The Melting of Platinum and the New Metallurgy of Deville and Debray

"It is therefore necessary to have a method of treatment more expeditious and more practical than that now adopted. It is for this reason that we are proposing an entirely new metallurgy for platinum."

HENRI SAINTE-CLAIRE DEVILLE
AND JULES HENRI DEBRAY

All the platinum so far described as having been worked into useful articles had been prepared from the powder form by hot forging, and all attempts at its melting had succeeded only on a most minute scale. The time was approaching, however, when melted platinum was to become available to industry. The first effective procedure was devised by Robert Hare, the young son of a brewer of the same name in Philadelphia who had emigrated from England in 1773 and who later became Speaker of the State Senate of Pennsylvania. While attending the lectures on chemistry given by James Woodhouse at the University of Pennsylvania and also helping his father in the brewery business the younger Robert Hare undertook research in his spare time in the cellar of the house in which he lodged on the corner of Dock Street and Walnut Street (1). He was deeply interested in the possibility of obtaining very high temperatures by means of an oxy-hydrogen blow-pipe and he was also aware of Lavoisier’s melting of a very small amount of platinum by the use of oxygen alone, described in Chapter 4. He felt that Lavoisier’s apparatus was both too unwieldy and too expensive, while he reasoned that an even higher temperature would be obtained by the combustion of hydrogen and oxygen together. He therefore designed and built the apparatus illustrated on the following page, based upon a barrel from the brewery and not noticeably less unwieldy or less complicated than Lavoisier’s equipment! By supplying a lamp or a candle with a continuous stream of oxygen and hydrogen kept in storage vessels and expelled by hydrostatic pressure through a common orifice, Hare was able to melt a number of substances, among them platinum, that had hitherto been regarded as extremely refractory. He had in fact achieved the highest temperature as yet attained.
The apparatus designed and built by Robert Hare in 1801 for the melting of platinum and other refractory substances. Based upon a barrel from his father's brewery, it comprised two separate storage vessels for hydrogen and oxygen, the gases being driven through a common orifice into the flame of a lamp, shown at the top left, mounted on an adjustable table.

Hare had become a member of the Chemical Society of Philadelphia, founded in 1792, of which James Woodhouse was President, and in December 1801 he demonstrated his apparatus before the society. His long and detailed account of the equipment and his experiments was immediately published in pamphlet form by the society and was reproduced in England in *The Philosophical Magazine* and in France in the *Annales de Chimie* (2).

Among his fellow boarders in the house was Benjamin Silliman (1779–1864) who had been invited to accept the chair of chemistry at Yale but having no knowledge of the subject had been sent to study at the University of Pennsylvania. He and Hare co-operated in improving the apparatus and in obtaining a higher purity oxygen by heating potassium chlorate in stone retorts. Silliman later recorded in his autobiography:

"The retorts were purchased by me at a dollar each and as they were usually broken in the experiment the research was rather costly, but my friend furnished experience and as I was daily acquiring it I was rewarded both for labour and expense by the brilliant results of our experiments." (3)

During the winter of 1802–1803 Hare had an opportunity of demonstrating
his blow-pipe to the discoverer of oxygen, Joseph Priestley, now approaching seventy, who it will be remembered had been informed by Benjamin Franklin twenty years earlier of Lavoisier's experiment. Priestley acknowledged that Hare's experiments were "quite original". (4)

For a number of years Hare was occupied in the brewery business, and then in 1818 he became for a short time Professor of Natural Philosophy at the College of William and Mary in Williamsburg but was soon appointed to the post he had long earnestly desired, Professor of Chemistry in the Medical School of the University of Pennsylvania. Here he took up the study of electricity, collaborating with Joseph Henry and corresponding with Michael Faraday. Silliman, on the other hand, annually demonstrated the fusion of platinum and of other substances by means of Hare's blow-pipe to his students at Yale.

**The Controversy with Professor Clarke**

Although Hare did not pursue his blow-pipe researches any further for a number of years he was aroused to great indignation in 1819 by what appeared to him an appropriation of his invention. A letter from a Mr. H. I. Brooke of Keppel Street in London to Thomson's *Annals of Philosophy* in 1816 described the design of a new form of blow-pipe which the writer had asked the instrument maker John Newman to construct (5). This came to the notice of Edward Daniel

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**Edward Daniel Clarke**

1769–1822

Professor of Mineralogy at Cambridge and a friend of Wollaston, Smithson Tennant and Humphry Davy, Clarke experimented with an improved form of blow-pipe from 1816 until his death, successfully melting small quantities of platinum. After describing his results in several papers, in 1819 he published a small book that provoked Robert Hare to an indignant response
Clarke, Professor of Mineralogy at Cambridge, who had been in the habit of submitting his mineral specimens to the ordinary blow-pipe. Clarke persuaded Newman to modify his apparatus to some extent and then proceeded to carry out a number of experiments with it, using hydrogen and oxygen in the carefully controlled proportions of two to one. He melted a range of substances, including platinum and palladium, and began to publish a series of papers, first in the Royal Institution's *Quarterly Journal of Science* and then in the *Annals of Philosophy* (6). In the first of these papers he wrote:

"Platinum was not only fused the instant it was brought into contact with the flame of the ignited gas, but the melted metal ran down into drops."

Wollaston then wrote to him suggesting that he tried to melt "ore of iridium" and this he claimed to have done successfully as well as melting a small quantity of iridium-osmium residue that had belonged to Smithson Tennant. After many further experiments, and after suffering a dangerous explosion of his apparatus, Clarke devised a wooden screen to protect himself or his man-servant, and again he melted platinum but only in small quantities. Then in 1819 he published a small book (7) describing the whole range of his work, the introduction including the sentence:

"The American Chemists lay claim to it as their invention in consequence of
experiments made in 1802 by Mr. Robert Hare, junior, Professor of Natural Philoso-
phy in Philadelphia.”

On receiving a copy of the book Hare immediately reacted angrily, address-
ing a long letter to his friend Silliman who had just recently founded the American
Journal of Science and Arts, quoting some lines of Virgil written on hearing that the
Roman dramatist Bathyllus had claimed some of his own verses (8). The
opening page of this diatribe is reproduced here. One of his more interesting
comments was:

“He (Clarke) would evidently wish the reader to adopt the false impression that
the facility with which platinum may be fused is owing to ‘the great improvements’
made fourteen or fifteen years after I had devised and used them. Will Britons tolerate
such conduct in their professors?”

The opening page of Hare’s letter to the American Journal of Science
in which he attacked Clarke for what he considered to be the appropriation
of his invention. The Latin lines from Virgil read in translation:

“I indeed have made these verses but another has received the honour.
So your birds make nests, not for yourselves,
So your sheep bear fleeces, not for yourselves,
So your bees make honey, not for yourselves.
So your oxen do not bear the plough for yourselves.”

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The letter also contained a series of drawings of the various forms of the compound blow-pipe as devised by Hare over the years. Clarke died in 1822 and there is no evidence that he ever responded to or acknowledged this rather harsh piece of criticism, or that he pursued his work on the melting of platinum any further.

On his part, Hare again took up the subject after a long interval. In 1836 he made a visit to England and attended the meeting of the British Association for the Advancement of Science, held that year in Bristol, meeting the leading scientists of the time including the seventy year old John Dalton, then a Vice-President of the Chemistry Section, and contributing several short papers on improvements in chemical apparatus. In August 1837 he wrote to Dalton to report his melting of a more substantial quantity of platinum:

"I beg leave through you to communicate to the British Association for the Advancement of Sciences that by an improvement in the method of constructing and supplying the hydro-oxygen blow-pipe, originally invented by me in the year 1801, I have succeeded in fusing into a malleable mass more than three fourths of a pound of platina. In all I fused more than two pounds fourteen ounces into four masses, averaging of course nearly the weight above mentioned. I see no difficulty in succeeding with much larger weights."

This letter was duly read to the British Association by Dalton during its meeting in Liverpool a month later (9), but Hare was still not satisfied. In September 1838 he exhibited to the Chemical Society of Philadelphia an even larger specimen of platinum, writing to Silliman:

"I have by improvements in my process for fusing platina succeeded in reducing twenty-five ounces of that metal to a state so liquid that, the containing cavity not being sufficiently capacious, about two ounces overflowed it, leaving a mass of twenty-three ounces. I repeat that I see no difficulty in extending the power of my apparatus to the fusion of much larger masses." (10)

After a further interval of some eight years Hare, towards the end of his occupation of the chair of chemistry, announced the melting of both iridium and rhodium, specimens of which he had obtained from Johnson and Cock. (11)

Hare took no commercial advantage of his long series of investigations, but his work did lead to two further developments in quite different directions. First, his oxy-hydrogen blow-pipe was adapted to good effect by the Scotsman Thomas Drummond (1797-1840) who served in his earlier years in the British Ordnance Survey where he devised a source of intense white light by directing the flame on to a block of lime. This was designed as an improvement to navigational safety, and his invention began to be installed in lighthouses in 1829, later being adopted for the theatre from where the expression "in the limelight" originated.

Working with this means of illumination in Paris, Marc Antoine Gaudin (1804-1880), a former student of both Dumas and Ampère who was employed by the Bureau of Longitude, presented a paper to the Académie des Sciences in 1838 in which he described his method of preparing a crystalline form of lime
from which he made crucibles (12). In these he was able to melt an alloy of 10 per cent iridium and 90 per cent platinum, almost certainly the first occasion on which a synthetic alloy of platinum had been produced. He commented on the lustre, the malleability and the extreme resistance to corrosion of his alloy.

The second and more significant outcome of Hare's work was due to his assistant in the University of Pennsylvania. This was Joaquim Bishop (1806–1886) who after working in the jewellery trade and then in a brass foundry became Hare's instrument maker in 1832 and took part in the experiments on platinum. Leaving Hare in 1839, he set up in business for himself and so founded the platinum works that bore his name for very many years and that will be dealt with more fully in a later chapter.

The Work of Deville and Debray

Hare noticed that if he maintained his molten platinum in an oxidising atmosphere it gradually freed itself from any base metals present by oxidation, and it was this observation that led to the next major step forward in the history of platinum, this taking place in Paris in the eighteen-fifties at the hands of Deville and Debray and constituting a revolution in the platinum industry.

Henri Sainte-Claire Deville was born in St. Thomas, one of the Virgin Islands, the son of a prosperous ship owner who had emigrated from France. He was sent to Paris to be educated, studying medicine but also attending the lectures of Thenard at the Sorbonne. In 1839 he set up a small private laboratory in which he began to make original investigations on organic substances including essential oils. On the recommendation of Thenard he was appointed Professor of Chemistry at Besançon in 1845 at the age of only twenty-six. When Balard was appointed Professor of Chemistry in the College de France in 1851 Deville succeeded him at the École Normale where he remained for the rest of his life, converting a most inadequate laboratory for the training of teachers into one of the outstanding centres of research in Europe. Here he found Jules Henri Debray, a native of Amiens who had been a student there since 1847 and whom he appointed as his assistant in 1855, the association developing into a great friendship and a most fruitful collaboration with Debray eventually succeeding him as professor.

The ten years following Deville's appointment were characterised by quite exceptional activity and achievement in the field of high temperature reactions. First he succeeded in producing aluminium by the reduction of its chloride with potassium, later with sodium, and his results being brought to the attention of Napoleon III by Dumas, he was given a government grant to establish a pilot plant at Javel. This was followed by the erection of a larger works at Nanterre, Deville and his colleagues Debray and Paul Morin subscribing capital to form the Société de l'Aluminium de Nanterre.

With production established, Deville returned to his laboratory and again gave his mind to the need for better methods of producing high temperatures. In
1856 he had published a long study of the use of coal gas and oxygen in blow-pipes and their application to both melting and welding in which he referred to the earlier work of Gaudin (13). At first Deville and Debray used the equipment to produce manganese, chromium, nickel and cobalt in a state of purity, using crucibles made of lime or magnesia.

They then turned to the platinum metals and for four years pursued their researches with great activity. Already in the 1856 paper Deville had made the point that his melted platinum had properties quite different from those of the powder metallurgy product. He had enjoyed the co-operation of a Parisian gold-smith and manufacturer of "doublé" or rolled gold, Auguste François Savard, and he commented:

"Cast and refined platinum is a metal as soft as copper, as confirmed by the Paris Mint; it is whiter than ordinary platinum and does not have the porosity that has so far proved to be an obstacle in the manufacture of an impermeable doublé of platinum."
Savard, whose firm, founded in 1829, still exists in the Rue Saint Gilles, had put his furnaces and rolling mills at Deville’s disposal and had made a very thin piece of platinum-clad copper that completely resisted the action of nitric acid.

Deville and Debray’s final design of a furnace for the melting of platinum, illustrated here, comprised two cylindrical blocks of lime bound together with steel strip. A hollow was formed in the lower block to contain the metal, a pouring channel being provided to the edge. The upper block was also hollowed out to form a roof which was pierced to receive the coal gas and oxygen. The whole unit could be tilted for pouring the molten platinum. By this means platinum was not only melted in quantity for the first time but could also be refined to some extent by exposure to an oxidising atmosphere, while the lime served to absorb any slag formed by the oxidation of base metal impurities.

Following this, Deville and Debray went on to devise a process for refining native platinum. Their preliminary results were described to the Académie des Sciences in 1857 (14) and in the same year both French and British patents were filed, not in Deville’s name but in that of Debray, and assigned for some reason to the Société de l’Aluminum de Nanterre (15). The British rights were at once

Jules Henri Debray
1827-1888

A native of Amiens, Debray studied at the Ecole Normale and then became first an assistant and later a collaborator of Deville’s, eventually succeeding him as Professor there in 1881. Their association was extremely close, and their joint work on the melting of platinum and its alloys extended over many years.
François Auguste Savard
1803–1875

The founder of a firm producing rolled gold in Paris in 1829, Savard turned to the production of platinum-clad copper, brass and silver in 1854. During the researches of Deville and Debray he put at their disposal both his furnaces and his rolling mills so that they could investigate the physical properties of their alloys. He also produced extremely thin coatings of platinum on copper from their melted metal that displayed complete freedom from porosity. His company continues in operation to this day.

Photograph by courtesy of M. Jean Pierre Savard

acquired by George Matthey whose long career in the platinum industry will be described in the next chapter, while the French patent was shortly afterwards acquired by Desmoutis and Chapuis.

The response from Russia was even more positive. Just at this time the government in St. Petersburg was considering restarting the minting of a platinum coinage, and in June 1859 their representative, Academician Boris Semenovich Yacobi (Known in Western Europe as Moritz Hermann Jacobi), Industrial Adviser to the Ministry of Finance, visited Paris to study the techniques of Deville and Debray. His visit coincided with the publication of a long paper by them, On Platinum and the Metals that Accompany It (16), in which they detailed not only the properties of each of the six platinum metals but gave a complete scheme for their analysis and finally proposed a simple and economical process for yielding a ductile and industrially useful iridium-rhodium-platinum alloy directly from the Russian mineral. The process included the preliminary alloying of the native platinum with lead to separate osmiridium and earthy matter, the lead alloy then being cupelled to leave the platinum rich material ready for melting.

280
Deville and Debray demonstrated their process to Jacobi, who was so impressed that he asked his Minister of Finance to sponsor further research on melting and on the working up of the residues that had accumulated in great quantity in the refinery in St. Petersburg. An agreement was quickly concluded by which the Russian government financed the setting up of furnaces and of an oxygen plant in the École Normale and Deville and Debray were enabled to carry out their experiments on much larger quantities of material. On February 23rd they received from St. Petersburg some 56 kilograms of mineral from the Demidov workings at Nizhny Tagil, demonetised coinage and refinery residues. On June 15th “after three and a half months of incessant work day and night”, they delivered to Jacobi 42 kilograms of ingots, rolled sheet and cast objects, together with an ingot of iridium weighing just over a kilogram. Their loss of platinum amounted to only 120 grams. This remarkable piece of work was described in detail in a further long paper (17), of which the opening page is reproduced here, with full particulars of the amounts of lead, oxygen and reagents consumed.
An original drawing of the lime-block furnace devised by Deville and Debray for the melting of platinum. The two cylinders A and B were hollowed out and pierced at E to admit the oxygen-coal gas burners. The molten platinum was poured through the channel on the right by tilting the furnace by means of the lever C. This type of furnace remained in use in the industry for many years until the development of the induction furnace.

Jacobi also enjoyed the use of the melting furnaces and rolling mills of Savard as well as of the facilities of the Paris Mint through the co-operation of its Director, Professor Pelouze, and in the December of 1859 he was able to send to the Minister of Finance thirty-eight medals struck in several alloys of platinum containing 5, 10 and 20 per cent of iridium. These were first shown to the Académie des Sciences by Pelouze, together with an ingot of iridium weighing 267 grams which Jacobi presented to the Académie (18). Unfortunately, despite Jacobi's recommendation in a pamphlet published in 1860 (19), the Russian government abandoned all thoughts of a new platinum coinage.

Despite this disappointment, Deville and Debray continued their intense work, elaborating their methods of preparing platinum and the other metals of the group in commercial quantities and in a high state of purity. In 1860 they laid before the Académie two ingots of platinum weighing together 25 kilograms (20) while two years later they reported to them on the industrial progress so far made with their melting process (21). In this they referred to the casting of an ingot of platinum weighing 100 kilograms by George Matthey, "the mass becoming so liquid that it filled exactly with metal every part of the mould and reproduced all its imperfections with unexpected precision". In a footnote to one of their earlier papers (16) they had already recorded in referring to their two licensees that

"Today these procedures are functioning and are being perfected every day in the hands of the clever craftsmen to whom they have been confided."

282
Boris Semenovich Jacobi
1801–1874

Born in Potsdam in Germany and known in his early years as Moritz Hermann von Jacobi, he left to make his career in Russia and was appointed Professor at the University of Dorpat in 1834, later moving to St. Petersburg to take charge of the Physics laboratory of the Academy of Sciences. In 1839, by then serving also as Industrial Adviser to the Russian Ministry of Finance, he visited Paris and sponsored further investigations by Deville and Debray but failed to persuade his government to re-introduce a platinum coinage.

The New Standard Metres

Jacobi was again destined to play a part in the work of Deville and Debray. In 1867 a Great International Exhibition was held in Paris, he was among the visiting scientists and he took the opportunity to join in discussions on standard weights and measures in which the French were deeply interested because of their long sustained efforts to spread the use of the metric system. With Jacobi’s support a committee of delegates from a large number of countries was formed and strongly recommended the universal adoption of metric weights and measures, this resulting in the setting up of the International Metric Commission in 1869.

“For the construction and verification with the best appliances of modern science of new international standards of the metre and the kilogram”.

The Franco-Prussian War delayed things, but in 1872 the first full meeting took place with twenty-nine countries represented, leading to the Convention du Metre signed in Paris in 1875. This finally achieved the support of all the
In 1873 the President of France, Louis Adolphe Thiers, together with a number of his ministers, paid a visit to Deville’s laboratory in the École Normale to witness the melting of ten kilograms of iridium–platinum for the production of the new standard metre. Deville is standing in front of the door looking thoughtful; Debray is at the opposite end of the furnace, while their assistant Clement is tilting the lime-block to pour the alloy. The President is holding a protective glass in front of his eyes.

important countries and the establishment of the still existing International Bureau of Weights and Measures with its headquarters in Paris (22).

An examination of the original standard metre, the Mètre des Archives, made by Janety in 1796 and described earlier in Chapter 10, showed that the ends were no longer plane, but the Convention decided that they would not go back to the original definition of the metre as one ten-millionth of a quarter of the world’s meridian, as there was no agreement as to its exact value. They preferred to use the Mètre des Archives “in the state in which it is found” but to convert its length from an “end” standard to a marked “line” standard.

The next question to be decided was the most suitable material from which the new standard and its copies should be made, and in 1862 Deville and Debray put forward a suggestion that an alloy of platinum with 10 per cent of iridium offered the best possibilities. It has to recommend it high density, high melting point, great resistance to humidity and air, a fine grain, perfect polish, great hardness and full malleability. Deville and Debray claimed to have put in ten years of study, assisted by many other people, before they arrived at the possibility of preparing this material in a satisfactory form and were satisfied.

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that it was better than anything else available. One of their greatest troubles had been encountered in the preparation of large ingots of this alloy, completely free from blisters and cavities. The only method available in those days of detecting their presence was the undertaking of very careful density determinations. Deville himself carried out large numbers of these, working long hours into the night and exhausting his strength in the service of the posterity that he dreamed of but could not hope to see (23). In one way and another the attempts to produce a sufficiency of homogeneous metal occupied several years at the hands of Deville himself and his assistants, the Norwegian O. J. Broch, the Belgian J. S. Stas, and George Matthey (24). Time after time the metal failed and, even after attaining the necessary qualities at its original preparation, was found to have taken up iron during the subsequent mechanical fabrication.

A detailed account of these matters and of the major role played by George Matthey will be given in the next chapter.

During this work an immense number of analyses of the platinum metals and mixtures thereof had to be undertaken, and the conscientiousness of Deville and his collaborators was such that continual advances were made in the accuracy of the determinations. The final methods were set out by Deville and Stas in 1877–1878 and these remained the last word on the subject for a generation or more afterwards (25). All these labours connected with the metre filled up the last years of Deville’s life, but he had the satisfaction of seeing them completed before he died in 1881.

Conclusion

The important invention of the lime furnace by Deville and Debray enabled platinum to be melted commercially on a large scale for the first time and remained the sole means of effecting this until the coming of the induction furnace a great many years later. But it must not be thought that this at once solved all the problems of the fabricator of platinum. It provided him with a means of preparing alloys but it was not the answer to all the questions raised in handling pure platinum. Here problems of purity gradually grew to be of paramount importance and it became evident that not only were the gases of the blowpipe capable of introducing impurities (and not only gaseous ones) into the melt, but that at the high temperature involved the refractory was capable of yielding them too. The former could introduce oxygen, iron dust, and carbon and sulphur products from the coal-gas; the latter calcium and silicon from the reduction of the oxides of these elements in the lime. So the forging of sponge continued for a long time, and was still used by refiners for many years.

In addition to the introduction of melting, Deville’s work covered the commercial analysis, the refining, the alloying and the fabrication of all the six members of the platinum group metals. Over twenty-five years of careful experimental work in these fields by such an experienced scientist put at the disposal of the platinum industry a rationalised technique that formed the basis for the
For sixty years, until the development of the Ajax-Northrup high-frequency induction furnace in 1918, the melting of platinum and its alloys was carried out on an industrial scale in the lime block furnace introduced by Deville and Debray, with an oxy-hydrogen flame and the tilting of the furnace to pour the molten metal into an ingot mould.

operations of all the firms working in it for at least the next thirty or forty years. In the hands of Deville, science and practice were brought together and an important industry made possible.

In July 1981 to commemorate the centenary of Deville’s death, an appreciation of his life and work was compiled by Dr. J. C. Chaston (26) who concluded his contribution with these words:

"The platinum industry has, since then, expanded to an extent far beyond anything he could have foreseen, but among those who laid its foundations there are few who deserve commemoration more than the modest, hard-working research worker and teacher, platinum chemist and technologist, Henri Sainte-Claire Deville."

The successful adoption of Deville and Debray’s method of melting platinum by leading refiners in England, France and Germany will be described in the following two chapters.
References for Chapter 15

1. E. F. Smith, The Life of Robert Hare, Philadelphia, 1917
4. E. F. Smith, *loc. cit.*, 8
7. E. D. Clarke, The Gas Blow-pipe, or Art of Fusion by Burning the Gaseous Constituents of Water, London, 1819
12. M. A. Gaudin, *Comptes rendus*, 1838, 6, 861–863
15. French patent 18532, British patent 1947, of 1857
16. H. Sainte-Claire Deville and H. J. Debray, *Ann. Chim.*, 1859, 56, 385–496. This was also published as a pamphlet
19. B. S. Jacobi, About Platinum and its Use in Coinage, Imperial Academy of Science, St. Petersburg, 1860 (in Russian)

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Joining P. N. Johnson as an apprentice at the age of thirteen, he retired as Chairman of Johnson Matthey and Co. Limited when he was eighty-four. During this extraordinarily long career he developed the refining and fabrication of platinum from a laboratory scale to a successful industrial operation upon which his successors have been able to build. He was elected a Fellow of the Royal Society in 1879.

From a portrait in the possession of Johnson Matthey

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