Henri Sainte-Claire Deville

HIS OUTSTANDING CONTRIBUTIONS TO THE CHEMISTRY AND METALLURGY OF THE PLATINUM METALS

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The centenary of the death of Henri Sainte-Claire Deville, teacher, chemist and technologist, is a reminder of the quite exceptional part he played in laying the foundations of the modern platinum industry.

Pasteur said of him that throughout thirty years "he bore aloft in France and in Europe the sceptre of Mineral Chemistry"; the Académie des Sciences, in honouring his memory with the posthumous award of its Prix Jean Reynaud, described his work on dissociation as "one of the purest gems in the Crown of French Science"; he and Michael Faraday visited each other back and forth over a period of 30 years, and in 1877 George Matthey wrote

Henri Sainte-Claire Deville
1818–1881

Professor of Chemistry at the École Normale in Paris, Deville followed up his researches on the production of aluminium by studying the metallurgy of the platinum metals. In 1857 he and Jules Debray devised the lime-block furnace fired by a mixture of oxygen and coal gas which for the first time made it possible to melt platinum and its alloys on a large scale. Their method remained in use until the development of the induction furnace in the 1920s that "the great bond of sympathy between us, beyond that of personal friendship, has been the advancement of a special branch of science which so greatly interests us—the treatment and separation of the platiniferous group of metals for scientific purposes". He set off to master the problems of inorganic chemistry at high temperatures and on the way he revolutionised the platinum industry.

Henri Sainte-Claire Deville was born on March 2nd, 1818 on St. Thomas in the Virgin Islands where his father, an emigré from Bergerac in France, was a prosperous ship-owner who was accustomed to deputise for the Dutch governor when the latter was away in Europe. Henri and his elder brother, Charles, were sent to Paris to be educated. At first he studied medicine but, attending the science lectures at various schools, he came under the influence of Thénard's lectures on chemistry. Berzelius came from one of Thénard's lectures and said "I have been a teacher of chemistry for 20 years, but not until now have I seen how it should be taught". Thénard for his part recognised the quality of his student and influenced Deville's appointment in 1845 as Professor of Chemistry at Besançon and as Dean of the Faculty of Science newly created there.

Professor at the École Normale

Six years later Deville moved to Paris as professor at the École Normale Supérieure, where he remained for the rest of his life, his laboratory becoming one of the outstanding research centres of the Continent. From 1853 he also served as substitute lecturer for Dumas at the Sorbonne, being appointed titular professor there in 1866.

From the first he displayed those special talents that guided him throughout his career. He was an enthusiastic teacher, illustrating his lectures with "unexpected figures of speech and analogies" and using original teaching aids which, as Le Chatelier said, "remained vivid in the memory because they produced an impression in our minds, unconscious perhaps, but nevertheless deep and deliberately so planned".

He was a persuasive communicator, as he showed in 1855 when his proposals that the new metal, aluminum, would be ideal for lightweight body armour, cuirasses and helmets so impressed the Emperor Napoleon III that he was given a grant for a pilot plant for its production.

Very early he developed a pattern of working that he followed unchanged. At the centre was his laboratory, which was unusually spacious. Here, in the words of Dumas he considered that

> "the head of the laboratory must himself be a model of diligence, devoted completely to his work, patient, working with his own hands; the first to set to work, the last to stop".

Dumas went on to say

> "from the moment he entered the laboratory at the École Normale to the day he was kept away from it by the illness to which he was to succumb, Deville was the most assiduous, the most unassuming, the happiest of those whom the love of science had brought together there".

Throughout, his approach to chemical problems and ideas was direct and clear-cut. He had no use for abstractions. He would have agreed with A. N. Whitehead's precept that "it is a safe rule to apply that when a mathematical or philosophical author writes with a misty profundity he is talking nonsense". His starting point was nearly always based on analytical studies, which he claimed gave the investigator the clearest possible insight into inorganic reactions.

High Temperature Reactions

The ten years following Deville's appointment at the École Normale were ones of quite exceptional activity and achievement. From the outset he was attracted to dry methods of chemical analysis and this may have directed his interest to high temperature reactions generally. His first major project brought out all his skills as an experimenter and as a chemical engineer. In 1854 Deville, seeking to obtain a dichloride of aluminium, repeated Liebig and Wohler's procedure of passing the vapour of aluminium chloride over heated potassium and obtained beautiful bright

Jules Henri Debray
1827–1888

First a pupil then an assistant and later a collaborator of Deville's. Debray eventually succeeded him as Professor at the École Normale. Their association was extremely close, and their joint work on the melting of platinum and its alloys extended over many years

globules of aluminium. Impressed by the possibilities of the new metal, he investigated production on a larger scale. He quickly found that sodium could be used in place of potassium, and was much safer to handle, so he set about making sodium on a factory scale by reducing sodium carbonate with carbon in the presence of lime. The alkali metal could be cast into ingots with comparative safety, and in four years the cost of a kilogram was reduced from 2000 to 10 francs. In the process for reducing aluminium, as finally developed, ingots of sodium were mixed with the double sodium aluminium chloride, made from purified bauxite, charged into pans, and heated in an iron tube to 200 to 300°C. It was found that the inclusion of cryolite in the charge increased fluidity and helped in the collection of the metal. In 1855 Dumas was responsible for introducing Deville to the Emperor, as noted above, and a few months later the first ingot from the pilot plant set up in Jarvel was presented to the Académie. Very soon a company, Nanterre Société d'Aluminium was formed, Deville, Debray, Morin and other chemists subscribing 50,000 francs, and a works was built at Nanterre. Deville returned to his laboratory.

The difficulties encountered in some of his researches—particularly on silicon, boron, and titanium—impressed Deville with the need for better methods of producing high temperatures. In 1856 he, with his former pupil, collaborator, and successor as professor, Jules Henri Debray, published an extensive study of the use of city gas or hydrogen and oxygen in blowpipes and their application to welding and melting (1). At first, Deville and Debray used the equipment to produce good-sized specimens of a number of metals with a hitherto unattained degree of purity. Chromium and manganese were reduced from their oxides with sugar charcoal, and nickel and cobalt from their oxalates. Crucibles were made from lime or magnesia, and it was shown that these would react with silica and other impurities and slag them away.

Four Years of Intense Activity

The two investigators then turned to the platinum metals and four years of intense activity followed, during which they developed the lime furnace for melting platinum and the platinum metals. Their final design, shown here, remained virtually unchanged for 70 years or more. It consisted of two cylindrical blocks of lime, bound with steel strip. A hollow was formed in the lower block to contain the molten metal, a pouring channel being provided to the edge. The upper block was also hollowed, forming a roof pierced in the centre to receive the burner. The original lime blocks were fired from chalk mined at the outskirts of Paris.

The results of their studies were published in 1859 in a paper "Platinum and the Metals which Accompany it" which has never really been accorded the recognition it deserves as a classic (2). It describes for the first time the properties of each of the six platinum metals in the massive form. Using a small lime furnace the authors were successful in melting all the platinum metals except osmium (which they obtained as a dense chalky mass), determining their properties, and for the first time measuring their density and observing such physical characteristics as their ductility and ease of working. They showed that the six metals could be arranged in two groups, according to their specific gravities, three heavy and three light, as below (values in brackets are those now accepted).

	Specific Gravity
Platinum	21.15 (21.45)
Iridium	21.15 (22.65)
Osmium	21.4 (22.61)

	Specific Gravity
Palladium	11.8 (12.02)
Rhodium	12.1 (12.41)
Ruthenium	11.3 (12.45)

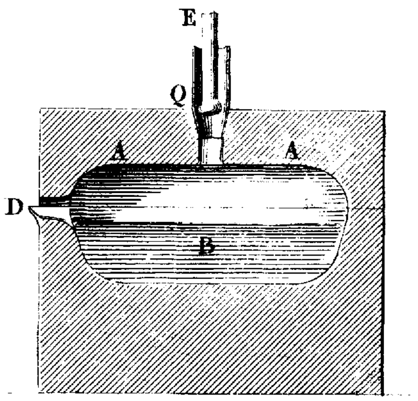
and they observed correctly the order of their fusibility.

In the second part a complete scheme of analysis of the platinum metals was set out in detail.

Finally they proposed a novel, simple, and economical fire extraction process for producing a ductile and industrially useful ternary iridium-rhodium-platinum alloy directly from the Ural minerals. These were extensive alluvial deposits of the following general composition:

	Per cent
Platinum	77
Iridium	3.7 – 5.7
Rhodium	0.3 – 3.3
Palladium	1.5
Gold	0.4
Copper	4
Iron	12
Native Osmiridium	0.5
Earthy matter	1.4

Although of course nobody could have known it at the time, these were to constitute the source of over 95 per cent of the platinum recovered in the world for the next 60 years or so, until the end of the First World War. Deville and Debray showed that if the mineral, after cleaning away osmiridium and earthy matter, was melted in a lime furnace using an oxidising flame, any osmium with palladium, gold and any silver would distil off (and could be collected) while copper and iron would oxidise, combine with the lime, and be slagged off. Thus a platinum-



An original drawing of the lime-block furnace devised by Henri Sainte-Claire Deville and Jules Henri Debray for the melting of all the platinum metals except osmium. The upper cylinder A *was hollowed out and pierced at* Q *to receive the oxygen-coal gas burner* E, *the lower block* B *also being hollowed out to hold the platinum, which was cast through the pouring hole* D *by tilting the furnace. George Matthey acquired the British patent in 1858 and after some initial difficulties successfully operated this type of melting unit for many years*

The opening page of one of Deville and Debray's papers on the metallurgy of the platinum metals giving a detailed account of their experiments and the treatment of native platinum carried out for the Russian Government

DE LA

MÉTALLURGIE DU PLATINE

ET DES

MÉTAUX QUI L'ACCOMPAGNENT,

PAR MM. H. SAINTE-CLAIRE DEVILLE ET H. DEBRAY.

Nous avons exposé, dans le LVI^e^ volume de ces *Annales*, un projet de métallurgie nouvelle du platine fondée sur l'emploi des moyens de la voie sèche : notre travail était fini et publié, lorsque le Gouvernement russe, par l'intermédiaire de M. Jacobi, conseiller d'État et membre de l'Académie des Sciences de Saint-Pétersbourg, nous proposa d'étudier, sur une échelle relativement assez grande, toute la partie pratique de la question que le manque de matériaux nous avait obligés de négliger momentanément. Nous avons accepté cette mission avec empressement, en nous imposant à nous-mêmes la condition de diriger nos travaux de telle manière qu'ils pussent être adaptés le plus complétement possible aux besoins du Gouvernement russe. La Monnaie de Russie reçoit en effet chaque année des quantités de minerai de platine de l'Oural assez variables, qu'elle traite elle-même par un procédé qui sera bientôt

iridium-rhodium alloy would remain and could be cast into ingots. Refinements to the process included the preliminary alloying of the mineral with lead or galena to separate the native osmiridium and earthy matter, and the addition of crushed lime to provide additional slagging material to the melt in the lime furnace. The lead alloy was subsequently cupelled to leave the platinum-rich material for melting. Finally, in order to control the composition of the ternary alloy within desired limits, it was proposed that calculated amounts of iridium, derived from roasted osmiridium, should be added to the melt. It was possible to recover the osmium from the osmiridium mineral by simple treatments, but there was little use for the metal or its compounds and Deville preferred simply to roast the mineral and allow the volatile osmium tetroxide to escape up the chimney stack with the furnace gases.

As long ago as 1813 Berzelius had approached Wollaston through their mutual friend Marcet to enquire "if it would not be possible to have a little malleable platinum not separated from its natural alloy with palladium, rhodium, etc. to make a crucible". Those he had brought recently were "noticeably purer than those I formerly had and for that very reason unfortunately were more susceptible to attack by other substances". Wollaston laughed at the idea and countered with a caustic ill-considered suggestion that if greater durability were required then the user might alloy the platinum with a little silver! How Berzelius was to do this was not explained.

Yet in fact the ternary alloy now proposed by Deville was ideal for nearly all the known applications at the time—for laboratory apparatus, for acid boilers, and for chemical plant generally.

In 1873 the President of France, Louis Adolphe Thier, 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

Also it was just about as stable at high temperatures in air as pure platinum; and not susceptible—like richer iridium-platinum alloys—to loss of alloy constituents by selective oxidation. A calculation suggests, for instance, that an alloy of the composition given below would evaporate unchanged in composition in air at 1500°C:

Platinum	balance
Iridium	1.5 wt.%
Ruthenium	0.025
Palladium	0.003
Rhodium	up to 20%
Silver	0.003
Gold	0.0015

The precise values could be permitted appreciable deviation from the above.

Russian Interest

The first, and very prompt, reaction to this work came from the Russian government, who were considering the reintroduction of a platinum coinage which had previously been in circulation from 1828 until its withdrawal in 1846. The industrial adviser to the Department of Trade and Industry of the Ministry of Finance, the Academician Boris Yakobi, known also as Moritz Jacobi, at once saw the advantage of the Deville process as a means of providing a coinage alloy. In particular, it seemed that it should eliminate the trouble of the iron-contaminated insoluble residues which had accumulated and plagued the refinery in the wet process used earlier. An agreement was quickly concluded by which the Russian government financed the setting up of furnaces and plant for producing oxygen at the École Normale to form a pilot plant in which Deville and Debray treated 56 kilograms of mineral, demonetised coinage, and refinery residues. The samples were received on 23 February, 1860 and by 15 June, "after $3\frac{1}{2}$ months of incessant work, day and night" they delivered back 42.080 kilograms of alloy in the form of rolled sheet ("thin" and "very thin"), cast ingots, and polished plates together with samples of the platiniferous lead before and after cupelling and an ingot of cast iridium weighing 1.805 kilograms. There was a loss of 580 grams of material by "an explosion during roasting". The loss of platinum in the whole operation was put at 120 grams. An exceptionally full and detailed account of this test was given in a second paper in *Annales de Chimie et de Physique* (3), with particulars of the amounts of galena, lead, fuel, and reagents consumed. The one omission was the cost of labour.

Unfortunately, at about the time this work was concluded the Russian government abandoned all thoughts of a new platinum currency and no further progress was made in applying Deville's process in this direction.

As far as can be ascertained, none of the European refiners, George Matthey, the firm of Desmoutis, Chapius and Quennessen, nor Hereaus ever showed the slightest interest in producing the ternary alloy or in exploiting its application, although Quennessen had been in constant touch with Deville throughout his experimental work and had apparently carried out all the rolling.

Difficulties with the Lime Furnace

George Matthey first heard of the work on platinum through M. Paul Morin, one of the chemists associated with the Société d'Aluminium de Nanterre, whom he met in Paris in 1855 when he was visiting the Paris Exhibition. Patents on the process of melting platinum in a lime crucible were taken out in July 1857 in France (Patent No. 18532) and in England (Patent No. 1947) in the name of Debray and were assigned to the Société d'Aluminium.

However, in August the English rights were offered to the London firm and in September George Matthey went over to Paris to meet Deville and Debray, taking with him a quantity of platinum and residues to be melted. He was sufficiently impressed with all he saw that by December he acquired the British rights to the process for 12,500 francs, or £500.

In London, Matthey at first found very great difficulty in melting platinum in the lime furnace, and it was not until the end of May 1861, after a visit from Deville's laboratory assistant, that success was achieved. The main problems were concerned with the pressure of the gases and in particular with the production of oxygen, for which the most favoured process was by heating manganese dioxide in iron pipes in a reverberatory furnace. Progress thereafter was rapid, and in 1862 Deville and Debray reported (4) that one of them

> "had recently had the opportunity of witnessing our process applied with great success by a clever English manufacturer, Mr. Matthey of London. An ingot of platinum of 100 kilogrammes (3215 oz.T) was melted in a lime furnace with lighting gas and oxygen. The mass became so liquid that it filled exactly with metal every part of the mold and reproduced all its imperfections with unexpected precision. The experiment occupied 4 hours but it took about half this time to heat the furnace itself".

The oxygen was produced by decomposing 22 kilograms of potassium chlorate mixed with the same weight of manganese (dioxide).

By this time it is evident that the use of the lime furnace was expanding in Europe. Deville and Debray noted that Hereaus used iron moulds—which they had abandoned—but had adopted the procedure of placing a strip of platinum about 1 mm thick at the bottom of the mould to act as a protection against the first impact of the stream of molten platinum. Deville claimed that platinum tubes made from melted platinum were free from the porosity found in tubes made from Wollaston-type material made from pressed sponge. Deville and Troost described an experiment in a paper published in 1863 in *Comptes Rendus*, and (5) translated in *Chemical News*, in which air was passed through a platinum tube 1 mm thick surrounded by hydrogen contained in an outer porcelain tube. No porosity was observed at 1000°C but at 1100°C the air emerging from the tube made from pressed platinum contained up to 22 per cent of hydrogen. A tube made by George Matthey from melted platinum showed no porosity at either temperature.

By the early 1860s Deville's real interests had passed on to the phenomena of dissociation at high temperatures, and for the rest of his life his most memorable work was to be in this field.

Problems with the platinum metals continued, however, to engage much of his working time. At the time of the Great International Exhibition in Paris in 1867 Jacobi had been very active in discussing the need for establishing standard weights and measures, and on his return to Russia recommended general recognition of the metric system and proposed the formation of an International Bureau of Weights and Measures. Deville found himself drawn into the project and after a good deal of experimental study recommended that the alloy of 10 per cent iridium with platinum should be adopted for all standards. For many years subsequently he was closely involved in melting and casting the ingots required and in personally conducting density measurements to determine their porosity as well as making extensive chemical analyses.

Deville's work received wide recognition both in France and throughout Europe.

He died at his rather modest summer home at Boulogne sur Seine just a hundred years ago on July 1, 1881, at the comparatively young age of 63. It is recorded that throughout his life at the conclusion of a long investigation he was prone to suffer acute fatigue, from which he needed periods of relaxation for recovery. The long and tedious years spent in density determinations and in analytical checking during the manufacture of the prototype metre standards were said by his biographer, Gray, to have taken a heavy toll of his strength. He was devoted to his elder brother Charles and the bond was strengthened when one of his five sons married Charles's daughter. He refused to allow his name to be put forward for election to the Académie before his brother had been chosen. The death of Charles in October 1876 was a profound personal tragedy, while his health was seriously affected by poisoning from osmium tetroxide which certainly caused intense irritation to his eyes.

On this centenary of his death the platinum industry has good reason to look back at the contributions it received from the laboratory at the École Normale where open house was held each Sunday:

> "After each week there was a brisk clean-up, early on Sunday morning, and then the doors were open to all. Students, alumni, friends, philosophers, mathematicians, industrialists, naturalists, and scientists of all varieties found these informal gatherings pleasant and instructive".

J. B. Dumas later wrote:

> "You came away at ease with others and with a feeling of contentment with yourself. You had learned something, you had furnished your bit to progress: there you were surrounded by great talents and eminent minds, who did not haggle over crumbs of praise, but were prompt to express admiration, were strangers to envy, ignoring jealousy and practising the utmost tolerance. These memories will be the eternal honour of the École Normale"

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.

Acknowledgements

For much background information I am indebted to an excellent bibliographical essay on Sainte-Claire Deville by Ralph E. Oesper and Pierre Lemay in "Chymia–Annual Studies in the History of Chemistry", 1950, 3, 205–221. A short biography by a contemporary J. Gray, "Henri Sainte-Claire Deville, sa Vie et ses Travaux" was published in Paris in 1889 and includes a bibliography, claimed to be complete, of over 200 books, pamphlets and papers.

References

1 *Ann. Chim. Phys.*, 1856, **46**, (3), 182–203
2 *ibid.*, 1859, **56**, (3), 385–496
3 *ibid.*, 1861, **61**, (3), 5–146
4 *Comptes Rendus*, 1862, **54**, 1139; *Chem. News*, 1962, **6**, 150–151
5 *Comptes Rendus*, 1863, **56**, 977; *Chem. News*, 1863, **7**, 294