

Frédéric Kuhlmann

PIONEER OF PLATINUM AS AN INDUSTRIAL CATALYST

By John Graham Smith

Department of History, University of Leicester

The name of Kuhlmann is familiar in histories of catalysis as one of the earliest pioneers of the modern processes for the manufacture of nitric and sulphuric acids. Yet the man and his work are little known. On the one hundred and fiftieth anniversary of his patents we consider the significance of some of his work.

Frédéric Kuhlmann was surely one of the most energetic and versatile industrialists of his day (1). As a manufacturer he was the founder, and for some half-century director, of an enterprise which had become by his death the third largest chemical firm in France (2). To his entrepreneurial skills he added those of a resourceful technologist, with some 50 patents to his name (3). At the same time he commanded respect as a scientific researcher, teacher, and academician, being the author of over 70 papers ranging widely over chemical science, technology and agriculture (4). The researches

surrounding the discovery for which he is today best remembered, the manufacture of nitric acid by catalytic oxidation of ammonia (5), reflect this diversity of interests.

Kuhlmann's orientation towards chemistry no doubt owed something to his early upbringing at Colmar in Alsace, a region noted for its dyeing and textile printing. Dyestuffs formed the subject of his earliest researches, when in his late teens he came to Paris to learn chemistry in Vauquelin's laboratory. Kuhlmann's own style as a scientist clearly shows the influence of Vauquelin: his researches were to be characterised by a meticulous and methodical analytical approach, and although not shy of theory he constantly took pains to stress the final authority of experiment. The



Frédéric Kuhlmann 1803–1881

Despite being the first to use a platinum catalyst for the oxidation of ammonia to nitric acid, his life and work are not well known. In addition to his technical ingenuity and his commercial ability, Kuhlmann had the simple curiosity of the scientist, his attention frequently being diverted by a curious occurrence or an unexplained observation in his manufactory. As a public figure he played a prominent part in the life of his region, and was a valued administrator in the Chamber of Commerce and other bodies

chemist J.B.A. Dumas remarked that from his long contact with Vauquelin, Kuhlmann had retained "the simple habits, sound sentiments, and respect for common sense that characterise all the pupils of his school" (6).

In 1824 Kuhlmann left Vauquelin's laboratory for Lille, which was to be his home for the rest of his life. Here intellectual life centred on the Société des Sciences, de l'Agriculture et des Arts, where he presented many of his researches, and on the public lecture courses created by the municipality in physics, natural history and applied chemistry. It was to take up the newly founded chemistry chair that Kuhlmann moved to Lille, and the course he taught there for the next 23 years helped to prepare the way for the eventual creation in 1854 of a university Faculty of Science, with its famous first doyen, Louis Pasteur. Kuhlmann no doubt valued his teaching rôle for the contact it gave him with local industry. It helped him to keep in touch with industrialists' problems and needs, and it was in this way that he began his own career as a manufacturer, when in 1825 he mounted a small lead-chamber plant at nearby Loos to provide a local supply of sulphuric acid. He thereafter progressively took up the production of Leblanc soda, hydrochloric and nitric acids, bleaching powder, fertilisers, and other materials, and to his original plant he added further works in the Lille area and, in 1847, at Amiens.

Kuhlmann's abiding concern with the application of science to the improvement of industry is clear from the outset of his work at Lille. In his first published paper to the Société des Sciences, in 1824, he used chemical analysis to educate textile producers in the error of their ways when they threw out spent lyes from which they might extract alkali for re-use. A similar attitude governed his own manufacturing operations. In another early paper, on sulphuric acid manufacture (1827), we find him weighing the respective merits of rival modes of working the chambers, and using his chemical insight to track down losses and improve manufacturing efficiency. The pursuit of effi-

ciency was to be a leading theme in his industrial researches, which were often particularly directed towards avoiding unprofitable by-products by an intricate integration of his operations.

The combination of scientist and manufacturer is particularly evident in the researches behind Kuhlmann's discovery of the catalytic production of nitric acid. He seems to have been led to his discovery only indirectly, through a primary interest in a long-standing theoretical debate about the formation of nitrates—and specifically saltpetre—in nature.

The Saltpetre Controversy

Since the introduction of gunpowder in the Middle Ages, saltpetre had become a material of prime military as well as industrial significance, for which supplies continued to depend on the natural formation of nitrate deposits on certain stones and earths (hence the name "salt of stone"). Such formations occurred abundantly in tropical climates and rather less readily in the temperate zones of Europe, where saltpetre makers exploited the nitrates that accumulated in the earthen floors of stables and such-like places, or which grew as an efflorescence on the walls of buildings. Whereas England, with her colonial possessions, could rely on imports from India, France was concerned to be self-sufficient and in the late eighteenth century made great efforts to develop production.

At the same time, advances in gas chemistry cast important new light on the manner in which saltpetre was formed. Hitherto, it had variously been imagined to derive from a supposed generation of nitric acid in the air, which then deposited to form nitrates; or from a transformation of vitriolic acid by an inflammable principle yielded by the decay of organic matter; or to be a vegetable product, formed by plants, from which it passed to the animals that ate them, finally to be released when the plant and animal materials decomposed (7). These vague old notions gave way to a much more precise interpretation when the discovery of oxygen and nitrogen led Lavoisier to recognise

that nitric acid (the anhydride) is a compound of these gases. The formation of saltpetre was now revealed to depend fundamentally on an oxidation of nitrogen, and since this gas in its elemental form was known to be highly inert it seemed plain that the nitrogen involved must derive from organic compounds rather than from the atmosphere: organic decay was conceived to release nitrogen which in its nascent state joined with oxygen from the air. The long-mysterious process of nitrification thus seemed at last to find a simple explanation as a process closely analogous to the slow oxidation of sulphurous peats, by which sulphuric acid and sulphates were formed.

This appealing interpretation was not to go unchallenged for long, however. It came to be vigorously disputed in the 1820s by a certain Longchamp, who offered instead a theory involving fixation of atmospheric nitrogen by a chemical mechanism in the soil (8). Although his ideas were dismissed by Gay-Lussac and others, Longchamp reopened a debate on nitrification that was to continue for another half century, and it was this that provided the immediate context for Kuhlmann's researches.

Kuhlmann's own interest in saltpetre dated from 1825, when he was consulted by the local gunpowder authority regarding some experiments to be conducted at the Lille refinery (9). In the work that followed, he recognised the presence of ammonia in the nitrifying materials, a discovery that provided the germ for the key idea he was to elaborate in the years to come: that ammonia is in some way involved in the nitrification process. Kuhlmann went on to develop a mechanism that accounted for the promotional rôle of ammonia in terms of what we would now call a catalytic reaction. His inspiration here came from the highly original theory of the lead-chamber process advanced in 1806 by Clément and Desormes (10). This had attributed the formation of sulphuric acid in the chambers to the oxidising action of cyclically regenerated nitrous gases—in effect the first intermediate-compound theory of catalysis—and Kuhlmann conjectured that in nitrification ammonia might play an analogous rôle. He sug-

gested that carbonate of ammonia (from organic decay), by its alkaline action induced the oxidation of atmospheric nitrogen to form nitric acid and hence nitrate of ammonia; this then yielded up its acid to such other bases as chalk (carbonate of lime), thereby itself reverting to carbonate of ammonia ready for further action. The ammonia in this way served as an intermediary or vehicle (or to use an analogy Kuhlmann himself became fond of, as a shuttle) in the nitrification of the chalk, in a manner that explained how although present only in small amounts it could nevertheless produce unlimited effects. Characteristically, Kuhlmann appealed to experiment to demonstrate the plausibility of his scheme, observing a reversible reaction when he brought together carbonate of lime and nitrate of ammonia in solution. Cyclical reactions of this kind were to hold a deep fascination for Kuhlmann, and he came to see them as important "levers" underlying many of the processes of nature as well as a number of industrial operations (11).

A Platinum Catalyst

By the time he came to publish his researches in 1838 Kuhlmann had come to see a further rôle for ammonia, however, and it is in this that the historical significance of his work primarily lies. He now believed that ammonia, formed by organic decay (and perhaps in other ways), not only served as a promotional agent but was also itself the immediate substrate from whose oxidation the nitric acid resulted. In this way he offered a third and original theory of nitrification, distinct both from Longchamp's fixation of nitrogen and from the Lavoisian direct oxidation of organic matter. It was to find support for such a theory that Kuhlmann turned to experiments on the laboratory production of nitric acid under the influence of a platinum catalyst. And he now made his discovery that ammonia could indeed be oxidised to nitric acid by passage with air over heated platinum sponge (or even under the influence of a red hot porcelain tube), similar reactions also occurring with volatile ammonium compounds and with cyanogen. On the other hand nitrogen gas gave

Jusqu'à présent on n'a pu se procurer l'acide nitrique qu'en l'extrayant des nitrates naturels ou des matériaux salpêtrés.

En profitant de l'action que le platine en éponge, le noir de platine, et quelques autres métaux ou corps dans un état de grande division ou de porosité, exercent sur différents corps pour en déterminer la combinaison chimique, je suis parvenu à fabriquer de l'acide nitrique et des nitrates.

Les éléments de l'acide nitrique tel que nous le connaissons sont l'azote, l'oxygène et l'hydrogène.

Je suis arrivé à déterminer la production de cet acide en employant l'ammoniaque, l'air et la vapeur d'eau, qui contiennent les mêmes éléments.

J'exécute cette combinaison à l'aide de la chaleur, en faisant passer l'ammoniaque, l'air et l'eau à travers une couche de corps poreux, parmi lesquels je donne la préférence à l'éponge de platine.

In the French Patent, number 11331, dated 22 December 1838, Kuhlmann records that his preferred method for the production of nitric acid and nitrates uses a heated bed of platinum sponge

no reaction under such conditions, nor was it oxidised by nascent oxygen from manganese dioxide, points supporting the greater likelihood of his own theory over Longchamp's.

How Kuhlmann came to think of experimenting with platinum is uncertain. It is likely, though, that the immediate inspiration owed less to contemporary studies of platinum, on which Kuhlmann seems to have been incompletely informed, than to a discussion of nitrification by Dumas, in his "Traité de chimie", which Kuhlmann acknowledged as an important influence on his own nitrification studies. A further factor that Dumas had there pointed to as promoting the natural oxidation of nitrogen was a supposed "condensation" of the gases by the action of porous bodies. (Saltpetre makers had long known that nitrification required materials in porous form—chalk, for example, rather than marble.) Dumas had cited a striking example of the powerful effects of porosity in the case of charcoal, which, if first impregnated with hydrogen sulphide gas and then immersed in oxygen, condensed the oxygen with such energy as to induce reaction of the gases even in the cold. And he added, "It is also known that almost all porous bodies determine the combination of hydrogen and oxygen in the manner of platinum sponge" (12). Kuhlmann similarly believed porous

bodies to have a significant influence on nitrification, and he seems to have regarded platinum sponge simply as a porous body active in particularly high degree, making it a useful laboratory analogue of natural conditions.

One remaining question led Kuhlmann to pursue further his researches with platinum. He wanted to know how extensive might be the formation of ammonia itself in nature, as a basis for nitrification, and for guidance on this he turned again to laboratory experiment. His attempts to form ammonia by direct combination of nitrogen and hydrogen over a platinum catalyst met with no success (only with the much later work of Haber was such a reaction achieved with significant yield). But he found that under the influence of platinum, ammonia could indeed be formed by the reaction of hydrogen with nitric acid or with the various nitrogen oxides. From these and other reactions he concluded that ammonia was formed whenever hydrogen encountered nascent nitrogen in suitable conditions, and was encouraged to believe that the formation of ammonia in nature was widespread.

Kuhlmann's theories seem to have quickly become common currency. He claimed in 1840 that "My theoretical ideas on this point [the formation of nitrates from ammonia] are today generally adopted by chemists" (13), and he

was particularly gratified that they had found the sanction of Liebig. Of course there were possible objections, which Kuhlmann did not hide. In particular, even platinum produced no detectable conversion of ammonia at the temperatures of natural nitrification. To this he could only answer by appealing to slow reaction over time. We now know, of course, that the answer to this and to other puzzles was to lie not simply in time but in microbiology. Nevertheless, by calling attention to the rôle of ammonia Kuhlmann did make a significant contribution to the elucidation of the modern nitrogen cycle, according to which nitrogen passes through the various major forms of elemental gas, ammonia, nitrates and organic materials, in a complex series of interlocking transformations. It is a cycle that would have delighted Kuhlmann!

Industrial Applications

Although Kuhlmann presented his researches with platinum as subsidiary to his larger theoretical concerns, he also clearly recognised their interest in their own right:

“By these experiments I think I have called the attention of chemists to the powerful agent they can find in platinum sponge, to produce numerous and varied reactions with gaseous or vaporisable materials, of organic as well as inorganic nature. Since the discovery of M. Doebereiner and the important work of M.M. Thénard and Dulong, platinum sponge had remained almost ignored in the field of experiment; it had remained an object of curiosity, whereas it was to become, in many circumstances, an agent more effective than heat or electricity. I have shown that its rôle should no longer be limited to igniting the gas of hydrogen lamps; that by its singular property this body is capable of an infinity of applications in our laboratories, applications which will not be slow to cross the threshold of the factory.” (14)

Kuhlmann here underestimated earlier progress, but his work did provide an impressive demonstration of the versatility and potential of platinum and he was congratulated on the range of his researches by a commission of the Academy of Sciences (15). Kuhlmann was naturally alert to possible industrial applications. The catalytic formation of hydrogen

cyanide in some of his experiments suggested one such manufacture (developed a century later to supply the plastics industry (16)). In other experiments he had found that vinegar could be catalytically converted to ethyl acetate, which he thought might open up a cheaper route to the production of alcohol. But the applications he evidently took most seriously, since for these he secured patents, were the manufacture of nitric and sulphuric acids (17).

On nitric acid manufacture Kuhlmann wrote prophetically in 1838:

“I have made known the possibility of obtaining, artificially and at will, nitric acid and consequently nitrates without having recourse to the slow process of nitrification. If, in present circumstances, the transformation of ammonia into nitric acid by means of platinum sponge and air presents no economy over our existing processes, there might come a time when this transformation will be able to form a profitable industry. One can say with assurance that a knowledge of the facts I have demonstrated is such as to reassure the country completely regarding the difficulties or even the impossibility of procuring saltpetre in sufficient quantity in the event of a maritime war, and to lead to a total abandonment of the old method of supplying saltpetre for the needs of the State.” (18)

His patent of 22nd December 1838 briefly indicated the passage of ammonia, air and steam over a heated bed of “porous bodies”, preferably platinum sponge. Whether he made any attempt to develop such a process industrially we do not know. If so it seems to have been short-lived, for when in 1846 we find him again speaking of the national importance of producing nitric acid from ammonia, there is no longer any mention of platinum. Instead his attention had now turned to manganese dioxide, which his subsequent researches had shown could provide the basis for another of those cyclical mechanisms in which he took such pleasure, serving as a vehicle for the progressive oxidation of ammonia by cycling between higher and lower oxidation states (19). As is well known, the industrial development of the platinum process had to await the further researches of Ostwald in Germany in the early 1900s and the stimulus of World War I.

Kuhlmann did, however, attempt to exploit

the patent he simultaneously secured for the manufacture of sulphuric acid by the catalytic oxidation of sulphur dioxide. This process had, of course, been discovered and patented in England seven years earlier by the obscure Peregrine Phillips, though whether Kuhlmann knew this is uncertain. At all events Kuhlmann's patent reveals a more sophisticated plant and a deeper awareness of the problems, and whereas Phillips planned to produce only ordinary acid, Kuhlmann perceptively saw that a chief virtue of the catalytic process was its ability to furnish the fuming acid, oleum (it was primarily as a source of oleum that it was to come into general use half a century later). Kuhlmann's plant clearly borrowed from existing lead-chamber and Leblanc soda technology. Sulphur was burned in a furnace evidently similar to those he used to feed his chambers. After passing through flues to deposit dust, the mixture of sulphur dioxide and air was directed through red-hot pipes — made of platinum, cast iron, or stoneware — containing platinum sponge suitably dispersed among fragments of glass or other inert material. (Alternatively, a heated reaction vessel could be used, with the platinum arranged in layers on a series of perforated plates.) The gases, now charged with sulphur trioxide, were next passed through a series of large water-cooled lead pipes, in which at points nearest the furnace fuming acid was collected and a little further on acid of lower strength. To facilitate the condensation and promote the draught through the system a current of steam was here introduced. Condensation was completed by passage through a long series of demi-johns part-filled with water, terminating in a chimney to create the draught (an arrangement commonly used in France to capture the acid fumes from soda furnaces).

A supplementary patent that closely followed affords further insight into Kuhlmann's work. He here emphasised that his process could burn materials other than sulphur — such as pyrites or hydrogen sulphide — which he hoped might result in easier reaction, by avoiding the dust in the gases from commercial sulphur. He also now extended his patent to cover the use of

oxygen gas as an alternative to air, for he had noted that pure oxygen gave a faster reaction and more complete condensation. In the event Kuhlmann was not to succeed (20). We are told that his large-scale trials failed, partly because of the great difficulty he encountered in satisfactorily condensing the acid gas when mixed with a large excess of air, and partly because he found that the platinum rapidly lost its power. Moreover, to obtain fuming acid it proved necessary to dry the air, creating an added complication. Only from the late nineteenth century was the modern contact process successfully developed, when ways were found to obtain sufficiently pure sulphur dioxide to avoid catalyst poisoning, and when the proportions of the gases were properly regulated for optimum reaction.

Other Fields of Research

Besides providing the context for his work on catalysis, Kuhlmann's investigations of nitrification were also the starting point for some of his other principal fields of research. It was a natural progression to examine the rôle of nitrogen in crop nutrition, and in a series of papers beginning in 1843 Kuhlmann became an early contributor to the grand debate on the nitrogen question that so preoccupied agricultural chemistry in the mid-nineteenth century (21). Contrary to Liebig, he believed in the importance of nitrogenous as well as mineral fertilisers, supporting his position with comparative field trials near Lille in the early 1840s. He considered that plants assimilated their nitrogen as carbonate of ammonia, and to explain how such a volatile compound could be held available in the soil he conceived another of his ingenious cyclical reaction schemes. Although he was mistaken in the details of his agricultural theories, his work perceptively highlighted some of the principal questions that were later taken further in the well-known researches of Boussingault and Ville (22). Another of Kuhlmann's major interests, the chemistry of building materials, had its origin in the efflorescences on walls that were commonly ascribed to nitrification (Kuhlmann in

1840 showed that they were often in fact carbonates and sulphates).

Much of Kuhlmann's research was closely linked with the problems and opportunities of his locality, but he kept in touch with the larger world of science through his contacts with the Academy of Sciences — of which he was elected a corresponding member in 1847 (23) — and through the friendships he enjoyed with prominent scientists in France and abroad. The most illustrious of these was Liebig, whom Kuhlmann no doubt met when they were both students in Paris. Kuhlmann published German versions of many of his papers in Liebig's *Annalen*, and Liebig dedicated to Kuhlmann one of his agricultural writings. Kuhlmann's house near Lille was described as something of a scientific gathering place. Dumas, conveying news of Kuhlmann's death to the Academy in 1881, recalled how:

"Placed at a cross roads for England, the northern lands, France, and the countries of the south, his house became a hospitable resort for scientists of all lands, certain of finding there the most noble and generous welcome. Many of them have disappeared, but how many among us still, who in losing M. Kuhlmann lose a friend, look back with emotion on the indelible memories left in their hearts by these gatherings where the most various nations sent their representatives from all points of the horizon, brought by a common sentiment, the love of Science and the disinterested cultivation of truth." (24)

It was at such a gathering in 1850 that Dumas, then Minister of Trade and Agriculture, had presented to Liebig the decoration of the Legion of Honour (25). Dumas similarly spoke of Kuhlmann's factories as a magnet for industrialists. From an early date, he tells us,

"the works of the French chemist were regarded in England as one of the finest schools of improvement. They have not ceased to be visited by the heads of the principal factories from across the Channel, who came there to borrow new processes, or to seek precise evaluations of processes proposed by inventors of greater or lesser authority." (26)

One can only regret that a man whose career illuminates so instructively the chemical world of his day has never been the subject of a full biography.

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