the remaining liquid retained a strong bitter taste. Kuhlmann also incinerated the roots, analyzed the cinders (7.45 % of the original matter), and found they contained a variety of inorganic salts of potassium and calcium as well of silica.<sup>26</sup>

According to Kuhlmann his analytical (qualitative) results indicated that the principal components of the roots were two coloring substances (one red, the other tawny), a vegetable acid, ligneous matter, mucilaginous substance, gum, sugar, a bitter component, an odorant resin, and different inorganic salts.<sup>26</sup>

In a paper published in 1826 Pierre Jean Robiquet (1780-1840) and Jean-Jacques Colin (1784-1865) mentioned that although Kuhlmann had been the only one who had published a theoretical paper about the separation of the coloring matter of madder, he had made a mistake in assuming that his red dye was a pure substance.<sup>27</sup> Robiquet and Colin used a different extraction procedure to prove their point, in which they macerated the roots with 3 or 4 parts of water during only 8 to 10 min. The resulting red brown acid infusion, which gelled after a time that depended on its concentration, was completely soluble in alkali and provided lakes with a dirty color indicating that it was highly contaminated. According to Robiquet and Colin the contaminant was potassium carbonate. Eventually they separated the coloring principle, which they named *alizarin*. Further purification indicated the presence of a second dye, which they named *purpurin* because of its red purple color.

In following publications Kuhlmann recognized his error and attributed it to his assumption that the bicarbonate he had used was completely insoluble in concentrated alcohol.<sup>28,29</sup> The dissolved potassium salt would act over a particular fatty material contained in madder. As a consequence, Kuhlmann conducted more experiments in which he extracted all the coloring matter present in the roots with cold alcohol instead of water. After repeated extractions he obtained a solution colored from dark brown to orange depending on the dilution. The remaining residue was a grey powder totally exempt of dye. Kuhlmann found that upon addition of water the alcoholic extract became milky; addition of alkali changed its color to red violet and acids turned it live orange. He then went on to separate alizarin by evaporation of the alcohol, followed by addition of sulfuric acid and dilution with water. The resulting orange precipitate was purified by water washes, dissolved in ether, and recrystallized by evaporation and drying. The resulting alizarin sublimed as beautiful long needles colored gold yellow.<sup>28,29</sup>

Kuhlman reported that alizarin was sparsely soluble in cold water and a little more in hot water, it dissolved well in ether, alcohol, and turpentine. Experiments on the use of madder for dyeing different cloths led him to believe that the roots contained an additional dye. For this purpose, he treated the yellow acid liquor originating from the washing of the alcoholic extract with ammonia, lead acetate, heat, etc. and noticed the different resulting changes in color that took place. Eventually he succeeded in separating a viscous yellow extract, which he named *xanthine* and assumed it was the additional dye present in madder. He gave a detailed description of his procedure for separating large quantities of the dye and mentioned that it was very soluble in water and the resulting liquor had a sweet and highly disagreeable bitter taste. Xanthine was soluble in alcohol and slightly soluble in ether; addition of alkalis turned it red orange and acids yellow green. It was not precipitated by lead acetate or sub-acetate or any known metallic salt. Although it communicated only one color (brilliant orange) to cotton, the use of brighteners allowed changing it into red or rose. Being a practical man, Kuhlmann also discussed the properties and industrial uses of the dyes present in madder, as well as their application to cloths to obtain the desired coloration, the use of mordants such as alum, gallnut, sizing, and brighteners, etc..<sup>28,29</sup>

#### Quinquina

In 1825 Kuhlmann reported the analysis of the bark of a quinquina species imported into England from Colombia, which seemed appropriate for dyeing.<sup>30</sup> The bark was colored yellow brown on the outside and tawny red in the inside, had a very bitter taste, all the characters of quinquina, and provided a large amount of crystallized quinine sulfate. Boiled in water it produced a tawny yellow solution, which after evaporation and cooling deposited a purple red powdery precipitate, while the liquor retained its tawny color. It communicated a strong red color to warm wool or silk impregnated with aluminum acetate, but did not act upon cotton. Boiling the wool or cotton in a diluted soap solution made the color clearer and brighter. The color resisted the action of acids but the alkalis destroyed it in an irreversible manner. The bath, exhausted of the coloring matter, had a strong bitter taste and the quinine could easily be removed from it as a sulfate. Kuhlmann believed that this bark would be a valuable addition to dyeing and pharmacy if it could be obtained without difficulty.<sup>30</sup>

#### Berries of *phytolacca* (pokeweed)

Kuhlmann also studied the possibility of using as a dye the beautiful purple color of pokeweed berries. He reported that acids, even when concentrated, did not enhance the color; weak alkalis changed it to violet while concentrated alkalis destroyed it completely in a matter of hours. Initially, ferrous sulfate changed the purple color to violet but destroyed the dye after prolonged exposure, probably because the salt became oxidized and acted upon the coloring matter. Kuhlmann tried without success to apply the color to linen, cotton and wool, independently of the mordant used. The process was possible with silk treated with alum or tin mordant; in the first case the silk acquired a hortensia hue while in the second it was dark violet. These colors were very resistant to chemical reagents.<sup>31</sup>

#### Blue color from cottonseed oil

In 1861 Kuhlmann reported the preparation of a new blue color from the residue obtained during the bleaching of cottonseed oil with sodium carbonate or limewater.<sup>32</sup> This thick soapy brown material separated very easily from the oil and contained its most alterable components together with the alkaline oxides; according to Kuhlmann it was used to manufacture fatty acids by distillation. For this purpose, it was first boiled for several hours with weak sulfuric acid and the fatty portion separated by decantation and boiled to eliminate the water. The boiling concentrated the remaining acid while some sulfur dioxide was released. At the end of this process a deep blue green deposit was

found at the bottom of the tank, which became very dense upon cooling. The remaining green liquid was then steam distilled to produce the crude fatty acids. Kuhlmann wrote that replacing the sulfuric acid by HCl or phosphoric acid produced the same results. On further treatment of the substance with concentrated sulfuric acid the green tint disappeared and was replaced by a deep pure blue one.<sup>32</sup>

Kuhlmann found that this residue was a mixture of colored products mixed with sulfuric acid, sodium or calcium sulfate, and fats. He removed the first two by water washes and the fat by means of naphtha. He believed that the new blue residue was chemically pure, as shown by the fact that its combustion left no cinder. The purified substance was sparingly soluble in cold concentrated alcohol, ether, and alkalis and more soluble at higher temperatures. In the latter case it was re-precipitated by addition of an excess of HCl or sulfuric acid. The new blue precipitate was slightly soluble in carbon disulfide and chloroform. An elemental analysis indicated it contained, by weight, 69.87 % of carbon, 8.22 % hydrogen, and 21.91 % oxygen, corresponding to the formula  $C_{34}H_{24}O_8$ . Kuhlmann indicated that although he had been unable to crystallize this new substance by all the known procedures, he believed it was a new organic compound as shown by the different derivatives which could be prepared by reaction with nitric acid, bromine, chlorine, and iodine. He also indicated that he had been unable to fix the dye on different clothes.<sup>32</sup>

### Hydrogen fluoride and fluorides

In 1825 Kuhlmann published a paper regarding the polemic question about the composition of fluoric acid (hydrogen fluoride); some scientists like Berzelius, considered it was a compound of fluorine and oxygen while others thought it was a compound of fluorine and hydrogen. Kuhlmann wrote that almost everything had been said about the subject, but the question remained unanswered. He now believed that additional discoveries might throw light on the picture.<sup>33</sup>

Assuming that fluoric acid was an oxyacid, then the decomposition of fluorspar and calcium fluuate (today calcium fluoride) by concentrated sulfuric acid of relative density 1.842, would be a simple substitution of the base, or a simple decomposition caused by the strong affinity of sulfuric acid to calcium. If, on the contrary, the acid was a compound of the radical fluorine and hydrogen then it was necessary to accept the decomposition of the water present in the concentrated sulfuric acid: the hydrogen would combine with fluorine and the resulting hydrogen fluoride would be released as a vapor; the oxygen would combine with the calcium forming calcium oxide, which would then react with sulfuric acid and form calcium sulfate.<sup>33</sup>

Kuhlmann believed that the answer could be found by carrying this reaction with anhydrous sulfuric acid. For this purpose, he used the information published by Antoine Bussy (1794-1882) in 1824 about the so-called sulfuric acid of Saxs prepared at Nordhausen by distillation of iron sulfate.<sup>34</sup> After much experimentation Bussy had concluded that the Nordhausen sulfuric acid should be considered as ordinary sulfuric acid containing in solution a certain amount of anhydrous sulfuric acid ( $SO_3$ ). This solute was the source of its particular properties. Bussy also mentioned that in 1812 Augustus Vogel (1817-1889) had postulated, without offering any experimental proof, that fuming sulfuric acid was ordinary sulfuric acid transformed by an imponderable factor into a higher state of acidity. On the basis of these facts Kuhlmann thought that if the reaction of fluorspar with sulfuric acid of Saxs would yield fluoric acid then the latter had to be an oxyacid. For this purpose, he heated calcined fluorspar in a platinum tube and contacted it with a stream of vapors of anhydrous sulfuric acid or with the acid in a liquid state. No gas was released and none of the fluorspar was converted to calcium sulfate. The same experience conducted with sulfuric acid of relative density 1.842 showed the release of an abundant stream of fluoric acid. To Kuhlmann these results showed clearly that fluoric acid was a hydracid, which should be named *hydrofluoric acid* (hydrogen fluoride). His analysis indicated it contained, by weight, 94.941 % of fluorine and 5.059 % of hydrogen. Nevertheless, he wrote that during the reaction between calcium fluoride and HCl he had noted the release of a small amount of chlorine, the origin of whom he could not explain. If it came from a decomposition of the pure calcium fluoride, then the actual hydrogen content of HF should be lower than the one he had determined.<sup>33</sup>

### Preparation of pure HCN

In another paper Kuhlmann described in detail the preparation of HCN without the previous need of cyanide.<sup>35</sup> He first reported his finding that all mixtures of nitrogen volatile compounds and hydrocarbons, or of nitrogen compounds containing hydrogen and CO, produced HCN or ammonium cyanide. These results led him to repeat the experiments of Jean François Clouet (1751-1801) about the production of HCN by the action of ammonia on incandescent charcoal.<sup>36</sup> Kuhlmann found that it worked perfectly, except that the product was ammonium cyanide instead of HCN because the acid decomposed at the high temperature at which the reaction took place. The cyanide was accompanied by methane, as described by the reaction  $3C + 2N_2H_6 = (N_2C_2H_2, N_2H_6) + CH_4$  (using the nomenclature of that time). The strong action of charcoal on ammonia suggested using this reaction to prepare HCN anhydrous. For this purpose, Kuhlmann passed a stream of dry ammonia through a porcelain tube containing small pieces of red-hot charcoal; the resulting gas, composed mostly of ammonium cyanide, was bubbled through dilute sulfuric acid warmed to about 50 °C. The washed gas was HCN pure, which was then condensed in a vessel surrounded by a frigorific mixture. According to Kuhlmann, the acid thus obtained was as pure as that obtained from the decomposition of mercuric cyanide by means of HCl. The reaction of carbon with ammonia could also be

employed to prepare potassium ferrocyanide by passing vapors of ammonium cyanide through a solution of KOH containing ferrous hydroxide.<sup>35</sup>

### Platinum catalysts

In 1838 Kuhlmann read a memoir to the Académie des Sciences summarizing the results of his experiments on the catalytic effects of platinum sponge on different elements and mixtures. He mentioned that Johann Wolfgang Döbereiner's (1780-1849)'s discovery of the phenomenon was probably one of the most important contributions to science in the last years.<sup>37,38</sup> This was the first of three publications of Kuhlmann on the reactions taking place when the above gases were passed over a hot bed of sponge of platinum.<sup>36-38</sup>

His results were as follows: (1) When a mixture of ammonia and air flowed at about 300 °C over a sponge of platinum, the ammonia decomposed and its nitrogen completely transformed into  $N_2O_5$  at the expense of the oxygen of the air; (2) under similar circumstances a mixture of cyanogen and air formed  $N_2O_5$  and  $CO_2$ ; (3) any ammonium salt behaved as if the ammonia was free; (4) free nitrogen never combined with free oxygen, but under the influence of the sponge of platinum all its compounds converted into  $N_2O_5$ ; (5) a mixture of any of the nitrogen oxides,  $N_2O$ ,  $NO_2$ ,  $N_2O_4$ , and  $N_2O_5$ , with enough hydrogen converted into ammonia when passed over sponge of platinum, usually without the aid of heat. The reaction was so energetic that frequently it caused a violent explosion. Any excess of  $N_2O_5$  resulted in the production of ammonium nitrate; (6) a mixture of cyanogen and hydrogen yielded ammonium cyanide; (7) a mixture of  $NO_2$  and ethylene, passed over heated sponge of platinum, produced water, nitrogen, ammonium cyanide, and  $CO_2$ ; (8) under the same circumstances  $NO_2$  mixed with an excess of ethanol vapor produced ammonium cyanide,  $CO_2$ , ethylene, and a deposit of carbon; (9) free nitrogen did not combine with free hydrogen or  $CH_4$ ; but all its compounds converted into ammonia, (10) in these latter reactions, the presence of carbon, combined with nitrogen or hydrogen, gave rise to HCN; (11) all the gaseous or vaporizable non metals, without exception, combined with hydrogen under the influence of sponge of platinum; (12) acetic acid vapors mixed with hydrogen were totally transformed into ethyl acetate and water, by the action of the sponge of platinum held at a moderate temperature.<sup>38-40</sup>

Kuhlmann remarked that substituting the sponge of platinum by platinum black resulted in a substantially less energetic reaction, contrary to what was expected. The precipitated platina was unable to produce  $N_2O_5$ , was very weak in producing ammonia, and it never became incandescent as happened with spongy platina. Nevertheless, precipitated platina converted acetic acid into its ethyl ester faster than sponge of platinum and did it even at room temperature. To Kuhlmann, his results indicated that it was possible to obtain  $N_2O_5$  at will and hence, nitric acid and nitrates, without having recourse to a slow process of nitrification. He was sure that the time would come when "the transformation of ammonia into nitric acid, by means of the sponge of platinum and air...would constitute a profitable manufacture. The transformation of vinegar into acetic ester, assures us that divided platinum promises also equally important applications in the arts connected with organic matters" (the Ostwald process).<sup>38</sup>

### Nitrification

In another paper, Kuhlmann discussed the phenomena associated with nitrification and the new production of nitric acid and ammonia.<sup>39</sup> He wrote that nitrification was a natural phenomenon that had attracted the attention of scientists for many generations. Many explanations had been given but no general consensus had been achieved. In this publication he intended to add more information to try to clarify the picture. At some time during a previous work about the production of potassium nitrate, he had realized that animal matter, buried and out of contact with air, was totally unable to form nitric acid, but during their slow decomposition in the air, and in the absence of lime or chalk, it formed a certain amount of ammonium nitrate. This fact convinced him that ammonia had to enter normally as an agent during the development of nitrification, the same as done by potassium hydroxide, lime, and magnesia. He believed that the nitrogen of air or of animal matter combined with the oxygen of air under the influence of the carbonates of calcium, magnesium, or potassium. It was easy to understand that in the presence of a highly alkaline salt such as potassium carbonate, the elements of nitric acid, coming from the air or from animal matter, would be easily incorporated to form potassium nitrate. This was not quite the same with the carbonates of calcium or magnesium, which were unable to act as free bases. In this situation and in the presence of putrefying animal matter, humidity, and air, these carbonates, which had certain porosity, would partially transform into nitrates. For this, it was necessary to admit that only under the influence of porosity nitrogen had to be a strong tendency of nitrogen to combine with oxygen and that the acid formed displaced  $CO_2$  from natural carbonates. Kuhlmann wrote that he had been completely unable to get these gases to combine under strong conditions and under the influence of porous bodies. This combination occurred only under the influence of electrical sparks. Anyhow, it had to be remembered that nascent nitrogen in the presence of an excess of nascent hydrogen had to come from ammonia in preference above nitric acid, where the formation required the absorption of a free gas or under less favorable conditions. The circumstances changed when ammonia participated and provoked by its alkaline reaction the combination of the elements composing the acid. This argument was weakened by the fact that ammonium nitrate was present in a very small amount in the nitrates; the largest fraction was composed of the nitrates of calcium and magnesium. Chemists were aware of the fact that ammonium nitrate and carbonates gave by double decomposition the nitrates of calcium or magnesium and ammonium carbonate. The latter would, as explained above, provoke the formation of new quantities

of nitric acid. This phenomenon occurred thanks to the great easiness with which ammonium carbonate volatilized, particularly when in contact with a body exposing a large surface to air and not containing a large amount of water to hold it.<sup>39</sup>

Kuhlmann repeated his previous findings about the phenomena that took place when different gases or gaseous mixtures came in contact with sponge of platinum. His results proved clearly that nitric acid could not be obtained except by the decomposition of ammonia or cyanogen, that is, the nitrogen had to be taken from a previous combination. Hence, it was appropriate to assume that the formation of nitric acid depended upon the principles composing ammonia: ammonia under the influence of air, water, and porous bodies would absorb oxygen and become nitric acid and water. It had to be also understood that these were very slow processes. The theory of the transformation of ammonia into nitric acid could be accepted more easily if it was possible to prove that the formation of ammonia was not limited to the decomposition of nitrogenous substances. For this reason, Kuhlmann went on to discuss the artificial production of ammonia.<sup>39</sup>

Kuhlmann had already shown that all metals decomposed water slightly acidified with nitric acid, to form a certain amount of ammonia.<sup>41</sup> This result showed that part of the oxygen consumed had to come from the water and that the hydrogen had combined with the nitrogen of the acid to form ammonia. Kuhlmann went on to prove that ammonia could be formed by a variety of other reactions, for example, (a) between the nascent nitrogen and nascent hydrogen formed during the decomposition of animal matter, or by passing a mixture of  $N_2O_5$  (or  $N_2O_4$ ,  $NO_2$   $N_2O$ ) with an excess of hydrogen over hot sponge of platinum or black platinum, (b) passing a mixture of  $NO_2$  and ethylene produced ammonium cyanide, while a mixture of  $NO_2$  and alcohol produced ammonium cyanide and ammonium carbonate; (c) the reaction of sulfuric acid with an alcoholic solution of  $KNO_3$  formed abundant  $N_2O_4$  and ammonia; and (d) mixing nitric or nitrous acid with turpentine produced abundant ammonia.<sup>39</sup>

At that time Kuhlmann could not have considered the existence of microorganisms and their role in the process of nitrogen fixation (diazotrophs).

### **Efflorescence**

In a paper about nitrification and effervescence of walls, Kuhlmann repeated his hypothesis that ammonia played an important role in the natural formation of nitric acid. In an extension of this study he made a detailed study of the efflorescence formed on the surface of walls subjected alternatively to humidity and drying, a phenomenon normally attributed to nitrification.<sup>42</sup> He had observed that this phenomenon was particularly acute in the walls of Flanders (northern part of Belgium), where during spring many of the walls became completely white due to the humidity that had penetrated them during the winter. During the dry season the efflorescence had a mealy appearance and was usually formed by the reunion of a large number of very fine crystalline needles. Their formation was particularly intense on the sections of the wall made from mortar or where the mortar met the bricks or sandstone. Kuhlmann collected a large number of samples and found that they did not contain nitrates; they were generally composed of sodium sulfate and carbonate, crystalline or amorphous. Wherever the air had a constant humidity (e.g. cellar, basement, etc.) these salts crystallized as a silky quilt; in higher locations the salts became apparent immediately after their construction and in a mealy form. It seemed that humidity facilitated the reproduction of the efflorescence. In addition, it was easy to notice that in recently constructed basements (and hence very humid) there was also an exudation of potassium and sodium chloride.<sup>42</sup>

In order to determine the origin of these salts Kuhlmann analyzed in detail all the materials employed in the construction of the walls: the earth and coal used for manufacturing the bricks, the sand used to prepare the mortar, and the lime and the stones used for its preparation. Examination of all the raw materials left no doubt that the components of the efflorescence originated mainly from the coal used for making bricks and from the lime.<sup>42</sup> A more extended investigation proved that all lime stones, particularly hydraulic limes and natural cements, contained notable quantities of potassium and sodium.<sup>43</sup>

Additional experiments demonstrated that using fat lime and an alkaline silicate it was possible to prepare a lime having all the characters of hydraulic lime. The alkalis served to transfer the silicon to the lime and thus build the silicates that in contact with water would solidify partially. Similarly, Kuhlmann found that it was possible to manufacture cement by simply mixing powdered chalk with a solution of silicate of potash. The resulting cement hardened slowly in the air and turned sufficiently hard to be applicable for the restoration of public monuments, the manufacture of molded objects, etc.<sup>44,45</sup>

### **Etherification**

In 1839 Kuhlmann published a memoir reporting the results of his efforts to use anhydrous chloride to synthesize diethyl ether from alcohol. He repeated the known fact that several substances that had an affinity for water were able to transform ethanol into diethyl ether; for example, sulfuric, arsenic and phosphoric acids, the fluorides of boron and silicon, and zinc chloride.<sup>40</sup> Kuhlman found that tin dichloride reacted with alcohol to form a series of brilliant and colorless compounds, which crystallized easily and were rapidly decomposed by water into the original reagents. The reaction was highly exothermic. When conducted with an excess of alcohol at about 140 °C the reaction formed a considerable quantity of sulfuric ether, but when the salt was in excess it formed hydrochloric ether (ethyl chloride), ethylene, and sweet oil of wine (ethyl bisulfate). Similar results were obtained with the anhydrous chlorides of

antimony and iron; ferrous chloride in particular gave a remarkably clear reaction, the ether was produced at about 130 °C, without containing water or ethyl bisulfate, this was certainly the easiest and surest mode of immediately obtaining highly pure ether. Arsenic chloride was unable to etherify alcohol; aluminum chloride distilled with a large excess of ethanol at about 180 to 200 °C generated a large amount of ethyl chloride, but no ether; absolute alcohol absorbed a large amount of the gases silicon tetrafluoride and boron trifluoride and the resulting combinations were decomposed at about 140 °C yielding diethyl ether. The results indicated that all the above chlorides and fluorides combined directly with ether producing volatile compounds, which decomposed in contact with water. Pyroxylic spirit (methanol) substituted for alcohol produced an analogous effect.<sup>40</sup>

Kuhlmann found that alcohol and ether formed a large number of combinations in which they seem to play a role similar to water in the hydrates. No ether was formed when ethanol and methanol participated as the electronegative part in the combination; but it was with strong acids and a large number of chlorides that behaved as electronegative components. An interesting result was that whenever ether was formed, it occurred at a reaction temperature of about 140 °C; Kuhlman believed that this was the temperature in which the elements of alcohol began to become independent so as to be able to form new combinations.<sup>40</sup>

The reviewers of the Académie des Sciences found this work so significant that they recommended it be included in *Recueil des Savants Etrangers*, the journal for non-members of the Académie.

In an additional paper Kuhlmann added some information regarding the molar proportions of the reagents required to form free ethers (not combined with chlorides). For example, with tin chloride it was necessary to use two “atoms” of the salt and three atoms of absolute alcohol. If two atoms of the chloride were used per atom of alcohol, one atom of chloride would distill before the etherification and no diethyl ether would be formed. If two atoms of alcohol were used per atom of chloride, then one-quarter of the alcohol would distill before the reaction. With ferrous chloride it was convenient to use two atoms of alcohol per atom of the salt; a larger proportion of alcohol would result in the distillation of the excess before etherification. With sulfuric acid the situation was more complicated: two atoms of anhydrous sulfuric acid and one atom of alcohol did not form ether; a ratio of 1:1 of the reagents yielded as ether 25 % of the weight of the alcohol, and a ratio of 4 atoms of sulfuric acid per 3 of alcohol yielded as ether 44 % of the weight of the alcohol.<sup>46</sup>

### Crystallization phenomena

Kuhlmann wrote a series of paper about the phenomena he had observed during the crystallization of many substances.<sup>47-49</sup> He wrote that at the moment of the formation of certain bodies as the result of chemical reactions, they were particularly disposed to assume a crystalline structure, especially so when their origin had been determined by a gas current. For example, antimony oxides gave beautiful needles of antimony sulfide when acted upon by hydrogen sulfide at a high temperature, and hematite (iron oxide), under the same circumstances, formed an iron sulfide having the luster of natural sulfide. It was known that in nature, under an inverse action, the same sulfide turned slowly into iron sesquioxide,  $\text{Fe}_3\text{O}_4$ . Zinc oxide could also be transformed at a sufficient temperature into a white sulfide that crystallized in broad shining plates. The chloride and carbonate of thallium, under the action of a hydrogen sulfide stream, yielded initially pseudomorphic crystals, which, upon sublimation at a higher temperature, changed into the true form of the sulfides.<sup>47</sup>

Kuhlmann repeated these experiments using HF gas instead of hydrogen sulfide and chloride. Passing a stream of red brown hot HF over the oxides or carbonates of copper, zinc, lead, tin, chrome, nickel, and thallium, he obtained the corresponding fluorides having different colorations. Hence, his results indicated that when crystalline minerals were formed by the reaction with gases, their forms were pseudomorphic; but at higher temperatures many of the crystals modified their form, and this modification, “came from a natural attractive force which gave to the bodies new forms similar to those which they have in nature”. Kuhlmann named this force *force cristallogénique* and mentioned that during his study of the crystallization of pastes of amorphous silicon he had observed many cases in which the molecules of bodies already solidified had a tendency for further movements and for becoming compact masses and then assuming a crystalline form. The presence of water, heat, or simple vibrations, facilitated this change. The trend of molecules of the same nature to combine when their mobility was augmented by solution or liquefaction explained the formation of the magnificent crystals of calcium sulfate usually found in plastic clays or of different silicates in glass kept for some time in a state of fusion. Kuhlmann added that when microscopic crystals were soaked with water they transformed themselves into very hard large crystals. Hence, it was necessary to attribute to the solid particles a tendency to approach each other in certain direction to build voluminous crystals. When the solid molecules were not moistened, the crystallogenic force was hampered and led to the formation of bodies of little cohesion and no characteristic form. These arguments could be used to explain the formation of marbles, agates, and jaspers of different colorations. The graining of stones could have resulted from the spontaneous mobility of the solid material and not necessarily from accidental ruptures and subsequent infiltration of crystallizable substances.<sup>47</sup>

After mentioning a number of other minerals showing the same behavior Kuhlmann proposed a possible explanation for the formation of glaciers. Could it be that the large mass of these bodies was the result of the tendency of microscopic crystals in a sufficiently moist state to solder themselves together into larger crystals, when they descended from the regions of perpetual frost?<sup>48,49</sup>

Other examples were as follows: (1) a thin layer of aqueous mannitol was applied over a horizontal sheet of iron or glass, which had been carefully cleaned with KOH. After slow evaporation a crystalline layer replaced the liquid one; this layer was formed by a set of stars separated one from the other by straight lines, disposed as a metallic moiré; (2) a similar experiment with sugar syrup showed the formation of a persistent varnish, which exposed to humid air changed into a bouquet of sugar crystals separated by nude glass areas. This was a clear example that water had facilitated the molecular movement; (3) similar experiments conducted with aqueous solutions of the sulfates of iron, copper, zinc, and magnesium, and a large number of other salts, showed the formation of voluminous crystals, isolated or grouped, and separated by nude glass areas; and (4) application of an artificial mean for decreasing the free mobility of the molecules (e.g. addition of magnesia, alumina, zinc oxide, gums, etc. to the solution) caused crystallization to occur all over the surface of the plate. Kuhlmann added that the shape of the crystals, their grouping or not etc., depended on external factors such as the concentration and composition of the original solution, the chemical nature of the solute, and additives (e.g. gums).<sup>48</sup>

In the second and third parts of this paper Kuhlmann mentioned that he had reproduced these crystalline structures by means of photography or electroplating to manufacture patterns to be used in glass etching, porcelain and metal decoration, paper and cloth impression, etc. He gave a detailed description of the procedure to follow in each of these applications.<sup>48</sup> These applications were completed by others in which the pattern had been obtained by freezing water or various aqueous solutions (e.g. the sulfates of zinc, iron, and aluminum, mixed with gum) over a horizontal plate, or by crystallization of a mixture of solutes (Kuhlmann, 1865).<sup>49</sup> The latter method produced some extremely interesting patterns, for example, a crystal of sodium carbonate added to a solution of nickel sulfate formed a geode composed of blue amorphous nickel carbonate, lined in its interior with blue and green crystals of carbonate; a crystal of sodium carbonate added to a solution of cobalt nitrate produced a geode lined with superb crystals of cobalt carbonate colored ruby red, etc..<sup>49</sup>

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