Friedrich Wöhler and His Lifelong Interest in the Platinum Metals

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Friedrich Wöhler was perhaps the last great all-rounder of chemistry (1). A skilful experimenter, he was above all a laboratory rather than a theoretical chemist and he delighted in attacking problems in inorganic or organic chemistry at the workbench. New minerals and new elements fascinated him. More than half a century divides his first and last papers on platinum metals (2, 3) and over the years he made several distinct contributions to their chemistry.

He was born in 1800 at Escherheim, now a suburb of Frankfurt-am-Main, to Auguste Wöhler, one-time Master of the Horse to the Elector of Hessen-Kassel but by then a wealthy farmer, and Katherina Schröder, the daughter of a Professor of Philosophy. The Frankfurt Gymnasium, which he attended from 1814, had a classical bias and he did well there while at the same time developing private hobbies. During childhood he was an inveterate collector of minerals and then as an eighteen year old his interest turned to their chemistry. We have from letters he wrote to a schoolboy friend Hermann von Meyer a blow by blow account of his youthful experiments, conducted in his bedroom at home in Frankfurt (4). Oxygen preparation, phosphorus extraction, and eventually the isolation of potassium using a 100-plate battery were all achieved in spite of phosphorus burns and broken chlorine flasks. Meyer owned a chemistry text-book by Ferdinand Wurzer (1765–1844), Professor of Medicine at Marburg University since 1804, which Wöhler knew almost by heart. Though there was no chemical

Friedrich Wöhler
1800–1882
One of the first German students to benefit from a period under Berzelius, Wöhler became his life long friend and the translator of his works into German. While Professor of Chemistry at Kassel he investigated the separation of the platinum metals and devised a method of separating iridium and osmium that was used commercially. For many years afterwards he was professor of Chemistry at Göttingen, the University founded by King George II of England, and his interest in the platinum metals continued

instruction at Frankfurt Gymnasium Wöhler might have expected to find it on a medical degree course at Marburg in 1820, but there was none, so after a year he transferred to Heidelberg. There Leopold Gmelin told him not to bother with the chemistry lectures but to work in his laboratory, and in 1822 Gmelin and Wöhler published a joint paper on cyanide compounds, including the first preparation of the double cyanides of platinum and palladium (2).

His Year with Berzelius

After graduation in medicine in 1823, and thanks to Gmelin, Wöhler secured a year as assistant to Berzelius in Sweden. In a letter to Meyer (5) we have a glimpse of Berzelius's laboratory and life in Stockholm:

> "I lodge with the ship's captain. . . . At 7 a.m. I get up and translate some exercises from the Swedish. . . . At 8 a.m. I dress, cross the bridge and walk (no skis for me, I prefer galoshes) to Berzelius's house. There he sits at his table, which is covered with glass and platinum – his present work on fluorides can only be done in platinum. He wears a black coat – on which several reactions can be studied. . . . I sit down at the table, look at my lithium salts crystallising from yesterday, and get on with an analysis of a cyanic salt compound which I had the misfortune to discover and must now follow up. I carry on with the analysis of lievrite which I have carried out six times already but still have not finished because the results never agree. . . ."

When he arrived in Stockholm Wöhler had been lent a platinum crucible, probably one that Berzelius had from Wollaston in England but he now ordered his own from Frankfurt. Berzelius's accurate analytical results never cease to amaze the modern reader; before starting an analysis Wöhler had to purify by recrystallisation all his reagents and he learned in Stockholm the full discipline of Berzelius's methods. At the same time he met new apparatus and arranged for a spirit lamp burner, which was unknown in Heidelberg, to be sent to Gmelin. (Only 12 years later when Wöhler became Professor at Göttingen he found twenty-five platinum crucibles, a large platinum retort, massive platinum tubes and plenty of common apparatus but no spirit lamp or flexible tubing of any kind were available.)

Before leaving Sweden in September 1824 Wöhler toured with Berzelius, meeting Hisinger and Oersted, of whom Wöhler wrote in 1875: "he could not at that time have guessed what epoch-making change would result from the major scientific discovery he had only recently made" (6) (Oersted discovered electromagnetism in 1820).

Wöhler Returns to Germany

Berzelius's influence secured Wöhler a post in Berlin which he held till 1831. By now his Swedish was good enough for him to undertake the translation of Berzelius's influential "Lehrbuch" (7) into German: successive editions of this and the magisterial reviews of chemistry (8) which Berzelius wrote each year kept Wöhler up-to-date and provided him with the widest possible chemical education. German chemistry was in fact much influenced by the availability of Berzelius's writings and views. A lively correspondence, sometimes about chemistry, but always full of personal warmth, lasted till Berzelius's death in 1848 (9).

Chemical mythology credits Wöhler with being the first to prepare an organic compound, urea, from inorganic sources in 1828, an experiment which was later widely believed to have overturned the vitalistic view of the nature of organic compounds. He was not, however, the first, and the preparation did not have this result, but his admirers later in the century claimed for him a number of doubtful priorities. Whether he or H. C. Oersted (or indeed neither) first prepared a sample of reasonably pure aluminium before 1827 is also debatable (10). But Wöhler himself was not the kind of man who bothered very much with priorities and controversy. Unlike many of the major scientists of the nineteenth century Wöhler was a modest, unpretentious, good-humoured and well-loved man, who genuinely enjoyed teaching the students who flocked to his laboratory in Göttingen from many parts of the world.

H. C. Oersted's work on aluminium consisted of the preparation of aluminium chloride, which he then decomposed by potassium amalgam to leave "aluminium" after distillation (11). Wöhler in his paper (12) gave full credit to Oersted but reported that he had been unable to produce any metal from the chloride in this way. Instead, for the second stage he heated aluminium chloride with potassium metal in a platinum crucible, causing a very energetic reaction "but the metal of the crucible was not affected in any way". Soon afterwards he used the same technique to obtain beryllium and what he believed, probably erroneously, to be yttrium (13).

In 1855 Henri Sainte-Claire Deville (1818–1881) published a method for extracting aluminium, on a larger scale, from sodium aluminium chloride, $NaAlCl_4$. Napoleon III honoured both Deville and Wöhler and a medal was struck, 20cm in diameter, from Deville's first ingot, bearing Napoleon's head on one side and on the other Wöhler's name and the date 1827. Unfortunately this medal seems now to be lost (14). Wöhler later published with Deville two joint papers on compounds of silicon and three on boron (15).

Between 1821 and 1880 over 300 papers appeared in Wöhler's name, 23 with Liebig as co-author but only 19 with any other collaborators. He did not believe in adding his name to students' work carried out under his supervision. The span of time involved is illustrated by the opening of a paper (3) by Wöhler published in 1877: "Already, a long time ago, in 1824, I have observed that palladium ... when left in an alcohol flame slowly becomes covered with a layer of carbon". He had also observed that the palladium was left as a brittle fine skeleton and at that time he believed that palladium had an affinity for carbon (16). After Graham's work (17) on occlusion he now accepted that the phenomena were due to the absorption of hydrogen. Still interested in the subject, he obtained, through Liebig's influence, twenty ounces of palladium from the large amount that Wollaston had bequeathed to the Royal Society and carried out experiments with ethylene, finding no reaction at 100°C, though decomposition of the ethylene occurs at red heat and the hydrogen is released. Carbon dioxide he showed to be unreactive to palladium at all temperatures. He described how palladium absorbs hydrogen at low temperatures and releases it at higher temperatures; cool palladium with absorbed hydrogen became red hot in air as the hydrogen burned away.

International fame came to Wöhler in 1832 when he and Liebig published an outstanding paper on oil of bitter almonds (benzaldehyde) and the benzoyl radical (18). By this time he was Professor at Kassel and in 1835 he visited Paris for three weeks, meeting for the first time Gay-Lussac, Thénard, Arago, Chevreul and Dumas, a galaxy of talent which he described in letters to Berzelius. The wealth and social standing of the French chemists, the formality of their meetings and the quality of much of their work impressed him. Dumas, almost an exact contemporary of Wöhler, gave him to take home a pound of platinum residues, a black solid left behind when platinum ore had been digested in aqua regia. Writing to Liebig (19):

> "Dumas was most hospitable and personally arranged a demonstration of his vapour density method. He also gave me a large portion of platinum residues and this has encouraged me to work out a very practical method of separation. If you mix the residues with salt and heat the mixture in a stream of damp chlorine gas the iron-titanium is left behind while soluble chlorides of osmium and iridium sublime."

The Separation of Iridium and Osmium

Besides the private letter to Liebig there was another to Pelouze in Paris which was published in *Annales de Chimie* (20). Berzelius had just sent him for translation in manuscript a chapter on platinum for the Textbook, and then further material on what seemed to be a compound of iridium and osmium. Wöhler carried on with his own work and published a full account in 1834 (21). The first stage described above was now attributed to Berzelius but was worked out in more detail. By careful temperature control most of the osmium can be made to sublime while the iridium stays in the tube. After the heating the tube contents were extracted with water, the insoluble titanium and iron compounds filtered away, then the solution evaporated to dryness and roasted – more osmium left at this stage severely irritating the eyes. Sodium carbonate was fused with the remaining solid and the residue extracted with water. Finally the insoluble iridium sesquioxide was reduced in hydrogen to the metal. This method was used by platinum refiners until the twentieth century. In his letter to Berzelius (22) Wöhler noted that there seemed to be quite a high percentage of gold in the residues and wondered if it would be worth trying to buy platinum residues in bulk to extract the gold!

In 1839 the method was used to show that black speck impurities in a gold sample sent to him by a goldsmith were composed of osmium and iridium (23). A quarter of a century later Wöhler published a paper describing the various colours osmium salts exhibit with certain reagents and compared the reactions with those of ruthenium (24).

Iridium ammonium chloride and several mixed salts of iridium and platinum were prepared and described in 1857 (25). Just as Berzelius had received samples of minerals from all over the world and given them to students for analysis, Wöhler became recognised as an expert in his turn. A sample of a mineral from Borneo caught his attention in 1866 and the same mineral was sent to him from Oregon, U.S.A., in 1869 (26). He noticed that these were the first known examples of a natural sulphide of a platinum-type metal: in this case ruthenium with some osmium. An early American student (Ph.D 1847), Charles A. Joy (1823–1891), re-visited Göttingen in 1857 with his wife Laura and Wöhler named the mineral Laurite in appreciation of his friendship with the Joys: they stayed in correspondence for many years.

In a seven-line paper Wöhler described in 1874 the spontaneous reduction of palladium oxide in hydrogen (27), an excellent lecture experiment.

Wöhler's name appeared on the title page of Liebig's *Annalen* from 1838 till 1882, the publication developing from a vehicle for Liebig's polemics to a very sober journal of impersonal record.

A Lasting Influence on the Platinum Industry

Two of Wöhler's German students made important technical and commercial contributions to the platinum industry. Wilhelm Carl Heraeus trained as a pharmacist and then as a chemist at Göttingen, while Heinrich Rössler obtained a doctorate with work on double cyanides of platinum and palladium at Göttingen in 1866 (28). When the young Wilhelm Carl returned to the family pharmaceutical business he engaged, additionally, in chemical preparation and the refining of precious metal scraps. This led him to establish in 1851 the W. C. Heraeus Platinum Refinery, the forerunner of the Heraeus company which continues to this day as one of the major refiners and fabricators of platinum. Heinrich also returned to run, with his brother Hector, a family business which was later formed into the limited company known as the Deutsche Gold- und Silber-Scheideanstalt vormals Roessler. In time the name was simplified to DEGUSSA and this international enterprise also remains among the leaders in the platinum industry.

Another student, an American named Edgar Fahs Smith, discovered from a fellow student that at the Ph.D. oral examination Wöhler had a standard question on the separation of the platinum metals, so he learned 12 pages of Wöhler's text book by heart. Wöhler congratulated him not only on his chemistry but on the perfection of his language! Smith was in Göttingen in 1874 and he describes Wöhler as an energetic teacher (29). In 1880 four hundred of Wöhler's students subscribed to give him a gold medal: 75 of these were American.

Wöhler enjoyed a healthy old age, dying in his lodgings at the Göttingen chemistry building. Just before the end of his life he gave away to a friend a long-treasured relic of his period in Stockholm, Berzelius's own platinum spatula. He had lived to see Napoleon I occupy

Frankfurt in 1814 and to remark in a letter to Liebig after the Franco-Prussian war that the French eagles captured in 1870 were made of gilded aluminium. He was given many honours, including the Royal Society Copley Medal on his seventieth birthday.

When he died his early achievements seemed so remote in time that they were hard to assess. In retrospect he can be seen above all as a great disseminator of chemical principles and practice, part of the German scientific educational system which underpinned the great technological leap forward which took place during the second half of the nineteenth century.

The anonymous obituary for Chemical News in 1881 could not have been written for many of his contemporaries. It concludes:

> "As a colleague, a teacher, and in every relation of private life, Wöhler was esteemed and beloved for his kindliness and geniality of his disposition, his modesty and uprightness. Many successive generations of students, now dispersed over the world, can bear witness to his readiness to perceive and aid merit. He gave his pupils his own ideas, aided them in carrying out the necessary investigations and kept his share in the work a secret" (30).

References

1 There are several reviews of Wöhler's life including:
(a) R. Keen, in "Dictionary of Scientific Biography", ed. C. C. Gillispie, Scribner's Sons, New York, Vol. XIV, 1976, pp. 474–479; also Ph.D. thesis, Univ. London, "The Life and Work of Friedrich Wöhler, 1800–1882", 1976
(b) A. W. Hofmann, *Berichte*, 1882, **15**, 3127–3290. A comprehensive but uncritical obituary notice.
(c) J. Valentin, "Friedrich Wöhler", Stuttgart, 1949

2 L. Gmelin and F. Wöhler, *J. für Chem. (Schweigger)*, 1822, **36**, 230

3 F. Wöhler, *Annalen* 1877, **184**, 128

4 A. W. Kahlbaum, "Friedrich Wöhler, ein Jugendbildnis in Briefen an Hermann von Meyer", Leipzig, 1900

5 Ibid., p. 90

6 F. Wöhler, *Berichte*, 1875, **8**, 838

7 J. J. Berzelius, "Lärbok i Kemien", 1st Edn., Stockholm, 1808–1830, 6 vols. Wöhler revised the first two volumes and translated the rest, then saw two further editions – not published in Swedish – through the press by 1841

8 J. J. Berzelius, "Jahres-Bericht über die Fortschritte der physischen Wissenschaft", Tübingen, 27 vols., 1822–48; Vols. 4–20, 1836–41, bear Wöhler's name as translator

9 O. Wallach, "Briefwechsel zwischen J. Berzelius and F. Wöhler", 2 vols., Wiesbaden, 1901. A scholarly edition with extensive footnotes illuminating the history of this period

10 K. Goldshmidt, *Z. angew. Chem.*, 1925, **38**, 1057; I. Fogh, *Kgl. Dan. Vidensk. Math. Fys.*, 1921, **3**. These set out the opposing claims

11 H. C. Oersted, "Scientific Papers", ed. Frau K. Meyer, Copenhagen, 1920, Vol. 1, p. cxxiii; the most accessible version. Original papers in Danish were not fully translated in foreign journals of the time

12 F. Wöhler, *Ann. Phys. (Poggendorff)*, 1827, **11**, 146

13 F. Wöhler, *Ann. Phys. (Poggendorff)*, 1828, **13**, 577

14 An account of Deville's work and the medal is given in: J. Richards, "Aluminium: its History, Occurrence, Properties, Metallurgy and Applications", London, 1890

15 On silicon: H. St.-C. Deville and F. Wöhler, *Annalen*, 1857, **104**, 256; and 1859, **110**, 248. On boron 1857, **101**, 113; and 1857, **101**, 347; and 1858, **105**, 67

16 F. Wöhler, *Ann. Phys. (Poggendorff)*, 1824, **1**, 231

17 T. Graham, *Proc. Roy. Soc.*, 1868/9, **17**, 212 and 500

18 J. Liebig, and F. Wöhler, *Annalen*, 1832, **3**, 249

19 A. W. Hofmann, ed. "Aus Justus Liebig's und Friedrich Wöhler's Briefwechsel 1829–1873", Braunschweig, 1888, 2 vols. (This is in fact a poor digest of the original letters, largely preserved in the Bayerische Staatsbibliothek in München.) II, p. 77

20 F. Wöhler, Lettre à M. Pelouze sur l'extraction de l'iridium et de l'osmium du résidu noir de platine, *Ann. Chim.*, 1833, **54**, 317

21 F. Wöhler, *Annalen*, 1834, **9**, 149

22 O. Wallach, "Briefwechsel zwischen J. Berzelius and F. Wöhler", Wiesbaden, 1901, 2 vols., p. 544

23 F. Wöhler, *Annalen*, 1839, **29**, 336

24 F. Wöhler, *Annalen*, 1866, **140**, 253

25 A. Muckle and F. Wöhler, *Annalen*, 1857, **104**, 368

26 F. Wöhler, *Annalen*, 1866, **139**, 116; 1869, **151**, 374

27 F. Wöhler, *Annalen*, 1874, **174**, 199

28 An account of W. C. Heraeus and Heinrich Rössler is to be found in D. McDonald and L. B. Hunt, "A History of Platinum and its Allied Metals", Johnson Matthey, London, 1982, p. 326

29 H. S. Van Klooster, *J. Chem. Educ.*, 1944, **5**, 158; C. A. Browne, *J. Chem. Educ.*, 1930, **7**, 502

30 *Chem. News*, 1882, **46**, 183