The Pivotal Role of Platinum in the Discovery of Catalysis

THE PIONEERING WORK OF JOHANN WOLFGANG DÖBEREINER DURING THE 1820s

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By the early years of the nineteenth century the more important physical properties of platinum had become reasonably well understood and had formed the basis of several different applications, but one of its major properties—its remarkable function as a catalyst—was yet to be discovered. Tentative reports of its effect in the oxidation of methane and of alcohol had been made by both Humphry Davy and his cousin Edmund, but neither of them sought to interpret their findings in any detail. However, the subject was vigorously taken up in Germany by Döbereiner, whose thorough investigation of the effect of platinum on hydrogen was the key to the discovery of the phenomenon of catalysis.

Johann Wolfgang Döbereiner was born in 1780 in Hof an der Saale, a town some 40 miles north of Bayreuth. Originally intended for a career in estate management, he contrived to obtain sufficient tutoring to become apprenticed instead to a local apothecary at the age of 14. His three-year apprenticeship completed, he set off on a five-year journey which included

Johann Wolfgang Döbereiner 1780–1849

Professor of Chemistry at Jena for thirty-nine years, a friend and protégé of Goethe, and the founder of the study of catalysis, his discovery of the power of finely divided platinum to ignite a stream of hydrogen caused a considerable stir in European chemical circles

From a portrait in the possession of Goethe-Nationalmuseum der Nationale Forschungs und Gedenkstätten, Weimar periods of thorough if unofficial study of chemistry and mineralogy at Karlsruhe and Strasbourg. A succession of pharmaceutical and technological jobs followed, each enhancing his scientific experience and reputation but none affording much financial security. Indeed, by 1810 he found himself unemployed, in debt and with a sizeable family to support.

From this predicament he was rescued by the offer of the chair of chemistry and technology at Jena University. Jena lay in the State of Saxe-Weimar, whose ruler, Duke Carl August, was an enlightened patron of both the arts and science. He was keenly aware of the practical value of science for his State, and when seeking an occupant for the chair specified a man of "scientific genius with practical flair". This outlook found a sympathetic response in Döbereiner. In addition to his official duties as a professor he served as an impromptu consultant on a wide range of issues, added to his portfolio the post of Inspector of Mines and in 1820 was appointed Privy Councillor. Ever the practical man, Döbereiner directed in his will that his body be buried with no coffin and that two fruit trees be planted on the grave, "so that the products of the decay of my corpse may turn into organic matter and appear in another guise in new life".

Carl August had brought Goethe to Weimar in 1775 and a close relationship grew up between the three men. Carl August and Goethe provided Döbereiner with the best facilities that the State could afford; Döbereiner for his part stayed at Jena for the rest of his life despite offers of more lucrative and prestigious chairs as his reputation grew. Carl August became godfather to two of Döbereiner's children and Goethe to one. Goethe once wrote a poem for Döbereiner when he was ill, and another of his poems prefaced Döbereiner's book on his platinum research. After Döbereiner's death in 1849 the town of Jena erected a statue to his memory.

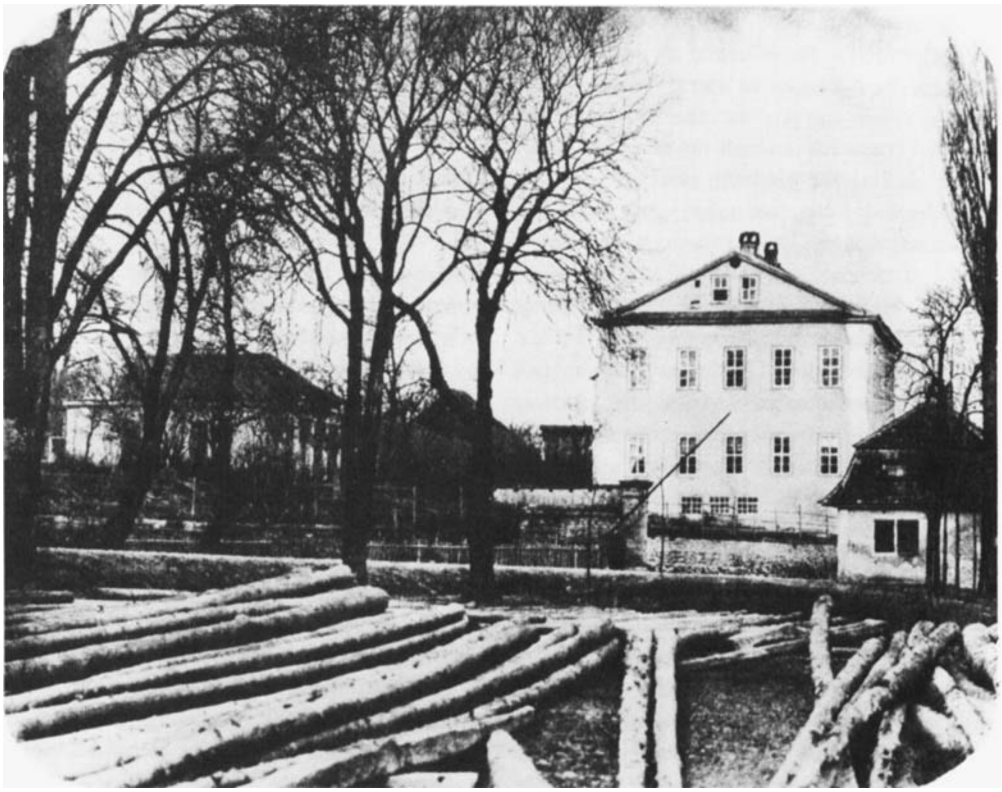
Apart from his wide-ranging work in applied chemistry, Döbereiner's reputation now rests on three aspects of his career. He was a very successful teacher and, at considerable personal expense, ran courses in practical experimental chemistry some years before Liebig's more famous courses at Giessen. Secondly, during the 1820s he developed his theory of "triads", an early pointer towards the Periodic Table. And thirdly there was his important pioneering work on platinum catalysis.

Earlier Experiments with Platinum

The precursor to Döbereiner's work on platinum is to be found in Humphry Davy's researches related to the miner's safety lamp. Davy discovered that a spiral of platinum wire in the vicinity of an ignited wick in the lamp would catalyse the continued oxidation of coal gas (methane) with sufficient vigour to glow white hot after the wick was extinguished. At least, that is how one would now describe his experiment; but Davy's central concern at the time was with the nature of combustion and safety in mines. He recognised that the addition of the platinum spiral was a useful modification to the miner's lamp, but of the phenomenon he had observed, he simply remarked that it was "more like magic than anything I have seen . . . it depends upon a perfectly new principle in combustion" (1).

Humphry's cousin Edmund Davy, working at the Cork Institution, was then carrying out a series of researches on the chemistry of platinum. In the course of this he found that platinum sulphate could be reduced by alcohol to platinum in finely divided form. The platinum powder, Davy observed, reacted strongly with alcohol vapour at room temperature, remaining white hot until all the alcohol was consumed. "This mode of igniting metal", he remarked, "seems to be quite a new fact in the history of chemistry; but the means of keeping it in a state of ignition is only another illustration of the facts previously pointed out by Sir H Davy" (2).

Edmund Davy's paper was published in German translation in 1821, and Döbereiner promptly set about repeating his experiments. The context, however, was crucially different. Döbereiner was then concerned with the chemistry not of platinum but of alcohol, so he



Döbereiner began his career as Professor of Chemistry in rooms in the palace of his patron, Duke Carl August of Saxe-Weimar-Eisenach, but these soon proved inadequate and in 1816 a large house was acquired, shown on the right of this illustration, for use as both a laboratory and a home. Later, in 1833, a new laboratory, visible behind the trees, was built for him to plans drawn up by the Duke's Minister of State, Goethe

emphasised not so much the glowing of the platinum powder as its ability to induce the oxidation of alcohol to acetic acid. He explained this ability in terms of the platinum electrochemically activating the alcohol towards reaction with oxygen. He also noted that the platinum was not used up by the reaction but could "be used again to acidify fresh, perhaps limitless, quantities of alcohol;—a circumstance which permits its use for the large-scale preparation of acetic acid" (3). In the event, Döbereiner did get as far as designing an "Essiglampe", but did not exploit the reaction commercially.

Döbereiner published his results in 1822. He spent the Christmas of that year with Goethe in Weimar and, among other experiments, demonstrated to him the action of Edmund Davy's platinum powder on alcohol. He continued to work on the properties of that powder during the winter, investigating also the properties of a form of finely divided platinum produced by ignition of ammonium chloroplatinate and extending the range of gases and vapours studied to include hydrogen.

The Crucial Experiments

The experiments that finally caught the imagination of the scientific world were carried out in the summer of 1823. On the 27th July Döbereiner prepared some platinum powder by ignition of ammonium chloroplatinate and exposed it to hydrogen. As he had expected, nothing happened. He then admitted some air to the hydrogen, and "there now followed in a few moments that strange reaction: the volume of the gases diminished and after ten minutes all the oxygen in the admitted air had condensed with the hydrogen to water" (4). Substitution of pure oxygen for the air made the reaction vigorous enough to char the filter paper holding the platinum powder.

Döbereiner was so taken by these experiments that he repeated them "at least thirty times" that day, and "always with the same result". He proposed a mechanism analogous to that used in his 1821 experiments on the oxidation of alcohol: "The entire phenomenon must be regarded as an electrical one, whereby the hydrogen forms an electrical chain with the platinum". He promptly dashed off an account of his work to Goethe and to the editors of three scientific journals; it was published a month later (a speed of publication that modern information technology seems unable to match).

On 3rd August Döbereiner produced an even more striking version of his experiment. Instead of the previous static arrangement, he directed a fine jet of hydrogen at the platinum from a distance of 4 cm, so that it was mixed with air before reaching its target. This had the effect of making the platinum immediately white hot and igniting the hydrogen jet. More excited letters were dispatched, commenting that "this experiment is most surprising and amazes every observer when one tells him that it is the result of a dynamic interaction between two types of matter, one of which is the lightest and the other the heaviest of all known bodies" (4).

Seven weeks later Döbereiner demonstrated his experiments to the meeting in Halle of the Gesellschaft deutscher Naturforscher und Ärtze. By then he was less confident of the mechanism he had first proposed: "Most likely a new natural principle is operative here, which will become apparent through further investigation" (5). In a small book published in October 1823 and dedicated to Carl August, in which he summarised his summer's experiments, Döbereiner suggested that the mechanism was "probably of a quite special nature, i.e. neither mechanical nor electrical nor magnetic" (6).

Döbereiner's work caused "a great sensation and excited the liveliest interest" in Paris, according to Liebig who was studying there at the time. It was reported in the daily *Journal des débats* on 24th August, the article concluding: "This beautiful discovery is going to open a new field of research in physics and chemistry" (7). The French chemists Thenard and Dulong, who had earlier investigated the decomposition of ammonia by heated metals and of hydrogen peroxide, immediately set to work; by 15th September they were able to present to the Académie des Sciences a paper extending Döbereiner's work to other forms of platinum and to other metals (8). Further papers followed, but the nature of the phenomenon remained obscure. On 29th November Liebig wrote to Döbereiner that, at a dinner for a group of leading scientists, "your beautiful and as yet inexplicable discovery was discussed in the most glowing terms". The same letter expressed strong, if tactful, reservations about Döbereiner's initially proposed mechanism.

News of Döbereiner's work reached England via a letter from the French chemist J. N. P. Hachette to Michael Faraday (9). Before the end of September Faraday had repeated the experiment and, in his laboratory notebook, had ascribed the phenomenon to the adsorptive powers of the divided platinum (10). At that time he was unable to pursue his investigations further, but he returned to the subject with great effect ten years later. Other English chemists also carried out experiments on the phenomenon.

Commendation of Döbereiner's Work by Jöns Jacob Berzelius

Döbereiner's experiments, then, provoked a great deal of interest and prompted many chemists in different countries to carry out further investigations. This was reflected in the summary of the year's events prepared by the Swedish chemist Berzelius. In 1821 Berzelius had taken upon himself the monumental task of reviewing the advances of physical science during the previous year and presenting them in a series of annual reports. These owed their

An incidental result of Döbereiner's discoveries was his invention of the first lighter. This employed hydrogen, generated from zinc and sulphuric acid, passing over finely divided platinum which then glowed sufficiently to ignite the gas. A number of different types produced in Germany and in England became very popular and many thousands of them were in use over a long period of time. Many elaborate and fanciful designs on enamel or porcelain were also developed including the two models illustrated here

Courtesy of the Danish National Museum

siderable influence to the fact that they were also published in German translation, initially by C. G. Gmelin and then by Friedrich Wöhler. When he came to assessing 1823, Berzelius wrote: "From any point of view the most important and, if I may use the expression, the most brilliant discovery of last year is, without doubt, that . . . made by Döbereiner" (11).

The warmth of this appraisal becomes all the greater when one considers Berzelius' earlier low opinion of Döbereiner. In July 1821 he had commented to Gaspard de la Rive, professor of chemistry in Geneva, "I do not know whether he (Thomas Thomson) or Döbereiner in Germany is the worst chemist in existence at the moment" (12). On 30th October 1823, however de la Rive found himself grudgingly writing to Berzelius: "We have had nothing new here since Döbereiner's experiment with his platinum; in view of the reputation of the said Döbereiner we were sceptical of it; it is, nonetheless, true" (13).

When writing his review of 1835, Berzelius was able to reflect on a wide variety of experimental and theoretical researches that had what he realised was a simple phenomenon in common. He gave to that phenomenon the name "catalysis", stressing as he did so that the name was intended to identify a particular phenomenon rather than to provide a single explanation (operation of a "catalytic force") for all instances of that phenomenon.

The First Practical Applications

Döbereiner immediately turned his discovery to practical ends. Already on 5th August 1823, he wrote, "I have already used this latest observation to construct a new lighter and a new lamp, and shall apply it to far more important ends" (14). One of those ends was eudiometry:

he was able to demonstrate its value in eudiometry at the Halle conference, and Michael Faraday was using it routinely for this purpose by the end of the year. He also used platinum to prepare sulphuric acid by catalytic oxidation of sulphur dioxide to sulphur trioxide, independently of Peregrine Phillips who patented the process in England in 1831, but he did not establish the technique on a large scale.

Indeed, the application most associated with Döbereiner is the lighter. Like Humphry Davy with his safety lamp, Döbereiner refused to patent his invention, published all the designs and spurned a large offer from an Englishman named Robinson for monopoly rights with the words "I love science more than money" (14). By 1828 some 20,000 Döbereiner lighters were in use in England and Germany alone, and it eventually found its way into most European countries. In spite of the invention of the safety match in 1848 by one of his former students, R. C. Böttger, the Döbereiner lighter was still in use at the beginning of the First World War. Part of its attraction lay in the scope it offered to the imaginative decorator: Döbereiner himself suggested that one could "embellish it with two alchemical symbols, namely the lion and the snake, and so arrange it that the snake takes the place of the capillary tube for the stream of hydrogen and the open jaws of the lion sitting opposite the snake hold the platinum" (15).

References

1 Letter from Davy to John Buddle, British Museum Add. MSS 33963 f. 114

2 E. Davy, *Phil. Trans. Roy. Soc.*, 1820, **110**, 108–125

3 J. W. Döbereiner, *Ann. Phys. (Gilbert)*, 1822, **72**, 193–198

4 J. W. Döbereiner, *J. für Chem. (Schweigger)*, 1823, **38**, 321–326; *Ann. Phys. (Gilbert)*, 1823, **74**, 269–273

5 J. W. Döbereiner, *J. für Chem. (Schweigger)*, 1823, **39**, 1–16

6 J. W. Döbereiner, Über neu entdecke höchst merkwürdige Eigenschaften des Platins, Jena, 1823

7 *J. des débats*, 1823, 24th August

8 P. L. Dulong and L. J. Thenard, *Ann. Chim.*, 1823, **23**, 440–443

9 Letter from J. N. P. Hachette to Faraday, 16th September 1823, I.E.E. Archives

10 M. Faraday, Royal Institution Laboratory Notebook No. 8, 81

11 J.J. Berzelius,Jahres-Bericht,1823/1825,4,60–61

12 H. G. Söderbaum, Jac. Berzelius Bref, Uppsala, 1912–1935, 3, letter of 23rd July 1821

13 Ibid, letter of 30th October 1823

14 W. Prandtl, Deutscher Chemiker in der ersten Hälfte des neunzehnten Jahrhunderts, Weinheim, 1956, p. 49

15 J. W. Döbereiner, Zur Chemie des Platins, Stuttgart, 1836, p. 76

Platinum 1986

A year ago Johnson Matthey published "Platinum 1985", the first of a new series of annual surveys of the world of platinum and the other five metals of the platinum group. This was designed to complement Platinum Metals Review by providing a comprehensive survey of the commercial aspects of these metals, including their supply and demand, international markets, major applications and related aspects, with supporting statistical data.

The second of these annual reviews, "Platinum 1986", has now been published. This concentrates on the events of the previous year, when the supply of primary platinum increased from 2,470,000 oz in 1984 to 2,510,000 oz, and in the same period demand in the Western World increased from 2,630,000 to 2,810,000. As the first of a series of occasional articles on topical subjects it includes a four page survey on fuel cells as a potential source of electrical power and as a major outlet for platinum.

Copies of "Platinum 1986" may be obtained from Mr. G. G. Robson, Johnson Matthey P.L.C., New Garden House, 78 Hatton Garden, London EC1N 8JP.