

# Henri Étienne Sainte-Claire Deville: A Physician Turned Metallurgist

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**Henri Étienne Sainte-Claire Deville (1818-1881) is well known for his work on metallurgy, on the separation and preparation of many metals on a large scale and in a very pure state, and developing the concepts and principles of the dissociation of gases. He was the first to prepare  $N_2O_5$  in crystalline state and to develop an inexpensive process for the industrial manufacture of sodium and aluminum. Among the many metals he separated successfully are silicon, magnesium, platinum, iridium, osmium, manganese, and chromium. His development of the platinum-iridium alloy led to its adoption for manufacturing the meter and kilogram standards.**

**Keywords** aluminum, Deville, dissociation, iridium-rhodium alloy, magnesium, metric standards, silicon

## 1. Life and Career

Henri Étienne Sainte-Claire Deville (1818-1881) (Fig. 1) was born in Saint-Tomas (Antilles) on March 11, 1818, the youngest of the three sons of a French immigrant who had become a prosperous ship owner and a leading citizen in the islands, which were then under Danish authority.<sup>[1-3]</sup> Even though the father never gave up his French citizenship, he took over the functions of the Danish governor of the Virgin Islands when the latter was away in Europe. When the boys reached the proper age, they were sent to Paris to be educated at the Institution Sante Barbe (which afterward became the Collège Rollin). There, Henri and his elder brother, Charles (1814-1876), were enrolled in the same class and received a solid foundation in the traditional classic curriculum. Charles became a geologist, a student, and later successor of Léonce Élie de Beaumont (1798-1874) at the Collège de France, while Henri became a physician and then turned to the physical and chemical sciences. Two classmates of Henri at Sante Barbe, Félix Polydore Bouley (1806-1835) and Félix Gaspar Ravaisson (1813-1900) (who afterwards became his colleagues at the Institut de France), had already taken note of his intelligent, sharp, impulsive, and charming personality.<sup>[2,3]</sup>

While following his medical studies at the Sorbonne, Henri took the opportunity to pursue his scientific interests and voluntarily attended other courses, particularly the ones on chemistry given by Louis-Jacques Thénard (1777-1857) at the Faculté de Médecine. Chemistry so much captured his attention that already by 1839, when he was only 21 years old, he installed a small and modest chemical laboratory in the Rue de la Harpe where he repeated the experiments of the courses he had attended and recorded in all details. In this manner, he achieved a very high degree of manual dexterity.<sup>[2]</sup>

Deville's first scientific paper was in the area of essential oils and resins (e.g., turpentine and balsam of elemi balsam of Tolu), particularly the isomeric reactions that took place in the presence of acids and other reagents.<sup>[4]</sup> The review committee of the Académie des Sciences, formed by Théophile-Jules Pelouze (1807-1867), Louis-Jacques Thénard (1777-1857), and Jean-Baptiste André Dumas (1800-1884), to examine his memoir was very enthusiastic about his findings. Dumas concluded the report with these words:

“Les difficultés du sujet abordé par l'auteur, le soin consciencieux qu'il a porté à toutes ses expériences et la nouveauté de quelques-uns de ses résultats, ont déterminé la Commission à proposer à l'Académie d'insérer son Mémoire dans le *Recueil des Savants Étrangers*”<sup>1</sup>

(The difficulties of the subject taken up by the author, the conscientious care that he has given to all of his experiments, and the novelty of some of his results, determined the committee to recommend to the Académie that his memoir be included in *Recueil des Savants Étrangers*). This was an unexpected honor for a young man of 21 years. He felt it in all its meaning, and from then on he devoted all his efforts and time to science.<sup>[2]</sup>

In the following years, Deville extended his research on essential oils and resins, and published additional papers about their properties and chemical reactions, particularly about turpentine, the isomeric transformations of which were attracting the attention of many chemists.<sup>[5-12]</sup> From resins and essences he recovered methyl benzoate, the first compound ester to be extracted from a natural product. From the balsam of Tolu he obtained a hydrocarbon, which, due to its resemblance to benzene, he named *benzoene*.<sup>[9,10]</sup> Toluene had been isolated in 1837 by Pierre-Joseph Pelletier (1788-1842) and Philippe Walter (1810-1847) by the distillation of pine oil; they correctly determined its composition and, noting that it contained the benzoic radical, named it *retinaphtha*. Deville believed his benzoene was isomeric with retinaphtha. Alexander Glenard

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<sup>1</sup>*Recueil des Savants Étrangers* was published by the Académie des Sciences, as an outlet for selected scientific contributions of non-members and aspiring academicians.

(1818-1894) and Boudault obtained retinaphtha by destructive distillation of dragon's blood (a bright red gum or resin exuded from the fruit of the palm *Calamus Draco*); hence, they proposed the name *dracycle*. Eventually, after the work of Cahours<sup>[13]</sup> on the products of the distillation of wood, the identity of the three products was established definitely, and the name benzoene was changed to toluene. By the end of the 19th century, toluene would play a key role in the development of dyes derived from coal.

In 1842, Deville married Mlle. Girod from l'Ain, the daughter of a general and deputy of l'Ain. They had five children. In 1843, Deville received his degrees of Docteur en Médecine and Docteur ès Sciences. In 1851, a happy event took place that would definitely change the course of his work. In the late 1840s, French higher education began to be reorganized. Public teaching affairs at that time were dealt with by the Conseil de l'Université de Paris, which was composed of a small group of illustrious persons in the fields of letters and sciences. Thenard was in charge of the science area, and he was a firm believer in the policy of appointing young men of promise to positions of responsibility. Having been assigned to organize the recently inaugurated Faculté des Sciences à Besançon, he did not hesitate to send three promising young men there: Victor Puiseux (1820-1883) for mathematics; Achilles Ernest Deless (1817-1881) for geology; and Henri Deville for chemistry. Thenard not only appointed Henri Deville to organize the Faculté de Médecine at Besançon, he also appointed him to the chair in chemistry and Doyen (dean) of the Faculty.<sup>[2]</sup>

Deville had hardly installed himself in his new position when the municipal administration of Besançon requested him to analyze the waters of the river Doubs and its nearby tributaries from the public viewpoints of nutrition and hygiene. The results of this research led to two publications in which Deville not only answered the queries of the city but also gave a more general description of potable waters.<sup>[14,15]</sup> For the first time, he demonstrated that they invariably contained silicon derivatives and nitrates, a fact that explained their fertilizing action.<sup>[2]</sup> His results were later confirmed by Jean-Baptiste Boussingault (1802-1887) and were shown to have an important bearing on agriculture.<sup>[3]</sup>

Much more significant work, related to polybasic acids (acids that can form many salts with the same metal, such as sulfuric and phosphoric), was done in 1845. Acid anhydrides (then called water-free acids) had been prepared only in the case of polybasic acids. Charles-Frédéric Gerhardt (1816-1856) had remarked that all these acids were known in the anhydrous form and that monobasic acids (forming only one salt with metals) could not be obtained in an anhydrous form. Deville, who did not like to be limited by unproven theoretical considerations, began to work on the subject and eventually succeeded in preparing nitric pentoxide ( $N_2O_5$ ) by passing dry chlorine over dry silver nitrate in a U-tube heated to 60 °C and by condensing the volatile product with a freezing mixture. Analysis proved the crystalline material formed to be  $N_2O_5$ .<sup>[16,17]</sup> Deville sent the samples of the colorless crystals in sealed ampoules to Dumas, who promptly showed them to the Académie. This exceptional finding placed Deville in the spotlight in the world of chemists.

Some time later, in 1851, François Ernest Balard (1833-1894) was appointed to the Collège de France and vacated the

position of Maître des Conférences at the École Normale (the purpose of this institution was the training of teachers for the secondary schools; there were no facilities of advanced work). The position was offered to Deville. It paid the modest sum of 3000 francs per year, which was much less than the salary of dean of the Faculté de Besançon. Deville nevertheless accepted it because it allowed him to be part of a medium where he was well known, as well as to pursue his scientific interests more freely. Within three years, Deville established his laboratory at the École Normale and worked there for the next 30 years. According to Dumas:

“L'École Normale, ignorée des chimistes jusqu'à ce moment, devint ainsi, sous l'influence d'Henri Deville, et de son école, l'un des principaux centers, dans le monde entier, du haut enseignement de cette science et l'une des sources les plus fécondes en nobles vérités. La Chimie minérale, qu'on disait épuisée, vint s'y rajeunir et briller d'un grand éclat.”

(The École Normale, until then ignored by chemists, became under the influence of Henri Deville and his school, one of the principal centers in the whole world for the teaching of this science, and a most fertile fountain of noble truths. Mineral chemistry, which was said to be exhausted, rejuvenated and shone with great splendour.<sup>[2]</sup>)

Among Deville's most distinguished students at the École were Henri Debray (1827-1888), Paul Hautefeuille (1836-1902), Desiré Jean-Baptiste Gernez (1834-1910), Henri Caron, Louis Joseph Troost (1825-1911), and François-André Isambert.

In 1853, Jean-Baptiste André Dumas (1800-1884) appointed Deville as deputy to his chair at the Sorbonne. This substitution lasted for 13 years until 1866. The following year Deville was appointed *professeur titulaire* (full professor). In 1861, Henri was elected to the Institut de France (receiving 50 of the 57 votes cast) replacing Pierre Berthier (1782-1861).<sup>[2]</sup>

After a few years of research, aluminum (Al) would come from his laboratory at the École Normale, not in the form of impure grains, which were easily attacked, but in the form of ingots that were almost as inalterable as silver (Ag) and were ready to be used in many applications.<sup>[18-24]</sup> After that came boron (B),<sup>[25,26]</sup> silicon (Si) in crystals similar to carbon (C),<sup>[19,27-29]</sup> and magnesium (Mg) in ribbons and wires,<sup>[30]</sup> yielding a light more brilliant than that of the electric arc. It was there at the École Normale that Deville taught the art of purifying and melting platinum (Pt), a metal that was reputed to be infusible by the strongest fire, and iridium (Ir), which was even more refractory.<sup>[31]</sup> Thanks to his methods, the bar metals that were prepared served as the kilogram and meter standards in many countries in the world, the standards differing between countries by no more than one-thousandth of a millimeter. In this laboratory, Deville also devised many new methods for the analysis of minerals<sup>[32-36]</sup> and measured the density of vapors at temperatures that had been thought to be unachievable.<sup>[37]</sup> He carried out the experiments that led to a new law of dissociation, which served to show the continuity between physical and chemical phenomena.<sup>[2,38-43]</sup>

Work on the preparation of different metals brought into focus the inadequacy of the available furnaces that were used to achieve the required high temperatures. Already by 1852

Deville had developed laboratory furnaces, which were heated by coke, oil, C, or hydrocarbons (including turpentine), that burned under forced draft. In 1856, he published an extensive discussion of the production of very high temperatures by means of illuminating gas fed with oxygen (O).<sup>[44]</sup> This procedure was quickly adapted by industry and led eventually to the application of autogenous welding. These furnaces allowed him to produce for the first time, in large quantities and with high purity, metals that were not easily melted [e.g., Mg and chromium (Cr)] by reducing their oxides with sugar, C, nickel (Ni), and cobalt (Co) by heating their oxalates.<sup>[2]</sup> In 1872, the International Commission on Weights and Measures commissioned Deville to prepare the alloy (90% Pt, 10% Ir) from which the standard kilogram and meter were to be manufactured.<sup>[3]</sup>

After visiting the laboratories of Michael Faraday (1791-1867) in London, Deville translated into French and annotated Faraday's book, adding some notes about stearic acid, lamps, illumination with gas, and dazzling lights.<sup>[45]</sup>

The discovery in 1859 of large petroleum fields in North America led rapidly to large investments in their development. During the International Exposition of 1867, many applications of the different fuels as sources of heat and light were exhibited. In the same year, the Emperor Napoleon III commissioned Deville to make a study of mineral oils with a view to their safe and efficient adoption in industry, especially transportation. Deville studied different procedures to eliminate the dangerous volatile fractions of the oils, their physical properties, and their coefficients of expansion. He needed to calculate the amount of free space necessary to avoid a rupture of the containers. He also determined the caloric value of these oils in equipment that simulated industrial conditions.<sup>[3,46]</sup>

In addition to the many scientific honors he received in France, Deville also was elected to be a member of many important foreign societies, among them the Royal Society of London, the Academy of Saint-Petersbourg, the Academy of Berlin, and the Société des Sciences Naturelles de Genève.

In 1882, the Académie des Sciences approved the recommendation of a committee composed of Joseph Louis François Bertrand (1822-1900), Henri Milne Edwards (1800-1885), Charles-Adolph Würtz (1817-1884), Boussingault, and Dumas, to award posthumously the Prix Jean Reynaud (10 000 francs), which was given every five years for the most meritorious work related to each class of the Institute, to Henri Deville. The committee report reviewed the discovery and work on dissociation by Deville and his collaborators, as well as the findings of others, and concluded their account by terming the law of dissociation "l'un des plus joyaux de la couronne de la Science française, l'honneur de Henri Sainte-Claire Deville et de son école" (one of the purest gems in the crown of French science, the honor of Henri Sainte Claire Deville and his school).<sup>[47]</sup>

Henri Deville died at Boulogne-sur-Seine on July 1, 1881.

## 2. Scientific Activities

Deville's most important contributions, particularly in the areas of metallurgy and dissociation, will now be described in detail.

### 2.1 Analysis of Mineral Substances

The analysis of mineral substances,<sup>[32-36]</sup> silicates in particular, was fraught with difficulties. The methods then available did not allow the individual dosage of the different elements to be determined, and the individual weight of several substances could only be obtained by difference. Deville solved this problem by a judicious combination of dry and wet methods of analysis using his *voie moyenne* (average route), which was characterized not only by its wide range of applicability but also by the extensive use of reagents, which were very volatile or easily destroyed by fire so that their excess could be removed easily. The new procedure allowed the individual determination of the components, a precise mass balance, and was particularly adapted to the analysis of natural silicates. In Deville's method, the sample was mixed with pure lime and was heated to "redness." The resulting mass was pulverized and then treated with nitric acid. A series of controlled calcinations was followed by the use of solvents that were either volatile or easily decomposed by heat. In this way, Si, Al, iron (Fe), calcium (Ca), and Mg were eliminated successively by decantation in the form of precipitates. Alkalis separated from other bases were easily determined by titration.

Deville studied the reactions of many metals, such as Fe, copper (Cu), zinc (Zn), Co, Ni, and chrome, particularly the formation of their carbonates. His first memoir on the subject was related to the type and composition of the carbonates produced with the carbonates of sodium (Na) and potassium (K).<sup>[32]</sup> According to Deville, the carbonates of Fe, Cu, Zn, Co, Ni, and chrome were produced in variable proportions with the carbonates of Na and K. Neutral carbonates, sesquicarbonates, and the bicarbonates of Na and K did not react in the same manner with metal solutions. In particular, the last two salts formed double salts that differed among themselves. Although Na and K carbonates were very similar, they did not always yield similar combinations with a given metal. Cu salts were an example. The addition of copper carbonate to a mixture of the two alkaline salts resulted in almost the sole precipitation of Na in the form of very brilliant crystals of a double carbonate, while K remained in solution. Deville was unable to produce with K a crystalline combination similar to that of the carbonate of Cu and Na. Other metals led to very similar results.<sup>[33]</sup>

The general procedure used for preparing samples of double carbonates was very simple: The metal salt was added very slowly and was agitated to yield a concentrated solution of alkaline carbonate. Ordinarily, a portion of the precipitates redissolved. However, another portion transformed into a rather voluminous mass of crystals as the liquor was deposited little by little, losing at the same time its coloration due to the presence of the metal substance contained therein. It seemed that the double carbonate was insoluble in the alkaline carbonate from which it evolved.

Ammonium carbonates yielded, with the carbonates of certain metals, combinations that had been partly investigated by Pierre Antoine Favre (1813-1880). Deville's procedure was particularly appropriate because of the easy preparation of the double carbonates of ammonium with Ni or Co, which was accomplished by contacting the nitrates of these metals with an excess of ammonium bicarbonate in a closed vase. In

this manner, it was possible to produce a salt in the form of mica-like plates that, by their composition, corresponded to the same salt as that produced with potassium bicarbonate.<sup>[34]</sup>

Deville also studied the preparation of different hydrates of double carbonates of ammonium with Mg, Co, Ni, and tin (Sn).<sup>[35]</sup>

## 2.2 Anhydrous Nitric Pentoxide

Deville succeeded in isolating anhydrous nitrogen pentoxide (then called anhydrous nitric acid) by treating dry silver nitrate contained in a U-tube with dry chlorine.<sup>[16,17]</sup> The silver nitrate was first dried at 180 °C under a current of dry CO<sub>2</sub>, while the chlorine (Cl) was dried by passing it over calcium chloride and concentrated sulfuric acid. No reaction took place at room temperature, but when the nitrate was first heated to 95 °C the apparatus filled with a dark red gas, which was proven to be hyponitric acid (NO<sub>2</sub>), easily identified by its color and easy condensation. The solid in the U-tube then was rapidly cooled to 58-60 °C and was kept at that temperature for some time, after which abundant vapors were generated. Cooling the exiting gas stream to -21 °C resulted in the deposition of brilliant and colorless crystals, which were similar to quartz. Deville noted that when the precipitation proceeded slowly from a very cold gas current, it was possible to obtain crystals having edges 1 cm long. Anhydrous nitric acid vapors mixed with carbon dioxide were colorless, but at the moment that a glass ampoule was sealed with a blow-pipe a certain amount of hyponitric acid developed and tinted the gas light red.<sup>[16,17]</sup>

According to Deville, anhydrous nitric acid crystallizes in the shape of six-face right prisms having a rhombic base, melts at about 29.5 °C, boils at about 45 °C, and has a very high vapor pressure at 10 °C. The analysis of this compound was very difficult due to the fast disengagement of gas that took place when the ampoule was broken. The dissolution of nitric pentoxide in water was very exothermic and occurred without coloration and gas release. The aqueous solution reacted with barium hydroxide, producing barium nitrate, which could be easily recognized by its crystalline form.

The decomposition of nitrogen pentoxide by heating began at a temperature slightly above its boiling temperature, a fact that made the determination of the density of vapors difficult. Dry ammonia reacted rapidly with nitrogen pentoxide, forming a nitrous vapor and a white salt composed entirely of ammonium nitrate. When the contact between the two reagents was slow enough, no formation of red vapors was observed, and the reaction was a simple combination of ammonia and anhydrous nitric acid.

Deville's results led Gerhardt to modify his conception about anhydrides. He now assumed that they were formed from two molecules of acids associated with the loss of one molecule of water, and this led him to devise a general procedure for their preparation. Experimental evidence justified his ideas, and Gerhardt had the honor of being the first to prepare organic anhydrides.<sup>[2]</sup>

## 2.3 Sodium and Aluminum

In many regions of France there exist large amounts of clays that owed almost one quart of their weight to a substance that

Antoine-Laurent Lavoisier (1743-1794) had predicted to be metallic.<sup>[18-24,48]</sup> It was generally believed that this earth was a simple substance, but Théodore Baron (1715-1768) and then Antoine-Laurent Lavoisier (1743-1794) in 1782 declared that it was an oxide of a metal that held the O so tenaciously that it could not be removed by heating with C. Until the time of Deville, it had been impossible to separate the metal by any of the available processes. Ordinary metallurgical processes, such as the electrolytic method of Humphry Davy (1778-1819), the ones used by Jöns Jacob Berzelius (1779-1848) for the extraction of Si, and those of Joseph-Louis Gay-Lussac (1778-1850) and Paul Thenard (1819-1884) for boron, had proven unsuccessful. In 1827, Friedrich Wöhler (1800-1882), while heating a mixture of aluminum chloride with K in a Pt crucible, obtained a powdery product, which he described as being able to decompose water at 100 °C.<sup>[49]</sup> The product caught fire when heated in contact with air and was attacked by all acids. No one thought that this material, which was described as Al, had any possible application. Eighteen years later, Wöhler repeated his experiments and obtained a number of globules not larger than a pinhead, but clearly metallic.<sup>[50]</sup> Wöhler did not determine the properties of this material, and thus it did not catch the attention of chemists, including Deville.

Around 1850, Deville became interested in the possibility of preparing a lower aluminum oxide, analogous to ferrous oxide, by reducing aluminum chloride with metallic potassium. He did not find the lower oxide he was looking for but did find a mass of the double chloride of Al and K mixed with voluminous globules of a white brilliant metal, inalterable to air, even at high temperatures, which were unable to decompose water vapor, were resistant to potassium nitrate and sulfur (S) at their melting points, and to nitric acid and hydrogen sulfide, but were easily attacked by hydrogen chloride and potassium hydroxide with detachment of hydrogen (H).

The remarkable physical properties of the metal led Deville to realize immediately the importance of his discovery, which he promptly reported to the Académie. In his exposition, he said<sup>[18]</sup>:

“On comprendra combien un métal blanc et inaltérable come l'argent, qui ne noircit pas à l'air, qui est fusible, malléable, ductile et tenace, et qui présente la singulière propriété d'être plus léger que le verre (densité = 2.56), combien un pareil métal pourrait rendre des services s'il était possible de l'obtenir facilement. Si l'on considère, en outre, que ce métal existe en proportions considérables dans la nature, que son minéral est l'argile, on doit désirer qu'il devienne usuel.”

(It is understandable that a metal white and unalterable like Ag, that does not blacken in air, that is fusible, malleable, ductile, and tough, and that presents the particular property of being lighter than glass (density = 2.56), how much useful such a metal would be if it would be possible to manufacture it easily. If in addition, we consider that this metal is abundantly present in nature, that its mineral is clay, it is desirable that it became common.)

The resources available to Deville at the École Normale did not allow him to pursue his work on the search for an easy method of production of Al. The Académie de Sciences was so impressed by the potential of the new element that they pro-

vided Deville with the necessary funds. In 1855, the results were promising enough for Dumas to approach the Emperor Napoleon III for further funding. Deville exhibited specimens of Al to the monarch, who was intrigued with the idea of fitting his troops with cuirasses and helmets of the new metal. Hence, Deville was given a government grant to defray the costs of pilot plant operations at Javel, and technical success was soon assured.<sup>[3]</sup>

The preliminary work at Javel was followed by technical installations at Rouen and at Nanterre. Deville was assisted especially by his colleagues Henri Debray (1827-1888) and Arthur Morin (1795-1880).

The first ingot produced at Javel was presented to the Académie des Sciences on June 18, 1855.<sup>[23]</sup> By 1856, Deville could state, "I now have no doubt that sooner or later Al will become an everyday metal." The first kilogram cost more than 30 000 francs to produce, but by 1859 the metal could be sold for 300 francs, and toward 1880 it had fallen to 80 francs per kilo. Massive bars of the metal were displayed at the Exposition of 1855, and it was clear that the new material would render inestimable service in many directions. Used at first for jewelry, it quickly outgrew this limited application, where non-oxidizability was valued more highly than lightness, Deville soon prepared Al bronzes, which were quickly used in the manufacture of, for example, tableware, art objects, household utensils, and marine instruments.<sup>[3,23]</sup>

The further introduction of electrochemical methods based on cheap electricity led the price of Al to drop to less than 6 francs per kilogram. This low price allowed the use of Al in many of the applications imagined by Deville.

The first stage in production was the preparation of aluminum chloride, a compound that is highly susceptible to humidity, followed by the removal of chlorine with an alkaline metal. The K used originally by Deville for the reduction of aluminum chloride cost more than 900 francs per kilogram. It was prepared by a rather capricious procedure and was very dangerous to handle. Deville examined the possibility of using Na with very satisfactory results. Unfortunately, Na was extremely rare and hardly known by the chemists. It existed only as a collector's item in the form of globules having an estimated price of 2000 francs per kilogram. At least 4 kg of K were needed to obtain 1 kg of Al, while 2.5 kg of Na was estimated to be necessary to achieve the same result (because the molecular mass of Na is 23, against 39 for K). In addition, Na minerals were more readily available than those of K. Hence, Deville's first efforts were given to developing a procedure for obtaining Na easily and cheaply. Eventually, he succeeded in manufacturing it at a cost less than 10 francs per kilogram. He also studied the properties of Na and showed that it could be melted in the presence of air without catching fire, cooled into ingots, and managed very easily and safely. It could be flattened between two sheets of paper, and could be cut and handled in air without accident, as long as the fingers and the instruments were dry. Slow oxidation of the metal appeared to proceed only at the expense of the moisture of the air. Na was flammable only in the vapor phase, and the rapid combustion of the metal occurred only at such temperatures above its boiling point that its vapor pressure became appreciable.<sup>[2]</sup>

The process for the production of Na, which Deville developed to factory scale, was based on the work of Joseph-Louis

Gay-Lussac (1778-1850), Louis-Jacques Thénard (1777-1857), and Brunner.<sup>[51]</sup> Deville's process involved the high-temperature reduction of a paste in oil of 717 parts of sodium carbonate by 175 parts of charcoal, in the presence of 108 parts of calcium carbonate as a flux.

Deville used as raw material bauxite, containing 46% of its weight as Al and readily available in large quantities in France. The name of the mineral comes from the location of large sources near Baux, in Arles, Provence. It is a hydrated alumina containing between 1 and 45 parts per 100 of ferric oxide, which gives it a color ranging from white to red. Bauxite is also found in large amounts in Hérault, Var, and Bouches-du-Rhône. Until that time, the mineral was exploited on a large scale, particularly for the production of alum for the glass and textile industries.

The first step in the process was the elimination of the iron, followed by conversion of the residue to sodium aluminate and then to alumina. The alumina then was mixed with carbon and marine salt, heated, and then treated with chloride to produce the double chloride of Al and Na, a product more suitable for rendering the metal. Treatment of the double chloride with sodium led to the separation of Al as metallic particles that could be isolated at high temperatures. Later on, Deville found that the separation of the metal was easily achieved by adding cryolite from Greenland as a flux (the same flux is used in modern times). All the technical difficulties, their solution, and details of the development of the industrial process are described in detail in Deville's book.<sup>[23]</sup>

In one of his many publications on the subject,<sup>[21]</sup> Deville gave a detailed description of the properties of Al, particularly the ones he had measured. For example, the electrical conductivity, measured with a Wheatstone bridge, indicated that Al conducted about eight times better than Fe. Al was slightly magnetic, was crystallized rather easily by fusion, and melted at a higher temperature than Zn and a lower temperature than Ag. Its density was 2.56, and its chemical properties located it between the precious metals and the common ones. It resisted the action of O at the highest temperatures achievable, and it was not attacked by water at room temperature or at its boiling temperature. Nitric acid at room temperature, diluted or concentrated, did not attack the metal, but it was easily dissolved by hydrogen chloride, diluted or concentrated. The attack was fast and energetic. At very low temperature, HCl gas attacked Al, yielding aluminum chloride. The metal was not attacked by hydrogen sulfide, did not amalgamate with mercury (Hg), and, when melted with lead (Pb), dissolved a very small amount of this metal. With Cu it produced a light, hard, and white alloy. It could be easily polished with 10% Cu, and with 25% Cu it was harder than bronze and could be filed with difficulty. It alloyed in the same manner with Fe and Ag.

A particular characteristic of Al was its facility in forming with C and Si an easily crystallized gray casting, which was grainy and fragile.

## 2.4 Other Metals

Once Al and Na became readily available, their presence gave rise to new discoveries. Na was found to be a powerful reducing agent, and Al was found to serve both as a reducing agent and as a solvent. As described by Deville<sup>[29]</sup>:



**Fig. 1** Henri Étienne Sainte-Claire Deville (1818-1881), second in the center, behind the bench (By permission of Edgar Fahs Smith Collection, University of Pennsylvania Library).

“Un caractère commun à tous les métaux et que présentent déjà les derniers métalloïdes, c’est la propriété de se dissoudre mutuellement et de former ces combinaisons d’un ordre particulier auxquelles on a donné le nom d’alliages. Les alliages se comportent souvent comme de véritables dissolutions des métaux les uns dans les autres, comparables presque en tout aux solutions aqueuses des sels . . . certains alliages de platine, de ruthénium, d’osmium et d’argent se forment au sein d’une masse fondue où le zinc, l’étain, le plomb servent de dissolvants, qu’il cristallisent pendant le refroidissement et peuvent être séparé au moyen des agents qui n’attaquent que le métal commun mis en excès . . . C’est le principe de la méthode qui a servi à la préparation de le bore et le silicium à l’état adamantin.”

(A common characteristic of all metals and also of the latter metalloids, is their capacity of dissolving mutually and of forming especial combinations called alloys. These alloys behave as true metallic solutions, having a behavior similar to aqueous salt solutions . . . certain alloys of Pt, ruthenium (Ru), osmium (Os) and Ag, form in the midst of a melted mass where Zn, Sn, and lead (Pb) serve as solvents. From there they crystallize by cooling and can be separated by agents that attack only the common metal present in excess . . . This is the principle of the method that has served me to prepare B and Si in the adamantine state.)

Si is almost as abundant in nature as Al. Berzelius isolated it in 1823 in the form of a rather stable powder by treating Si tetrafluoride with K, and he claimed that it was acid forming and gave rise to many silicic acids.<sup>[52-54]</sup>

In 1854, while studying the possibility of obtaining Al from impure sodium aluminum chloride by electrolysis, Deville ob-

tained a solid casting of a gray phase, which was grained and fragile, from which he succeeded in extracting brilliant metallic platelets, similar to the filings of Pt. This form of Si differed from the one found by Berzelius. Initially, Deville did not think that his Si was a true metal. He believed that it was actually to ordinary Si what graphite was to C. When attacked with hydrogen chloride, it released H, giving off a bad odor that indicated the presence of C. Si was easily separated from the cast by the continuous action of boiling HCl.<sup>[19,21]</sup>

Deville returned to these findings in 1856 and 1863. This time he found that passing a slow stream of silicon chloride vapors over pure Al produced very hard pure octahedral crystals. This was a third form of Si, called crystal or adamantine silicon.<sup>[27,55]</sup> Additional work done with Henri Caron in 1863 led to the development of a faster process for obtaining this crystallized Si. When treating potassium fluorosilicate with a mixture of Na and zinc sodium reduced the fluorosilicate while Zn dissolved the Si produced. Since the Zn was more volatile, it could be driven away at high temperature, leaving Si in the form of crystals. The resulting metal had, with even larger inalterability, all the chemical properties that Berzelius attributed to the residue of the incomplete combustion of ordinary Si. For example, it could be heated to white heat in a stream of pure O without changing its weight (and without generating CO<sub>2</sub> like silicon carbide). It resisted the action of hydrogen fluoride and nitric acid, and conducted electricity like graphite. A particular characteristic was the difficulty with which it was attacked by fused red-hot K, although eventually it was completely transformed into silica.<sup>[29]</sup>

In 1808, Thenard and Gay-Lussac had treated boric acid with K and obtained a greenish powder, which was composed

of potassium, potassium borate, and a third substance that they recognized as a new element and named *bore* (boron). B was separated from the mixture by simply washing it with cold or hot water. Thenard and Gay-Lussac determined some of the physical properties of B, studied many of its chemical reactions, and noted particularly the similarity of its properties with those of C, phosphorus (P), and S. For example, B would form borides similar to, for example, carbides and phosphides.<sup>[56]</sup> In 1856, Wöhler and Deville<sup>[25,26]</sup> prepared B by a method modified from that of Thenard and Gay-Lussac: the substitution of K by Na allowed them to obtain a large amount of amorphous B and thus to thoroughly study its properties. They confirmed that B burned in N, a relatively inert material, forming boron nitride. Using Al instead of Na or K yielded beautiful crystals of a hardness, refractability, and brilliancy similar to that of diamond. This is the B variety known today as adamantine boron or B diamond. Wöhler and Deville showed that there were three varieties of boron: 1) crystalline B or B diamond, which was extremely hard, transparent, and colored either garnet or honey yellow (the difference in color was caused by the presence of small amount of impurities, particularly Si, C, or even amorphous B; it resists the action of O but it is easily attacked by chlorine yielding boron chloride; and it is not attacked by a concentrated solution of caustic soda, although a dilute solution of NaOH or sodium carbonates dissolves it slowly; 2) graphitic boron, resulting from the dissolution of the element in Al, which can be prepared easily by treating potassium fluoroborate with Al, and presents itself in the form of opaque pale red hexagonal blades, having the form of natural graphite and graphitic Si; and 3) amorphous boron, which is obtained by heating a small Al globule with a large amount of boric acid. This last variety has all the properties reported by Thenard and Gay-Lussac. Contrary to graphitic boron, the amorphous form burns very easily in the presence of a flame.

Mg is a metal that is as white as Ag and lighter than Al that burns with a dazzling brilliancy yielding magnesia. Antoine Bussy (1794-1882) isolated it in 1831 using Wöhler's procedure for preparing Al (i.e., reacting magnesium chloride with Mg). Similar to the case with Al, Mg had been prepared in very small quantities, which were highly impure and inadequate for determining its properties. In 1857, Deville and Caron<sup>[30]</sup> returned to Bussy's procedure, except that they used Na instead of K. The reduction of magnesium fluoride with Na in the presence of calcium fluoride produced pure Mg in a yield that was 75% of the theoretical. Their method allowed them to prepare a large amount of Mg, which they purified by distillation in C vessels in a H atmosphere. Afterward, they made a detailed study of its properties. Mg was found to be as volatile as Zn at more or less the same temperatures. Sublimation did not leave any residue, and the sublimated material was white and surrounded by a small amount of oxide. In the pure state, it melted at a temperature close to the melting point of Zn. At a slightly higher temperature, it caught fire, producing a brilliant flame.<sup>[30]</sup>

## 2.5 Platinum

Word of the existence in Mexico of an infusible metal reached Europe as early as the middle of the 16th century. In 1749, William Watson (1715-1787) communicated to the

Royal Society his experimental results on Pt and its properties, and also those of William Brownrigg (1711-1800).<sup>[57]</sup> According to Watson, the Spaniards called the metal *platina di pinto* or *platina* because its color resembled that of Ag. Watson was unable to melt the metal even in the presence of borax or other fluxes. Four years later, William Lewis (1708-1781) published an extensive memoir describing the chemical properties of the element.<sup>[58]</sup> He indicated that pure platina was a white metallic substance, slightly malleable, permanent to fire, indestructible by nitre, unaffected by S, and soluble in *hepar sulfuris* (a mixture of various compounds of K and S that is made by fusing potassium carbonate and S). Platina was similar to gold (Au) in that simple acids did not attack it but aqua regia did. Hence, the common methods of Au purification with *aqua fortis* (nitric acid), *aqua regis*, or *regal cement* were no longer reliable when this metal was adulterated with Pt. Platina alloyed with an equal weight of other metals (e.g., Sn, Pb, Ag, Au, Cu, and Fe) making them stiffer and harder. It also alloyed with Hg, bismuth (Bi), Zn, and antimony (Sb).<sup>[59-61]</sup>

Afterward, the mineral also was discovered, for example, in the Urals, California, Australia, and Borneo, as it usually is present in auriferous sands. A crude analysis of the sands indicated that, in addition to Cu and Fe, they contained about 12% foreign matter and 80% Pt, and had variable proportions of five rare metals, called Pt metals. Pt and Os formed a compound that adhered to the steel mortars that were used in trying to pulverize the mineral. This compound resisted the action of aqua regia.

The small concentration in which Pt metals were present and the high price of the raw material were for a long time an obstacle for their serious study. The metals were separated in small quantities in very impure form and were found to resist, without melting, the temperature of the hottest furnaces. The properties of the material were extremely variable and depended on the mineral used for their preparation. Of the six metals present, three, Pt, Ir, and Os, were very heavy, having densities of 21.46, 22.38, and 22.44, respectively. The density of the other three metals, palladium, rhodium, and ruthenium, was 11.4, 12.1, and 12.16, respectively. All were attacked with difficulty by different reagents.<sup>[31]</sup>

It took four years of hard work for Deville and Debray to develop a dry method of analysis that was appropriate for both the Pt mineral and the residues, which accumulated in the industries where these materials were treated. Deville and Debray also measured new properties of the isolated metals or rectified previous ideas, which they proved to be wrong. For example, Os prepared by Berzelius had a density of 7, and Deville and Debray showed that the actual density was 22.44, the highest of all known bodies. In addition, when Os was heated in air beyond the fusion temperature of Zn, it burned, giving off vapors of osmic acid, which was highly smelly and toxic. This acid could be kept indefinitely under vacuum. It was easily reduced by organic matter, particularly nervous tissue, thus justifying its use as an indicator in histologic research. It melted at 40°C, boiled at about 100 °C, and appeared as vapor whenever Os-containing materials (except iridium osmure) were treated with aqua regia. In this manner, it was possible to separate it completely from the mother material.<sup>[31]</sup>

Deville and Debray also developed a method for the com-

plete separation of Ir from Pt. It was sufficient to melt the alloy of Ir and Pt with Pb, which dissolved it. During cooling, Ir crystallized first and Pt solidified afterward. To study these two metals, which the most powerful metallurgical furnaces were unable to melt, Deville and Debray used the large heat released by the combustion of H or illuminating gas with O. With the apparatus they developed for this purpose, they were able to melt 10 kg of Pt in less than 40 min. They also used this procedure to prepare alloys of Pt with Ir and Rh, which had several properties quite different from pure Pt.

This arduous work had hardly been finished when Deville and Debray were called to conduct a large-scale demonstration of the practical application of their results. It was known that in the Urals, particularly at Nijni-Tagilsk, there were Pt sands that were capable of yielding up to 1 g of Pt per 15.5 kg of sand. The Russian government had used Pt for several years in the fabrication of coins. Eventually, after large quantities of Pt were discovered in other regions of the world, it was found that the ratio of the value of Pt to that of Au, fixed at the origin, was substantially higher than their market value. Hence, it was advantageous to introduce forged coins into Russia and to obtain substantial profits from doing it. The resulting fiscal loss led the Russian government in 1843 to withdraw Pt coins from circulation, an act that left it with a stock of over 14 tons of coin metal, as well as significant amounts of residues that were very rich in Pt and Ir. Since the then available methods did not permit the recovery of Pt, the Russian government approached Deville with the request that he study on a large scale the procedures he had developed for treating Pt minerals. Russia financed the construction of large-scale gasometers and reverberation furnaces, which were installed at the École Normale and, at the end of the research project, were donated to the École Normale. Deville and Debray were provided with 32 kg of mineral from the Urals, 16 kg of Pt from coins, and 8 kg of raw Ir, a total of 56 kg of raw material containing 42.2 kg of Pt. With this opportunity, Deville and Debray were able to show on a large scale the economic value of their procedure. Within three months, they produced the metal in different forms (e.g., ingots, thin plates, and wire) with a total weight of 42.080 kg, representing a loss of only 120 g due to the many operations they had performed. All of the Pt manufacturers in Paris and London were enthusiastic about these results and promptly adopted the procedures developed by Deville and Debray.

In 1875, the International Conference of the Meter, comprising the representatives of 15 nationalities, adopted the French system of weights and measures. To bring the system into practice, it was necessary to select a metal that was able to provide the prototypes of the meter and kilogram that was less sensitive to mechanical action and atmospheric agents, and was capable of supporting, without melting, the high temperature to which it might accidentally be subjected. The properties of the Pt-Ir alloy developed by Deville and Debray made it particularly appropriate for this purpose, and thus it was adopted.

Now began for Deville the difficult task of preparing in a state of very high purity the large quantity of Pt and Ir that was necessary for manufacturing the prototypes required by the signatory nations, to test alloys of different composition, to study their properties, and, later on, to prepare the alloy that was finally adopted (containing 90% Pt and 10% Ir). Not only that, they had to verify its composition, eliminate from the

pieces fabricated the impurities introduced by the different fabrications steps, and, finally, bring all the prototypes to a common state of homogeneity. The standards prepared by Deville were incredibly accurate, with the meter standards differing by no more than 1/1000 of a millimeter, and the kilograms by less than 1/100 of a milligram. One of the most serious problems to solve was the inevitable appearance of puffs when manufacturing large ingots. These puffs appeared at the time of the solidification of the metal and were due in particular to the sudden release of the dissolved gas, which was retained as bubbles. The procedure selected was to submit the metal to strong mechanical compressions until a satisfactory density was achieved.

## 2.6 Dissociation

In Deville's time, the determination of the density of a vapor was one of the most important problems of physical chemistry. It provided not only important practical values (e.g., the molecular mass), but it also completed and controlled the analytical results.<sup>[39-43]</sup> It permitted the verification of the law of volumes of Gay-Lussac<sup>2</sup> and provided important information in favor of or against theories about the constitution of matter. Two procedures were then available: 1) Gay-Lussac's method, which was limited to very volatile substances; and 2) Dumas's method, which allowed the determination of the density of the vapor up to much higher temperatures. Dumas's method was applied to all volatile substances that could be heated without decomposition up to the melting temperature of glass (about 500 °C). Most known organic substances decomposed well below this practical limit, but this was not the case with mineral substances. In addition, the heating baths developed by Dumas for his procedure were limited to a temperature of about 300 °C.

In 1857, Deville and Louis Joseph Troost (1825-1911) initiated an extensive study of vapor densities.<sup>[37,38]</sup> They adopted the procedure of Dumas and improved it with some ingenious modifications. First, they substituted liquids baths that were maintained at a constant temperature with great difficulty with baths that used the vapors of a boiling liquid as heating medium, and, second, they substituted glass with Bayeux porcelain, which was able to sustain continuous temperatures of up to 1400 °C. With these modifications, it was possible to use the method of Dumas to determine densities at temperatures up to 1000-1200 °C. As heating media they used the vapors of Hg, S, cadmium (Cd), and Zn, which boiled at 350 °C, 440 °C, 860 °C, and 1040 °C, respectively, and were held in vessels made of forged Fe instead of glass.

Using their improved apparatus, Deville and Troost were able to determine for the first time, with high accuracy, the density of a large number of substances, including simple bodies metalloids and metals, chlorides, bromides, metallic iodides, and ammonia salts, all of which were carefully prepared with high purity. Their excellent measurements explained some embarrassing abnormalities in some physical generalizations that were at that time believed to be true. For example, Dumas had determined that the density of S vapor at 500 °C was 6.654,

<sup>2</sup>In a balanced chemical reaction occurring at constant temperature and pressure, the number of moles of each participant also may be considered as the number of volumes at the given conditions.

a value that decreased at higher temperatures and became constant at 2.2 at temperatures above 800 °C (S vapors are now known to be a mixture of S<sub>8</sub>, S<sub>6</sub>, S<sub>4</sub>, and S<sub>2</sub><sup>[62,63]</sup>). Selenium (Se) and tellurium (Te) showed the same behavior. These values were such that, on the one hand, O, and on the other hand, S, Se, and Te occupied the same volume under equivalent molecular masses at temperatures well above their boiling points. For example, equal volumes of these gases combined with double their volume of H to give the same volume of water vapor, hydrogen sulfide, hydrogen selenide, and hydrogen telluride. Hence, it was necessary to admit that, despite the chemical analogy of these four bodies, the volume of S, Se, and Te that combined with a volume of H was double that of oxygen, which formed water vapor without leaving a residue, and was only one third the volume of O.

Deville's measurements increased the growing number of abnormal vapor densities and led to the establishment of the fact that certain materials exhibit different molecular weights at different temperatures. Then it was possible to explain the abnormal densities as being the densities of a mixture of the original substance and its dissociation products.

The starting point of Deville's explanation of the phenomenon was its comparison with the change in phase of a pure compound. It was known that bodies did not pass abruptly from liquid to gas, and that there was a considerable temperature range within which they could exist in both states. The difference between the various states of aggregation of a body depended on the (relatively large) amount of heat (enthalpy) contained in each of the new phases. At each temperature, the equilibrium established was characterized by the vapor pressure. If during the phenomena of the change of state decompositions also took place, produced by heat, a different interpretation was offered. It was believed that for each body there existed a temperature below which the elements remained combined, and above which they became separated. The great law of the continuity of phenomena then had a unique and surprising exception.

Certain facts appeared to be inexplicable even from this viewpoint, and one in particular. It was known that the combination of H with O released very large amounts of heat, enough to melt Pt and Ir, as Deville and Debray had already shown. In addition, in 1847 William Robert Grove (1811-1896, the father of the fuel cell) had shown that adding Pt at its melting point to cold water resulted in the detachment of bubbles containing H and O.<sup>[64]</sup> In other words, the part of the water that had become heated in contact with Pt had separated into its elements, despite the fact that Pt was found to be unchanged by the phenomenon. Pt had long been known to facilitate certain reactions, for example, that of bromine (Br) with H, and certain decompositions, for example, that of ammonia nitrate. Berzelius had regarded these effects to be an attribute of Pt and had given them the name of *action* or *force catalytique*.<sup>3</sup>

These arguments did not satisfy Deville. To him all that these scientists had done was

“... que de meter un mot nouveau en place d'une inconnue... Toutes les fois que l'on découvre un fait exceptionnel, le premier travail, je dirai presque le premier devoir imposé à l'homme de science, est de faire tous ses efforts

pour le faire rentrer dans la règle commune par une explication qui exige quelquefois plus de travail et de méditation que la découverte elle-même...”

(... to replace an unknown by a new word... Every time that an exceptional discovery is made, the first task, I would say the first obligation imposed on a scientist is to make all the efforts to include it within common laws by an explanation that some times requires more work and meditation than the discovery itself...).<sup>[66]</sup>

Deville and Troost repeated the experiments of Grove and showed that the phenomenon took place with many other compounds, that is, within a certain temperature range, a compound could exist partly in the combined state and partly as a mixture of the elements that formed it. This limited decomposition was named by Deville *dissociation*, a term that is now universally accepted. Dissociation was a phenomenon similar to a change in phase such as boiling. At a given temperature, if the pressure increased beyond the vapor pressure, part of the vapor returned to the liquid state until the pressure decreased to the vapor pressure. In the case of dissociation, the amount of decomposition was fixed for a given temperature.

<sup>3</sup>Soon after Berzelius became secretary of the Academy of Sciences, he began publishing his *Arsberättelser öfver Vetenskapernas Framsteg* (*Annual Surveys of the Progress in the Sciences*). In them, Berzelius reviewed all of the literature of the preceding year, added his comments and opinions (sometimes very acid!), and he discussed questions related to the elements, their valences, and compounds. In the 1835 edition of the *Annual Survey*, Berzelius summarized the findings of different scientists on the formation of ether from alcohols, the enhanced conversion of starch to sugar by acids, the acceleration of gas combustion by Pt, the stability of hydrogen peroxide in acid solution and its decomposition in the presence of alkali and such metals as Mg, Ag, Pt, and Au, and the fact that the oxidation of alcohol to acetic acid could be accomplished in the presence of finely divided Pt.

In a brilliant stroke, Berzelius was able to understand that all of these processes, although apparently different, had a common denominator, which he called *catalysis* (either catalysis of inorganic reactions by metals or of biological reactions by enzymes). In the *Annual Survey*, he wrote: “In inorganic nature when compounds arise through the interaction of several substances, the available combining units strive for a state of better satisfaction. Thus the substances endowed with strong affinities combine readily on the one hand, while those more weakly endowed form combinations among themselves on the other. The agent causing the conversion of substances *does not participate in the new compounds formed but remains unchanged*, thus operating by means of an internal power, the nature of which is still unknown, although it was in this way that it revealed its existence. Thus it is certain that substances, both simple and compounds, in solid form as well as in solution, have the property of exerting an effect on compound bodies, which is quite different from ordinary affinity in that they promote the conversion without necessarily participating in the process. This is a new power to produce chemical activity belonging to both inorganic and organic natures. It will also make it easier for us to refer to it if it possesses a name of its own. I shall call it the catalytic power of substances, and decomposition by means of this power catalysis (from the Greek *kata-*, ‘down,’ and *lyein*, ‘loosen’).”<sup>[65]</sup> The observant reader will realize that the concepts about catalysis developed by Berzelius 170 years ago are not very different from those that are enunciated today in any introductory lecture about the subject. During Berzelius' lifetime, his ideas about this new principle of catalysis were bitterly contested and attacked, but in the 20th century they became an indispensable ingredient of both the theoretical and applied fields of chemistry and chemical engineering.

Deville used a very ingenious apparatus to perform the experiments required to test his theory. It was known that light gases diffused easily through porous bodies. Deville decided to use this property to physically separate H from O as they were formed and, thus, to thwart their recombination. The apparatus built for this purpose was very simple: two concentric tubes, the external one made of porcelain varnished on its two faces to make it impervious, and the internal one built of porous earth. Fragments of porcelain filled the space between the two. Through the annulus, it was possible to pass any gas desired. The whole setup was enclosed in a furnace that burned coal and allowed the production of temperatures up to 1100-1300 °C. Water vapor was then passed through the internal tube and, at the same time, carbon dioxide through the annulus. Part of the steam dissociated, and the H diffused through the porous wall and was carried away by the CO<sub>2</sub>. The CO<sub>2</sub> stream, carrying the diffused H, was washed with aqueous potassium hydroxide, and the H left when lit with a flame. Deville was able to show not only that water dissociated into its elements but also that the amount of decomposition increased with temperature.

In another set of experiments, Deville and Troost took advantage of the fact that if two reacting gases are diluted enough with an inert gas, the mixture cannot be ignited (what today we call the lower limit of flammability, or explosion). Thus, they filled a porcelain tube with porcelain fragments, heated it to a “white” heat and passed through it a mixture of CO<sub>2</sub> and steam. The heat decomposed the steam, but H and O did not recombine because they were highly diluted. The next set of experiments was the definite one. Deville and Troost used as a diluent the same gas that was to be dissociated. This procedure eliminated any possible external effect that had been caused by the inert carrier in the previous experiments. To show the decomposition of CO<sub>2</sub>, they made it flow through a porcelain tube heated to 1300 °C, and from the exit steam they recovered a highly diluted mixture of CO and O in the ratio 2:1. In other words, one volume of CO<sub>2</sub> had simply decomposed into two volumes of CO and one volume of O.

Despite the success of his experimental procedures to prove dissociation, Deville continued his research. He tried an additional experiment, again brilliantly performed. In his *Leçons sur la Dissociation*<sup>[39]</sup> (pp. 65-66) Deville states:

“On sait que l’étincelle électrique décompose un grand nombre de corps. Or, d’après toutes les probabilités, l’étincelle n’agit sur eux que par la chaleur énorme qu’elle développe; il m’a donc semblé que, si cette décomposition n’était pas toujours suivie d’un combinaison nouvelle des éléments séparés, cela peut tenir à ce que ceux-ci sont mis en contact immédiatement avec une atmosphère en mouvement et relativement très froide. En effet, la masse ou le nombre des molécules de gaz violemment chauffé, au moment de la décharge, est très-petit, à cause de la petitesse du trait de feux par rapport à la masse gazeuse ambiante don’t la température varié à peine. On réalise toutes ces conditions sans l’intervention de l’électricité, de la manière suivante . . .”

(It is known that the electric spark decomposes a large number of compounds. Now in all probability the action of the electric spark results from the large amount of heat it develops. Its

seems, to me, however, that since this decomposition is not followed by a new combination of the elements, it is due to the fact that there is an immediate contact with a moving and relatively very cold atmosphere. In effect the mass or the number of molecules of gas highly heated at the time of the discharge is very small due to the smallness of the fire tract in relation to the ambient gas, whose temperature hardly changes. All these conditions can be realized without the use of electricity in the following way . . .)

Deville then described his proposed apparatus, which was to be built of two concentric tubes, the same as the one described above, except that the central one, which was to be made of a silvered brass apparatus, was cooled by an internal flow of tap water. In this way, the temperature drop across the annulus walls could reach up to about 1500 °C. With time, this arrangement became known as the *Deville hot-cold tube*.

The hot-cold tube was used to demonstrate the decomposition of many other gases, for example, SO<sub>2</sub> into SO<sub>3</sub> and S, HCl into H<sub>2</sub> and Cl<sub>2</sub>, CO into CO<sub>2</sub> and C, CO<sub>2</sub> into CO and O<sub>2</sub>, and NH<sub>3</sub> into N<sub>2</sub> and H<sub>2</sub>.<sup>[40]</sup> The hot-cold tube gave Deville an excellent tool for explaining previous results. For example, the procedure of Thenard and Gay-Lussac for preparing K was based on decomposing potassium hydroxide with Fe at high temperature. Deville showed that this reaction was simply a decomposition of the hydroxide into K, H, and O, in which the O was retained by the Fe and the K was released together with H. This explained why iron oxide was found only at the exit of the tube, a fact that had totally surprised Thenard and Gay-Lussac.<sup>[38]</sup>

Deville also was able to explain inverse decompositions that until then had defied all explanation, for example, the decomposition of alkaline carbonates dissolved by hydrogen sulfide and the decomposition of sulfides dissolved by a stream of CO<sub>2</sub>.<sup>[42]</sup>

All of these experiments proved beyond any doubt the phenomena of dissociation, the variety of conditions under which they took place, and the influence of temperature, pressure, and removal of products. Eventually, Peslin<sup>[67]</sup> and Henri Le-Châtelier<sup>[68]</sup> undertook the thermodynamic analysis of the phenomenon and established the mathematical relations that describe it.

### 3. Epilogue

An interesting angle to the life of Deville is connected to Henri Le Châtelier (1850-1936) and his father Louis Le Châtelier (1815-1873).<sup>[69]</sup> Louis had been trained at the École Polytechnique and the École des Mines, and between 1855 and 1868 served as consulting engineer to the financial society Crédit Mobilier. One of the projects financed by the bank was the railway system not only of France, but also of Spain, Austria, and Russia. This position allowed Louis to be actively associated with many industrial advances, notably with the establishment of the Siemens-Martin process of steel melting and with the development of the Deville process by which aluminum was first successfully manufactured on a commercial scale.

In the same manner as Deville, Henry Le Châtelier received his first degree at the Collège Rollin from which he obtained

his diplomas of Bachelor of Letters and of Bachelor of Sciences. After graduation he entered the École Polytechnique (1869), and from there he moved to the École des Mines for his specialization studies. He voluntarily attended other lectures, including those of Henri Sainte-Claire Deville (1818-1881), at the Sorbonne. In 1899, he published a French translation of the papers of Josiah Willard Gibbs (1839-1904), and in 1904 he founded the journal *Revue de Métallurgie*. In 1925, with the collaboration of his daughter, Jean Roger, he published a book of more general appeal entitled *Science et Industrie*, in which he expounded his ideas regarding applied research, his political ideas, and his deep patriotism. He illustrated his ideas with funny remarks about friends, teachers, and scientific principles. He described his foremost teacher, Sainte-Claire Deville, as a discursive lecturer who furnished his students with little likely to be of service in the approaching examinations.

After Saint-Claire Deville discovered the phenomenon of dissociation and after chemical reactions were shown to be reversible, Le Châtelier tried to understand the principles of the thermodynamic equilibrium that he suspected were more general than what was thought at that time. In his fundamental memoir of 1888 on the subject,<sup>[68]</sup> he announced a certain number of results that eventually became classic. He defined chemical equilibrium, numbered the factors on which it depended, and, at the same time, explained the role of a catalyst. His conception was totally new. It was later elaborated on further by Wilhelm Ostwald (1853-1932) and became the basis of modern theories of catalysis.

Le Châtelier's work on metallurgy gave us the platinum-rhodium thermocouple, having the same composition as the alloy discovered by Deville, and one of today's accepted standards for measuring temperature.

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