Johann Wolfgang Döbereiner

THE DISCOVERY OF CATALYSIS AND THE REFINING OF RUSSIAN PLATINUM

By Donald McDonald

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Many of the most important contributors to the progress of chemistry in the eighteenth and nineteenth centuries have intervened in the story of platinum, fascinated by the extraordinary properties of the metal and the difficulties of rendering it malleable and fabricating it. For instance there was Baumé, who first introduced the idea of forging it like iron, and Wollaston, who made a scientific business of this proposal. Another and later one was the German chemist, J. W. Döbereiner, best known as a great practical teacher, as a founder of the study of catalysis, and, through his Theory of Triads, as a pioneer of the Periodic System for classifying the elements.

Döbereiner was born the son of a Bavarian coachman and his education amounted to nothing very much. At the age of 14 he entered a pharmacy as apprentice and, after three years of that, practised as assistant at several places including Karlsruhe, Bayreuth and Strasbourg. At the last he came into contact with scientific men like Gmelin and Bockmann, realised his educational shortcomings and determined to overcome them.

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 chemical circles, and he was the first to make use of what we now know as a supported catalyst.
(From a portrait in the City Museum at Jena)

He could not afford a university course, but assiduously attended lectures on chemistry, mineralogy, botany and philosophy, while trying to finance himself by means of three entries into business, all of which ended unfortunately. But in the meantime he had begun to write on scientific subjects and had attracted the attention of the well-known editor-publishers Gehlen and Schweigger, so much so that the former, in 1810, proposed him for an Extraordinary Professorship of Chemistry at the University of Jena.

Association with Goethe

Jena is twelve miles south-east of Weimar, then the capital of the small, and at that time independent, German state of Saxe-Weimar, ruled by an hereditary prince with, after 1815, the title of Grand Duke. From 1775 this position was held by Karl August, a highly intelligent patron of art, literature and science, and a supporter of the new liberal ideas that were beginning to creep into politics.

In order to forward these aims, he had appointed as his Minister of State no less a person than the young Goethe, who helped him to attract to Weimar and Jena a remarkable galaxy of intellectual talent. When in 1810 Gehlen offered Döbereiner's name to Karl August it was without much hope, as his protégé was not a graduate and had not even a school certificate. But Karl August was satisfied with Gehlen's recommendation and saw that the candidate was given a doctorate at half the usual fee, paid, as the minutes record, "in rather worn thalers". It seems that Goethe approved of the appointment and Döbereiner became his chemical assistant.

Now the intellectual fame of Saxe-Weimar had spread rapidly around Europe and attracted a flow of visitors, eager to partake in so much that was new and progressive. They came from all over the continent and among them was the Grand Duchess Maria Pavlovna from Russia. She was a daughter of the Czar Paul I and was married to Karl August's son; two of her brothers became the Czars

The Grand Duchess Maria Pavlovna

The daughter of Czar Paul I and the daughter-in-law of Duke Karl August von Weimar. Her interest in Döbereiner's work on platinum combined with her connections with the Russian court led to his being called upon to help in the refining of the platinum deposits that had recently been discovered in the Urals

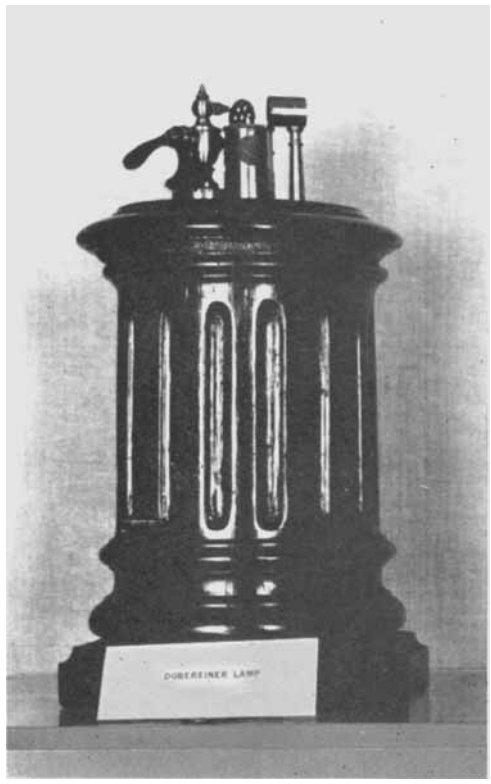
Alexander I and Nicholas I. The latter, who reached the Imperial rank at the end of 1825, desired to develop the natural resources of Russia, and his principal agent in this activity was his very able Minister of Finance, Count Egor Kankrin. Kankrin, in his *ex officio* capacity of Head of the Mining Department, interested himself very deeply in the discoveries of platinum deposits made in the Urals from 1824 onwards. This material was already in demand in Western Europe for both decorative and scientific purposes but, as the basis for neither of these was available in Russia, Kankrin, after consulting that great international authority Alexander von Humboldt, had decided to use it for coinage. To refine the native material for this purpose, he had commissioned the well-known Russian chemist Sobolevsky to make the necessary arrangements and this had been done in the Govern-

ment Mining Laboratory at St Petersburg. But neither Kankrin nor Sobolevsky was completely satisfied with the chemical methods with which they had started their operations and they were continually searching for advice for improvement.

As it happened chemistry was one of the interests of Maria Pavlovna and, through her brother the Czar, she was well acquainted with Kankrin's work and his problem with platinum. Similarly at Weimar, through her father-in-law Karl August, she was aware that Döbereiner had some experience in this same field. As early in his career as 1812 he had interested himself in refining some South American native platinum in order to provide himself with his own platinum apparatus and she had obtained for him some further supplies from Russia to help his work. Also, as chemical advisor to the Minister of State, he had to inspect the work of breweries and distilleries and this led him to a long research on the oxidation of alcohol and the possibility of making vinegar from it by direct chemical means.

Experiments with Platinum Black

In the course of all this work, he came upon the experiment of Edmund Davy in 1820 on the power of chemically-reduced platinum black to promote the oxidation of alcohol. He repeated this in 1821 and found that not only did it oxidise the alcohol entirely to acetic acid alone (without other less desirable products), but at the end the platinum black remained unchanged and available for more work. It therefore promised well for the direct production of vinegar from alcohol. Before taking this further, however, Döbereiner made some further experiments on platinum black, which he thought was a sub-oxide, and found that it absorbed large quantities of hydrogen and would then "imbibe" oxygen until the former was all oxidised to water. Then he turned his attention to that quite different form of platinum, the so-called sponge obtained by calcining ammonium chloroplatinate. He



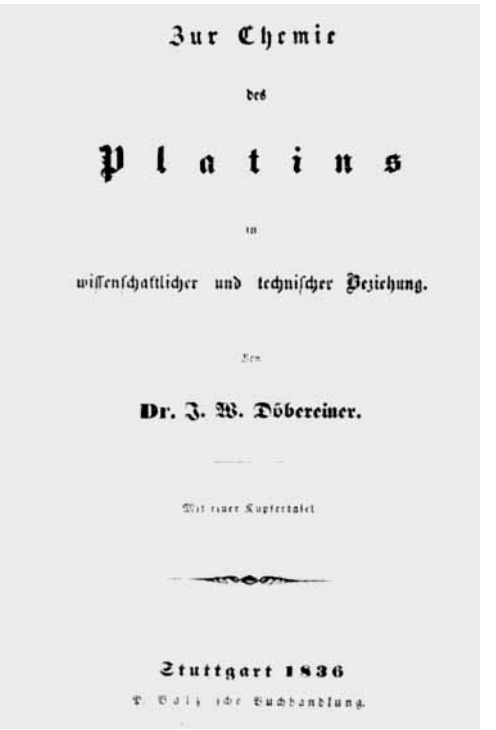
One of many types of Döbereiner lamp in which a jet of hydrogen, generated from zinc and dilute sulphuric acid, is ignited by a small amount of finely divided platinum. (By courtesy of the Science Museum)

wrapped some of this in filter paper and demonstrated its use in gas analysis by ensuring the combination of oxygen and hydrogen in mixtures containing them and so producing easily measurable changes in volume. Finally on August 3rd, 1823, he showed that if platinum sponge is spread out on a watch-glass and a stream of hydrogen is directed on to it in such a way that it mixes with air before touching it, the gas bursts into flame at once.

This discovery was very quickly developed into the Döbereiner lamp, an instrument which, under suitable circumstances, replaced the tinder box as a means of lighting domestic lamps and candles, a function which it continued until it was replaced by the phosphorus match. It is interesting to note in

passing that in 1832 Döbereiner discovered the power of platinum to oxidise sulphur dioxide to trioxide, but in this he had been preceded by Peregrine Phillips in England a year earlier. Also that he was the first to use what we call today catalyst carriers. The filter paper wrapping of 1823 was succeeded by a dried and ignited mixture of platinum sponge and potters' clay; and an improved version of the Döbereiner lamp had its platinum sponge applied in an adhesive coating on a coil of platinum wire. A final comment on Döbereiner's work on platinum is that his process for the direct production of vinegar was never used, because it was overtaken by a more convenient indirect one! But undoubtedly he occasioned a profound interest in this new phenomenon, to which Berzelius, the master of chemical nomenclature, gave the name "catalysis" in 1835.

So it is evident that Maria Pavlovna must have found a great deal to interest her in Döbereiner's laboratory and no doubt she reported it to Kankrin on her return to St Petersburg, presumably somewhere in the 1830s. It is evident that he was pleased to be in touch with the fresh mind of Döbereiner and moved at once to take advantage of it. Accommodation was arranged in Professor Osann's chemical laboratory at the University of Dorpat (now Tartu) and the services of a Dr Friederich Weiss of that University engaged. Döbereiner himself was of course unable to leave Jena for any long period, so his son, Franz Döbereiner, was sent to Dorpat to work with Weiss and to be the agent for full communication with Jena. Unlimited raw material was of course at their disposal and, no doubt, full access to the refining operations at St Petersburg. Their approach to the problem was by way of an attempt to free the solution of the native platinum in aqua regia from iron and copper by the addition of alkalies. This idea had been tried by earlier refiners without much success. Chabaneau had got himself into difficulties by using milk of lime for the purpose in Madrid in the 1790s. But meanwhile the


Zur Chemie

des

Platins

in

wiſſenſchaftlicher und techniſcher Beziehung.

Von

Dr. J. W. Döbereiner.

Mit einer Kupfertafel

Stuttgart 1836

The title page of Döbereiner's book on the chemistry of platinum

work of the English astronomer and chemist, Sir J. F. W. Herschel, in 1830 had clarified the subject considerably by showing that the lime will certainly precipitate the base metals and the rhodium and iridium, but will leave the platinum in the solution as long as it is not warmed or exposed to strong light. It was upon this that Weiss and Döbereiner based their improved process for the Russian refinery. It was brought into use there after Sobolevsky's death in 1841 and presumably continued until 1846, when the refinery was closed on the cessation of coining.

As far as is known, J. W. Döbereiner made no further contact with platinum after this, but maintained his distinguished teaching career until his death on March 24th, 1849. But among his many publications was a small book of a hundred pages on the history and properties of platinum, published in Stuttgart in 1836, which was remarkably comprehensive for its time.