

Melting the Platinum Group Metals

FROM PRIESTLEY, LAVOISIER AND THEIR CONTEMPORARIES TO MODERN METHODS

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Some fifty years ago Donald McDonald wrote in Platinum Metals Review on 'The History of the Melting of Platinum' (1) and Leslie B. Hunt marked the event's bicentenary in 'The First Real Melting of Platinum: Lavoisier's Ultimate Success with Oxygen' (2), which is also covered in the invaluable "A History of Platinum and its Allied Metals" (3). The topic is revisited and extended here, showing how oxygen, first isolated by Joseph Priestley and Carl Wilhelm Scheele, was used by Antoine Lavoisier to melt platinum. Work on the melting of the other platinum group metals (pgms) and modern methods for melting the metals are also discussed.

Early Attempts to Melt Platinum

Before 1782 little more than a 'partial agglomeration' of platinum had been achieved, mainly by hot forging from the powder which, although it sufficed to make many platinum artefacts, did not produce homogeneous molten metal (1–3). The first to melt impure platinum may have been Henrik Theophil Scheffer (1710–1759) who in 1751 melted platinum with copper, and later arsenic, in a furnace (4). Franz Achard (1753–1821) similarly melted the metal with arsenic (5). In both cases alloys of platinum, rather than pure platinum, are likely to have been melted. In 1775 Pierre Macquer (1718–1784) and Antoine Baumé

(1724–1804) unsuccessfully attempted to melt platinum in a porcelain crucible over a wood fire. Macquer and others (later including Lavoisier) then tried with burning glasses: a 56 cm diameter concave mirror which focused the sun's rays quickly melted iron but platinum gave only silvery-white glistening particles – the product probably contained impurities of carbon which lowered its melting point (1). In 1774 a magnificent 1.2 m diameter burning glass filled with alcohol was mounted on a carriage and installed in the Jardin de l'Infante, Paris, France: it melted many materials, but not platinum (1, 6). An illustration of this device is shown in Figure 1 (3).

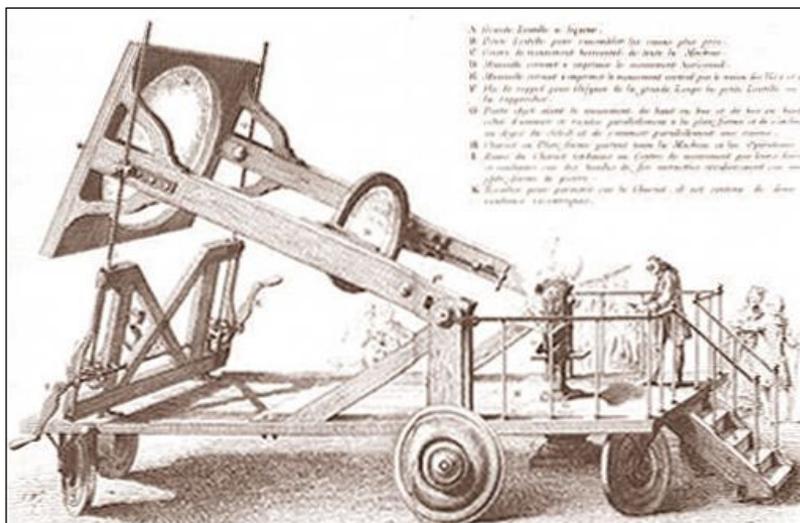


Fig. 1 The large burning glass built for the Académie Royale des Sciences and used in an early attempt to melt platinum (3)

Priestley, Scheele and the Discovery of Oxygen

Joseph Priestley (1733–1804) was born in Fieldhead, Birstall, near Leeds in the U.K., and died in Philadelphia, U.S.A. He was better known in the eighteenth century for his radical religious and political beliefs; opposition to these and his enthusiasm for the French Revolution led him to leave the U.K. in 1794. We remember him for his science: photosynthesis, optics, electrostatics, biology and physiology and above all chemistry (7). He discovered many new ‘airs’ – N_2O , NO , NO_2 , CO , SO_2 , NH_3 and SiF_4 – and investigated HCl , SO_3 , Cl_2 , PH_3 and N_2 . He discovered oxygen on 1st August 1774, by heating mercuric oxide (HgO) with a burning glass, and showed that it supported combustion (8–11). He called it ‘dephlogisticated air’, believing in phlogiston, the alleged principle of combustion, to the end. Phlogiston features in one of his last papers, which also describes experiments on dissolving platinum in *aqua regia* (12). In October 1774, travelling in France with his patron the statesman Lord Shelburne, Priestley dined with Lavoisier and told him that he had obtained ‘a new kind of air’ by heating HgO (11).

Carl Wilhelm Scheele (1742–1786), a Swedish pharmacist for whom chemistry was a rewarding hobby, rivals Priestley in the extent of his discoveries. He was the first to isolate chlorine (in 1774), HF and HCN , and did fundamental work on NH_3 , HCl , compounds of Ba , Mn , Mo , Ce , P and on several organic compounds. He made oxygen between 1773 and 1775 by heating MnO_2 , KNO_3 , HgO , HgCO_3 , MgNO_3 or Ag_2CO_3 , calling it ‘vitriol air’ (*aer vitrolicus*) or ‘fire air’ (*aer nudus*); he too was a phlogistonist until he died. His paper on oxygen was submitted in 1775 but not published until 1777 (13) so Priestley did not know of his work. Lavoisier did know, however. On 12th April 1774, he sent two copies of his “*Opuscules Physique et Chimique*” to Stockholm with a copy for Scheele. In September 1774 Scheele wrote thanking him and told him how to make ‘fire air’ from silver carbonate and a burning glass. His letter was rather vague and Lavoisier did not reply (14).

Lavoisier, Oxygen and the Melting of Platinum

Antoine Lavoisier (1743–1794) is a supreme figure in chemistry, a pivotal contribution being his refutation of the phlogistic theory (10, 15, 16). There is some controversy as to whether Lavoisier discovered oxygen independently (10, 17, 18) – he was not averse to letting people think this. However, in his paper on the melting of platinum (19) Lavoisier did grudgingly allude to Priestley’s priority: “...cet air, que M. Priestley a découvert à peu-près dans la même temps que moi, & je croi même avant moi...” (...this air, which M. Priestley discovered about the same time as I, and I believe even before me...) – although some of his later publications omit the last phrase. Unlike Priestley, however, he began to understand the real significance of oxygen. In 1778 he refers to a *principe oxygène* (20), and in the first edition of the 1789 edition of his textbook (21) – after melting platinum – he refers to *oxygène*, from $\text{O}\xi\upsilon\zeta$ (*acide*) and $\gamma\epsilon\nu\eta\zeta$ (*j’engendre* – ‘I beget’ or ‘I generate’). He believed oxygen to be an element which was a constituent of all acids.

Lavoisier’s Melting of Platinum

Priestley never attempted to melt platinum with ‘dephlogisticated air’ but the idea did occur to his friend, the Reverend John Michell (1724–1793), who wrote to him that “possibly platina might be melted by it”, recollected by Priestley in his book of 1775 (8) which Lavoisier may have read. In April 1782 Lavoisier directed a stream of oxygen from his *caisse pneumatique* (a storage device capable of producing a stream of hydrogen, oxygen or both, shown in Figure 2 (3)) onto hot hollowed-out charcoal containing powdered platinum. It is not clear from his paper whether it was solely oxygen or a hydrogen-oxygen mixture: he had means of producing and storing both gases. He reported to the Académie des Sciences on 10th April 1782, that “...le platine est fondue complètement, et les petits grenailles se sont réunis en un globule parfaitement rond...” (...the platinum melts completely, and the particles united in a perfectly round globule...) (19).

On 6th June 1782, Lavoisier demonstrated his discovery at the Académie to a visiting Russian

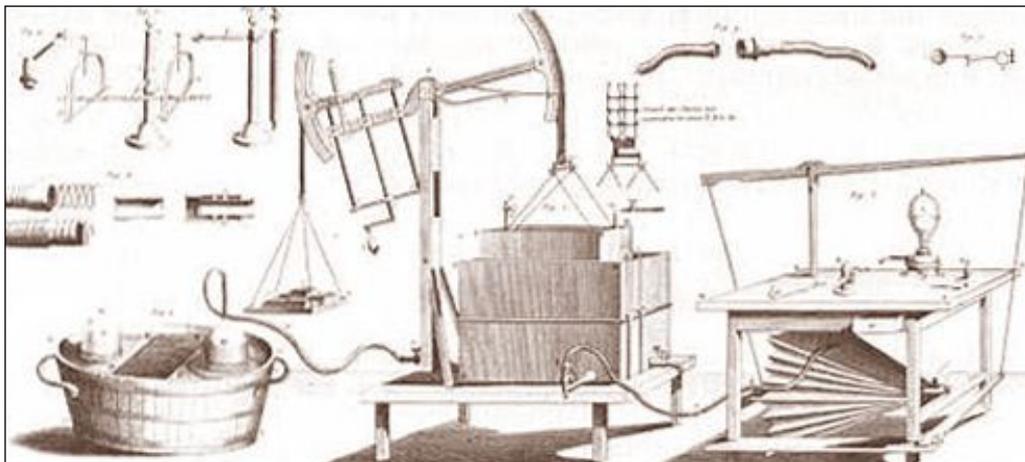


Fig. 2 A drawing by Madame Marie Anne Paulze Lavoisier of the apparatus designed by Lavoisier to burn continuous streams of oxygen and hydrogen (3)

nobleman. Benjamin Franklin (1706–1790), a friend and supporter of the often penniless Priestley, was also present, writing to Priestley that: “Yesterday the Count du Nord was at the Academy of Sciences, when sundry Experiments were exhibited for his Entertainment; among them, one by M. Lavoisier, to show that the strongest Fire we yet know, is made in a Charcoal blown on with dephlogisticated air. In a Heat so produced, he melted Platina presently, the Fire being much more powerful than that of the strongest burning mirror” (22), Figure 3 (3).

Although neither Lavoisier, Priestley nor Scheele could have realised it, the ability of oxygen to support combustion, a process which emits the

degree of intense heat needed to melt platinum, arises largely from the intrinsic weakness of its O–O bond (496 kJ mol^{-1}) (23). This weakness and consequent facile bond cleavage arises from electron lone pair-lone pair repulsions between the atoms in the O_2 molecule. The heat emitted from, for example, charcoal burning in an $\text{H}_2\text{-O}_2$ mixture arises from the formation of the much stronger C=O bonds in CO_2 and O–H bonds in H_2O which are the products of combustion.

Later Methods for Melting Platinum and the Other PGMs

Lavoisier’s method was not suited to large-scale production of molten platinum. In 1816 William

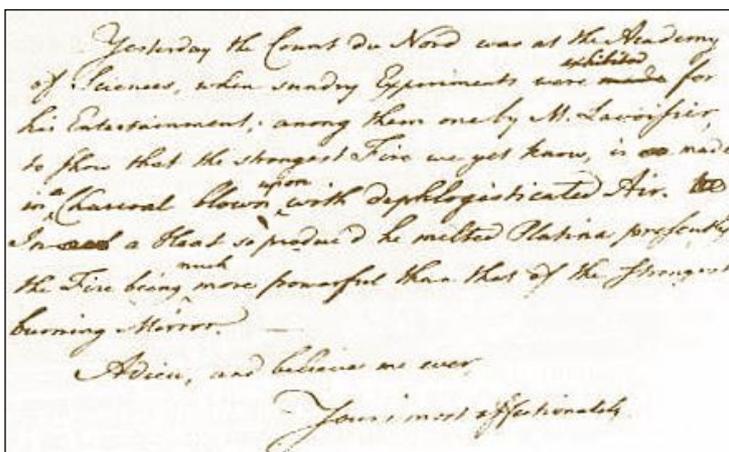


Fig. 3 The concluding paragraph of Benjamin Franklin’s letter to Priestley, dated 7th June 1782, the day after Lavoisier demonstrated his technique for melting platinum at the Académie (3)

Hyde Wollaston (3) wrote to the Cambridge mineralogist Edward Clarke (1769–1822), suggesting that he might try to melt iridium and the native alloy osmiridium. Clarke used a blowpipe with an H₂-O₂ mixture. Despite several explosions he melted 0.5 ounces of the metal, writing that it melted more quickly than did lead in a fire (24). He also melted palladium, rhodium, iridium and native osmiridium (25). Another early claim was made for melting of rhodium by a ‘hydro-pneumatic blow pipe’ (26). A different approach was to fuse the metal by placing it between the poles of a large voltaic battery. John Frederic Daniell (1790–1845), using seventy large copper/zinc-sulfuric acid cells in series, melted platinum, rhodium, iridium and native osmiridium (27).

The work of Henri Sainte-Claire Deville (1818–1881) and Jules Henri Debray (1827–1888) led the way to large-scale production of molten platinum. Their furnace used two large hollowed-out blocks of lime containing the metal, fired by a coal gas-oxygen mixture; the refractory lime absorbed the slag formed by oxidation of base metal impurities. They melted a 600 g sample of platinum in 1856 (28, 29), and this remained the method of choice for melting platinum until induction furnaces became available in the early twentieth century.

In 1855 George Matthey (1825–1913) visited the Paris Exhibition of 1855 and there met Debray, who in 1857 offered him the British rights for his method for melting platinum. By 1861 the process was in commercial use by Johnson Matthey and Company at Hatton Garden in London, U.K. In 1862 Deville came to London, and with Matthey melted a huge 100 kg ingot of platinum. The production of platinum, in the hands of Johnson Matthey, passed from a labora-

tory procedure to a full-scale operation, making the metal available worldwide.

Michael Faraday (1791–1867) tried but failed to persuade Deville to demonstrate his method at the Royal Institution of Great Britain. Instead, in one of his last discourses there, entitled ‘On Platinum’, Faraday demonstrated its melting by using a ‘voltaic battery’, mentioning that “if you go into the workshops of Mr. Matthey [you will] see them hammering and welding away [at platinum]...”. He noted that five of the six pgms had been melted, the exception being osmium. He wrote that ruthenium has the highest melting point, followed by iridium, rhodium, platinum and finally palladium (30). Faraday also referred to platinum in his celebrated “Chemical History of a Candle” (31).

Melting Points of the PGMs

It was not until the late nineteenth and early twentieth centuries that reliable pyrometers were devised for determining melting points (32, 33). Table I lists modern values for their melting and boiling points (34); osmium has the highest values for both (35).

Current Methods for Melting the PGMs

Early methods for melting the pgms used blow-pipe procedures, while Daniell used electricity. These days the same basic procedures are still used, albeit with newer techniques.

Oxy-hydrogen or oxy-propane blowpipes or torches are still in use for bench-scale repair of platinum jewellery (36, 37), and certainly temperatures as high as 2500°C and probably higher can be reached.

Three principal methods, all electrical, are currently used to melt the pgms for industrial use and

Table I Melting and Boiling Points of the Platinum Group Metals (°C) (34, 35)						
	Ru	Rh	Pd	Os	Ir	Pt
m.p.	2333	1963	1555	3127 ± 50	2446	1768
b.p.	4319 ± 30	3841 ± 90	2990 ± 50	5303 ± 30	4625 ± 50	3876 ± 20

for large-scale jewellery manufacture (see Figure 4). Induction heating, derived from Faraday's discovery in 1831 (38) of electrical induction, uses high-frequency alternating current passed through a water-cooled copper coil surrounding a refractory crucible containing the metal sample. Electron beam heating uses a refractory cathode, often tungsten or molybdenum: the electrons from this are accelerated *in vacuo* by a high-voltage direct current source to the metal (which becomes the anode) in a refractory container, the beam being steered by a magnetic field. Energies developed can reach 150 keV, and material can be melted at temperatures above 2100°C. Finally, in arc melting, which can be traced back to Humphry Davy's early experiments with a voltaic pile, the arc is struck under argon between a tungsten cathode and the metal which rests on a water-cooled copper anode. A direct current potential of 50 V to 80 V and a current of several hundred amperes is commonly used. The technique melts tungsten

(which has a melting point of 3422°C), and so can melt all six pgms. These methods have been well described, although without reference to pgms (39), and there is a recent history of the induction method (40).

For larger quantities of platinum or palladium (1 kg to 20 kg), induction heating is the quickest and most effective procedure. The metal charge is held in alumina or zirconia crucibles and is typically melted in air since oxidation is not a problem for these metals. Graphite or copper alloy moulds form the ingots and the molten metal is poured by an automated procedure.

For the higher-melting iridium and rhodium, induction heating is less suitable. For these, arc melting is used for smaller quantities, usually less than 1 kg, and is effected in an inert gas atmosphere with the charge held in a water-cooled copper alloy mould. A tungsten cathode generates and maintains the arc, which is moved over the metal to melt and consolidate it. Electron beam



Fig. 4 Industrial casting of molten platinum.
Image courtesy of Johnson Matthey Noble Metals

melting is used to make larger ingots: an evacuated chamber is used under a vacuum in excess of 10^{-4} Torr, with the metal held in water-cooled copper alloy moulds as for arc melting. As with the latter technique, several melting sequences are required with the ingot being turned over several times to ensure complete and even melting. Ingot sizes are typically between 2 kg and 15 kg (41). There is a recent paper in this Journal providing information on the melting of iridium (42).

Conclusions

The discovery and production of gaseous oxygen, by Scheele and Priestley, allowed the first melting of pure platinum by Lavoisier in the late

18th century. The other platinum group metals were melted during the early 19th century, and by the mid-19th century commercial-scale production of platinum had become possible for the first time. The methods developed during this period remained in use until the early 20th century, when modern methods of industrial scale production using electrical heating became possible.

Acknowledgements

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