La química en la historia, para la enseñanza.

# Henri Moissan The discoverer of fluorine

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### Resumen

A Henri Moissan (1852-1907) le debemos el descubrimiento del flúor y la síntesis de muchos de sus compuestos, la invención de un poderoso horno eléctrico, el descubrimiento de una variedad de nuevos compuestos químicos y formas alotrópicas, así como la preparación de varios sistemas metal-amoníaco. Moissan provenía de una familia muy modesta pero su fuerte interés en la química lo llevó a alcanzar el máximo galardón científico: el Premio Nobel de Química del año 1906.

# Abstract

To Henry Moissan (1852-1907) we owe the discovery of fluorine and the synthesis of many of its compounds, the invention of a very powerful electric furnace, the discovery of many new chemical compounds and allotropic forms, and the preparation of several metal-ammonia systems. He came from a very modest background but a strong interest in chemistry led him to the maximum science achievement: the Nobel Prize in Chemistry (1906).

# Life and career

Henry Moissan was born in Paris, on September 28, 1852, of a non-Jewish father and a Jewish mother. His father François Ferdinand Moissan was a junior employee of the Railroad Company of the East and his mother Joséphine Almédorine Mitel, was a seam-stress. There is a record that he had a sister by the name of Marie Julie Laurence, born in 1855, but no information about the existence of other brothers and sisters. When he was twelve years old his family moved from Paris to Meaux where his father enrolled him in the *Collège de Meaux*, a public school, in the area of *Enseignement Secondaire Spécial* (professional studies), a short study track for people of modest means that did not include the study of Latin

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and Greek and did not allow the graduate to continue university studies. Already by the age of fifteen Moissan was already showing a great attraction for chemistry. His mathematics teacher, James, showed an especial attention for the young man and provided him with additional lectures (Viel, 1999).

After graduation he started working with a watchmaker named Godailler, this would have also been his future profession had not been by the Franco-Prussian war of 1870 that marked the return of the Moissan family to Paris. Henri Moissan was too young to enrol in the Army but he made use of the regulations that allowed him to replace his sick father during the night watches. Thus he took place during the engagement of the Avrom plateaux, one of the many military operations that tried to liberate Paris from the Prussian siege (Viel, 1999).

In order to look into his future his father advised him to consider the possibility of becoming a pharmacist. At that time people who of did not have a bachelor's degree could only opt to the diploma of pharmacien de deuxième classe and with this purpose in 1871 he entered the Baudry pharmacy as an intern. There he remained until 1874. Having completed his official internship he registered at the *École de Pharmacie* to follow the three-year program that would lead to the desired degree. At that time his best friends were his high-schoolmate Jules Plicque who worked in the laboratory of Pierre Paul Dehérain (1838-1902) in the Museum of Natural History. Plicque was a chemistry enthusiast and the description he made of his activities influenced Moissan in such a manner that in 1872 he left his intern position and entered the Museum to work in the laboratory of Edmond Frémy (1814-1894). After one semester with Frémy he transferred to the laboratory of Dehérain (Leveau, 1908).

Between 1875 and 1876 Moissan did voluntary military service in Lille, in a unit of military nurses.

Dehéran noticed Moissan's brilliant aptitudes and convinced him to complete his basic studies so that he could follow university studies. When he was 25 years old he had learned enough Latin to obtain his *baccalauréat*, he now had to obtain his license in

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sciences to continue doctoral studies. The study of physics replaced now the study of Latin; he failed the first time he was examined but he was not discouraged and in 1877 he was awarded his licence.

During this preparatory stage Moissan delivered his first memoir to the Académie des Sciences (Dehérain and Moissan, 1874). It was a work done in collaboration with his master Dehéran and related to the absorption of oxygen and emission of CO<sub>2</sub> by plants maintained in the dark. After a large number of experiments they established that the amount of CO<sub>2</sub> emitted by the leaves in the dark was comparable to those produced by the lower animals and that it increased when the temperature was increased. They showed that the amount of oxygen absorbed by the leaves was larger than the amount of  $CO_2$ released. In addition, leaves maintained in an atmosphere deprived of oxygen continued to release CO<sub>2</sub> for several days at the expense of their tissues. Moissan continued this project alone and in 1879 he published a second memoir where he demonstrated in an undisputable manner that the emission of CO<sub>2</sub> in plant respiration was not directly related to the absorption of oxygen, that is, the ratio of  $CO_2$  to  $O_2$ absorbed was not constant (Moissan, 1879). The ratio changed according to the conditions and it was rather the result of reactions occurring in the interior of the plant than the immediate transformation of oxygen into CO<sub>2</sub>.

These two memoirs are the only ones written by Moissan in the area of plant chemistry. After that he moved into inorganic chemistry and started studying pyrophoric iron, a subject that would lead him to the doctorate in 1880 (Moissan, 1880a).

Examination of pyrophoric iron showed Moissan that the iron that this material contained was never formed of metallic iron alone but by its mixture with a large proportion of ferric and ferrous oxides (Moissan, 1877). Observation of the reduction of sesquioxide of iron by hydrogen led him to discover an iron oxide pyrophosphate that was an allotropic variation of Henri Debray's (1827-1888) ferrous oxide. Careful oxidation of iron led to the preparation of an allotropic variation of magnetic oxide (Moissan, 1879). This allotropism was also found to exist in the oxides of manganese and nickel. By examining different chromium oxides Moissan was forced to revise certain aspects of the history of chromium compounds. He prepared the sulfides and selenides of this metal and did a beautiful study of the principal salts of chromium that until then had been

obtained only by Eugène Melchior Péligot (1811-1890) (Moissan, 1880b).

On May 30, 1882, Moissan married Marie Léonie Lugan, the daughter of a pharmacist at Meaux that he had met through the good offices of Jules Plicquet. They had only one son, Louis Ferdinand, born on January 5, 1885, who studied chemical engineering at the *Institute de Chimie* in Paris, afterwards became pharmacien de première class (1913), and assistant of toxicology at the *École Supérieure de Pharmacie* in Paris. He participated in the First World War as a sub-lieutenant of infantry and was killed in action at Billy-sour Mangiennes (Meuse) during the first days of the conflict. Being bachelor and the only male in the family, his death signalled the extinction of the Moissan family (Viel, 1999).

In addition to his scientific activities, Henri Moissan was a well-known art collector, particularly of paintings. His collection included among others, works by Gustave Courbet (1819-1877), Eugène Delacroix (1798-1863), Siméon Fort (1793-1861), Henri Regnault (1843-1871; the son of Victor Regnault), Justin Ouvrié (1806-1879), and Edouard Alexander Saïn (1830-1910). At his death his son Louis donated the collection to the city of Meaux (Viel, 1999).

Henri Moissan passed away on February 20, 1907, after complication following an attack of appendicitis.

# Academic career

Henri Moissan served in many in academic positions: Répétiteur of physics at the Institut Agronomique (1879-1880); Maître de Conferences et Chef des Travaux Pratique at the École Supérieure de Pharmacie in Paris (1879-1883); Agrége des Sciences Physico-Chimiques (1882); professor of toxicology (1887); professor of mineral chemistry (1899); consultant to the Director of the Ecole (1900); honorary professor of the École de Pharmacie and professor of chemistry at the Faculty of Sciences, University of Paris (1900). He was a member of the Académie de Médecine (1888), Conseil d'Hygiene, the Aluminium Committee of the Ministry of War, the Collège de France, and of the chemistry section of the Académie des Sciences (1891) where he replaced Auguste Cahours (1813-1891).

#### Honors

Moissan received many honors for his contribution to science and industry. He was awarded the La Caze prize from the Académie des Sciences (1887), the Humphry medal from the Royal Society (1896), and the Hoffmann medal from the Chemical Society of Berlin (1903). He also received awards from the Franklin Institute of Philadelphia (1898), the Société d'Encouragement pour l'Industrie Nationale (1898), and the Société Industrielle du Nord de la France (Kuhlmann Foundation) (1898). In 1900 he was nominated Commandeur de la Légion de Honneur.

Moissan became a foreign member of the Royal Society of London; corresponding member of the Academy of Sciences of Berlin, Academie of Sciences of Munich, Academy of Sciences of Saint-Petersburg, Brussels, Amsterdam, New York, Turin, Royal Society of Denmark, Royal Society of Uppsala, Harlem, Manchester, Bunsen, Academy of Sciences of Budapest, honorary member, of the Society of Pharmacy of London, Paris, New York, etc. etc., and member of the Société de Minéralogie. In 1906 his friends and students presented him with a medal carrying his effigy.

Moissan is credited with over three hundred publications, his greatest works being *Le Four Électrique* (The electric-arc furnace) (Moissan, 1897), *Le Fluor et ses Composés* (Fluorine and its compounds) (Moissan, 1900) and *Traité de Chimie Minerale* (Treatise on inorganic chemistry) (Moissan, 1904; five volumes, 1904-1906).

In 1906 Moissan was awarded the Nobel Prize for Chemistry for "isolating and investigating the chemical element fluorine and for introducing the electric furnace into the service of science-exploits whereby he has opened up new fields for scientific research and industrial activity." He was the first French scientist to be awarded the Nobel Prize for Chemistry.

# Scientific activities (Lebeau, 1908; Gauthier, 1904; Stock, 1907; Ramsay, 1912)

Moissan was a many-facet scientist; his principal contributions were the isolation of fluorine, the manufacture of synthetic diamonds, the electrical furnace, and his researches on boron, calcium, metal hydrides, and metal-ammonia.

# Fluorine

In 1884 Moissan began working on the isolation of elementary fluorine. Frémy had already tried it and failed, he had electrolyzed molten metal fluorides using a platinum cathode and found that it was attacked by a gas having such a chemical activity that it was impossible to collect (Frémy, 1856). Frémy had shown the difficulty of the problem, without offering a solution. Moissan was well familiar with Frémy's experiences and was convinced that he should not use the same procedure. In his own words: "Je suis partie dans ces recherches d'une idée préconçue. Si l'on suppose, pour un instant, que le chlore n'ait pas encore été isolé, bien que nous sachions préparer les chlorures métalliques, l'acide chlorhydrique, les chlorures de phosphore et d'autres composés similaires, il est toute évidence que l'on augmentera les chances que l'on peut avoir pour isoler cet élément en s'adressant aux composés que le chlore peut former avec les métalloides. Il me semblait que l'on obtiendrait plutôt le chlore, en essayant de decomposer le pentachlorure de phosphore ou l'acide chlorhydrique qu'en s'adressant à la electrolyse du chlorure de calcium ou d'un chlorure alcalin. Ne doit-il pas en être de même du fluor?" (I have started my researches from a preconceived idea. If we suppose, for a moment, that chlorine has not been isolated but we are well familiar with the preparation of metal chlorides, hydrogen chloride, the chlorides of phosphorus and similar compounds, it should be clear that we can increase the probability of isolating the element by addressing ourselves to the compounds that chlorine forms with metalloids. It seemed to me that it should be highly possible to obtain chlorine by trying to decompose phosphorus pentachloride or hydrogen chloride, than trying to hydrolyze calcium chloride or an alkaline chloride. Should it not be the same for fluorine?) (Moissan, 1900).

Moissan found that very few combinations of fluorine with metalloids were known. Humphry Davy (1778-1819) had found that heating a mixture of a metallic fluoride with phosphorus, in a metal tube, generated a combustible gas that fumed in the presence of air (Davy, 1813). Davy assumed that it would be possible to isolate fluorine by burning it in an atmosphere of oxygen in a vase made of fluorspar. Moissan's first step in the search of a method for isolating fluorine was the preparation of phosphorus trifluoride and pentafluoride (Moissan, 1884, 1885). He succeeded in preparing these compounds in very pure form using different procedures, for example, heating dry lead fluoride with copper phosphide, and by halogen-exchange processes ( $PCl_3 + AsF_3$ ;  $PBr_2 + ZnF_2$ ). Moissan showed that both fluorides were actually gases and not liquids, as believed before. He determined their main physical and chemical properties, particularly those that might lead to a procedure for releasing the fluorine. Combustion of the trifluoride did not liberate the element, oxygen combined with it yielding a new gas, phosphorus oxyfluoride ( $PF_3O$ ) (Moissan, 1886a). All these studies provided the science of chemistry with a wide variety of new compounds and facts but did not solve the initial problem.

Moissan decided now to try to electrolyze some of the compounds he had prepared, particularly arsenic trifluoride, a liquid at room temperature. His electrolytic cell was composed of a platinum crucible serving as cathode and having a platinum wire along its axis that functioned as anode. To increase the electrical conductivity of the bath Moissan added potassium fluoride. During the electrolysis he noted that arsenic was deposited at the cathode while a gaseous sheath formed around the anode. The gas was poorly absorbed by the bath and thus did not generate arsenic pentafluoride. Eventually, the extremely dangerous properties of arsenic trifluoride forced him to stop this series of experiences.

Having acquired enough experience electrolyzing liquid fluorine derivatives, he decided to try the electrolysis of anhydrous hydrogen fluoride, liquefied in a U tube made of platinum that was submerged in boiling methyl chloride at 249 K. Moissan reasoned that due to the extreme affinity that fluorine had for silicon, they would combine at room temperature and probably with incandescence. For this reason he put a piece of crystalline silicon at the exit of the electrode where the mysterious gas was released during electrolysis. On June 26, 1886, he performed the experiment and was witness to the combustion process he had expected.

The discovery of the new element was announced by Debray during the session held by the Académie des Sciences on June 28, 1886 (Moissan, 1886b, c, d). The Académie appointed a committee formed by Marcelin Berthelot (1827-1907), Debray, and Frémy to verify this sensational result. When Moissan tried to repeat the experience it failed miserably, no current passed through the bath and no gas was released. The committee abandoned his laboratory greatly disappointed. When Moissan examined the test he realized that the bath of his original experiments had contained accidentally small amounts of potassium fluoride that made it conducting. He was now able to repeat his experiment successfully in front of the committee who witnessed the brisk combustion of different elements (silicon, manganese, iron, arsenic, and antimony) with fluorine.

Afterwards, Moissan determined the physical properties of fluorine and prepared a large variety of inorganic and organic fluorides. He prepared ethyl fluoride, methyl fluoride, and 2-butyl fluoride. Together with Berthelot they determined the heat of the reaction between fluorine and hydrogen (Moissan, and Berthelot, 1889).

#### Boron and derivatives

After his extensive research on fluorine, Moissan dedicated his efforts to the study of boron and its derivatives. His first results indicated that all the procedures used by Jöns Jacob Berzelius (1779-1848), Joseph-Louis Gay-Lussac (1778-1850), Louis-Jacques Thénard (1777-1857), Henri Saint-Claire Deville (1818-1881), and Friedrich Wöhler (1800-1882) to prepare the element led to boron that was highly impure. He then studied very carefully the reduction of boric anhydride with magnesium and determined the conditions required to obtain highly pure boron (Moissan, 1892a). Subsequently, he discovered boron triiodide and the boron phosphides (Moissan, 1891, 1892b). He also prepared boron pentasulfide and established for the first time the pentavalence of boron. (Moissan, 1892c). Afterwards, in collaboration with Henri Gautier he measured the specific heat of the element and found that it did not satisfy Dulong-Petit's law (Gautier and Moissan, 1893).

#### Artificial diamonds

Initially, Moissan thought that since fluorine was a mineralizing agent it should facilitate the transformation of amorphous carbon into crystalline carbon. He studied many combinations of fluorine with carbon but was unable to transform the amorphous carbon into another form. He then reasoned that science did not have the powerful means that Nature had used to manufacture crystalline minerals; he also felt that artificial diamonds were probably very small so that it was necessary to use a microscope to follow the experimental work. He believed that it was very probable that in natural deposits diamonds were also present in microscopic sizes. He proceeded to study the diamond sands of Brazil and the blue earth of the Cape (South Africa) and discovered the presence of very small natural diamonds that he believed should be similar to the ones that he expected to manufacture (Moissan, 1893b). At the same time he found that the diamond earths contained graphite, a carbon variety that formed at relatively high temperatures.

From these findings he got the first hint for preparing diamonds at high temperatures.

He then proceeded to burn with oxygen a large number of diamonds of different origin and varieties. Analysis of the ashes showed the presence of a constant impurity of iron. Hence he initiated his research on the solubility of carbon in iron with very encouraging results: the variety of carbon obtained was also graphite. He now believed that other carbon solvents could be used usually equally well for the same purpose. In the blue earth of the Cape he found that diamond was accompanied by many mineral species. Although this did not prove that these different minerals came from the same medium where diamond had originated, it did not disprove that some of them have the same origin. Among the many impurities he detected the presence of titanium. This element was present in the blue earth in the form of many oxides. Unfortunately, the metals in which he was particularly interested were the least known ones. Some of them had been described only as infusible powders, while others had been prepared in minute quantities and in a very impure form. Unfortunately all his experiments did not lead him to produce diamonds, in every case, the extracted carbon was graphite.

Meanwhile, Georges Friedel (1865-1933) and others had observed a curious fact in a meteorite found at Cannon Diablo, Arizona. This celestial body, of ferronickel nature, contained a variety of diamonds, from transparent to black ones, and accompanied by carbon of medium density and graphite. Moissan obtained a small sample of the meteorite and was fortunate to study in situ a very small diamond of the boort variety that resisted the action of the milling wheel used to cut the meteorite. The diamond formed a needle enclosed in the metal and surrounded by a sheath of carbon in which it was possible to identify graphite. To Moissan this composition indicated the medium in which the diamonds had been synthetized: Carbon was originally dissolved in a bed of molten iron, the surface of the iron had suddenly cooled subjecting the core to very high pressures because solid iron containing carbon in solution expanded during solidification (Moissan, 1893a).

Moissan concluded that it should be possible to realize the synthesis of diamond in a liquid metallic medium under the influence of large pressures. This was a very difficult experimental task, but Moissan remembered that under high-pressure the saturated carbon melt increased in volume when it solidified, the same as did water when turning into ice. Sudden cooling of the melt could create thus the high pressures required; the only problem was finding the envelope, which would resist these high pressures. He reasoned that one-way of solving the problem was to plunge the molten melt in cold water; solidification would create the required external envelope. On doing so he found that the metallic ferrules thus formed were cracked, but had a smooth surface that had seemingly tried to resist the pressure. Treating the ferrules with the appropriate reagents allowed dissolution of the metallic mass and destruction of the graphite. Moissan obtained a small amount of residue formed of small transparent crystals that he identified as having the same physical and chemical properties as natural diamonds. He was also fortunate to recover in these artificial products what he believed were diamond varieties, from black diamond to carbon, transparent and crystallized.

This diamond synthesis was communicated to the Académie on the meeting that took place on February 6, 1893 (Moissan, 1893c). Although the scientific problem seemed to have been solved, not so it's practical side: Diamonds formed in very small amounts and of highly irregular shape.

Moissan's claims of having synthetized diamonds have been criticized and discarded by several people. For example, Bundy et al. (1955) reported that Charles Parsons (1854-1931) had tried for thirty years to synthesize diamonds and trying to duplicate Moissan's results (Bundy et al., 1955). Parson concluded that he had been misled by his results as regarding as diamond various transparent singly refracting spinels, which were very resistant to chemical reagents and would not burn (Parsons, 1907). Later on Sidgwick wrote that calculations based on the Nernst equation indicated that the two allotropes (graphite and diamond) could exist only under extreme conditions, such as 300 K and 15 GPa, and 1500 K and 40 GPa (Sidgwick, 1950). Eyring and Cagle concluded that considerations of the geological formation of diamonds indicated that they were formed at great depth and under conditions thermodynamic stability. The information in the literature contained no certain example of artificial diamonds but Eyring and Cagle thought that the problem could be technically solved. Bundy et al. claimed that according to the phase diagram of carbon diamonds could be formed at the very extreme conditions of 3 to 10 GPa at temperatures in the range of 1000 to 3000 K,

conditions well beyond those attained by Moissan (Eyring and Cagle, 1953).

Nowadays, equipment for achieving the stable diamond region for hours has been developed by the General Electric Company and used to produce, without doubt, synthetic diamonds.

#### Electric furnace

The synthesis of diamond had the important consequence of leading Moissan to invent his electric furnace and providing mineral chemistry with new and powerful auxiliary equipment.

Moissan constructed and operated his new electric furnace on June 1892, at the École Supérieure de Pharmacie. It was fed by a 45-ampere current and 40 volts generated by a small dynamo. It was a modest apparatus composed of two superimposed blocks of chalk. In the lower block there was a groove through which went two carbon electrodes of 8-10 mm diameter. A small crevice at the center of this block held a small crucible of sugar charcoal, of less than 2 mL diameter and located below the arc between the two electrodes. Eventually, Moissan moved this prototype to a laboratory in the École Normale Supérieure where he could feed it now with double the original voltage. The new results showed the need to impose higher and higher currents and this meant moving the furnace through many institutions, such as Societé Gramme, the electrical substation at the Gare de *l'Est*, the Edison Company, etc., etc. All these relocations were accompanied by improvements in the structure of the furnace; for example, limestone blocks replaced the chalk blocks and it was now possible to reach temperatures of about 3700 K (Moissan, 1897).

Moissan results went further than the synthesis of artificial diamonds: he found that metallic oxides considered before, could now be easily fused and vaporized. For example, calcium oxide, barite, strontia, and magnesia were easily fused and distilled. Similar results were obtained with metals hardly fusible like iron, and platinum. These could be melted and brought to their boiling temperatures in minutes. The action of carbon upon oxides permitted preparing refractory metals such as chromium, manganese, molybdenum, tungsten, titanium, uranium, vanadium, and zirconium very easily. Using an excess of carbon yielded metallic carbides. Calcium carbide was found to react with water to form acetylene, allowing transferring a laboratory curiosity into industrial production. The manufacture of calcium carbide became one of the most important uses of white coal and resulted in the installation of many metallurgic industries in the mountain area of France.

The action of water on many of these carbides provided Moissan with a reasonable explanation about the origin of petroleum deposits. The carbides were very stable compounds, even at very high temperatures, and were certainly present at high depths in the earth. Their decomposition by water explained the formation of gaseous, liquid, and solid hydrocarbons, and could also be the cause of certain volcanic eruptions.

Between 1892 and 1907 Moissan published more than one hundred papers on the results attained with his electric furnace, covering the following subjects: (a) fusion, crystallization, and vaporization of metallic oxides, (b) preparation, fusion and volatilization of metals considered refractory, (c) study of the properties of different varieties of carbon, and (d) preparation of a very large number of binary compounds and metallic alloys, among them, silicides, borides, phosphides, and, particularly, carbides (Moissan, 1897).

Royère has traced the story of the development of the electric furnace from Moissan's design to today's high temperature devices (Royère, 1999).

# Calcium and derivatives

Moissan started preparing calcium in 1898. This metal had been manufactured industrially by electrochemical means, in small quantities and in a very impure form. Moissan modified the procedures used by Liès-Bodart and Jobin and obtained highly pure crystalline calcium (Moissan, 1898c). Treatment of calcium iodide with an excess of sodium liberated calcium, which then dissolved in the alkaline metal from where it crystallized. It was also possible to separate pure calcium by treating the solution with absolute alcohol that destroyed the sodium. Having now pure calcium, Moissan proceeded to study its properties as well as prepare derivatives such as calcium hydride and calcium nitride (Moissan, 1898a, b). He discovered that the reaction of calciumammonia yielded very pure white calcium carbide, in contrast with the same highly colored compound prepared in the electric furnace. Calcium phosphide allowed him to prepare phosphine gas.

#### Hydrides

Alkaline hydrides had long been assumed as compounds similar to alloys and having like them, a

metallic character. Moissan prepared the hydrides of potassium, sodium, cesium, and rubidium and showed that they did not conduct electricity and that the hydrogen was supposed to exist in combination as a non-metal, in contrast to its condition in palladium-hydrogen alloy (Moissan, 1905a). The hydrides reacted with  $CO_2$  to yield the corresponding fomates, and with  $SO_2$  to produce hyposulfites, with the simultaneous release of hydrogen. These reactions were particularly important because they connected inorganic chemistry with organic chemistry.

Reaction of the hydrides with alkyl halides yielded the pertinent hydrocarbons. Accidentally Moissan found that the action of different reagents was highly dependent on the absence or presence of water. For example,  $CO_2$  absolutely dry reacted with potassium hydride at 54°C yielding potassium formate. In the presence of traces of water the formation of formate took place already at -80°C (Moissan, 1905b).

# Ammonia metals

Another area of Moissan's research was solutions of metals in ammonia and methylamine (ammonia metals). He expected that at very low temperatures these would react like sod-ammonium that gave up its sodium, to fix hydrogen and yield the ammonium group  $(NH_4)_2$ .

Moissan prepared calcium ammonia and lithium ammonia and checked the possibility of hydrogenating lithium-ammonia in liquid hydrogen sulfide or with ammonium chloride. He was unable to find products other than ammonia and hydrogen. He abandoned this route and prepared ammonia amalgam using liquid ammonia in the absence of water. He demonstrated unequivocally that during decomposition these amalgams yielded ammonia and hydrogen in the volumetric ratio of H to NH<sub>3</sub>. Nevertheless, the amalgam did not allow the production of the ammonium radical.

Finally, he turned to the electrolysis of ammonia salts, particularly of solutions of salts in liquid ammonia. One of these researches, published after his death, described the electrolysis of a solution of mercury iodide in liquid ammonia. He had observed that during the passage of current blue filaments were formed on the platinum cathode. When the current was stopped these filaments decomposed suddenly yielding hydrogen and a grey cloud of mercury. The blue compound was readily soluble



Figure 1. Stamp issued on the occasion of the 1906 Nobel Prize of Chemistry.

in mercury and the solution presented the properties of an ammonia amalgam (Moissan, 1907).

# Epilogue

Moissan's electric furnace has a picturesque angle in Jules Verne's novel (1985) *The Secret of Wilhelm Storitz.* After Verne's death his son Michel published many of the remaining manuscripts as novels. In this particular one, related to the subject of invisibility by achieving the same refraction index as the surroundings it says: "In a corner, many instruments and equipment, bowls, a portable furnace, a Rhumkorf coil, an electric furnace built according to the Moissan system and capable of achieving temperatures from 4,000 to 5,000 degrees, several retorts and alembics, samples of those metals or metalloids included in the category of rare earths, a small acetylene, and a gasometer for feeding the lamps connected to it."

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# References

- Bundy, F. P., Hall, H. T., Strong, H. M., Wentorf, R. H., Man-Made Diamonds, *Nature*, **176**, 51-55, 1955.
- Davy, H., Some Experiments and Observations on the Substances Produced in Different Chemical Processes on Fluor Spar, *Phil. Trans. Royal Soc.*, 103, 263-279, 1813.
- Dehérain, P. P., Moissan, H., Sur l'Absorption de

l'Oxygéne et l'Émission d'Acide Carbonique par les Plantes Maintenues a l'Obscurité, *Ann. Soc. Nat.*, 19, 321-333, 1874.

- Eyring, H. and Cagle, F. W., An Examination into the Origin and Possible Synthesis and Physical Examination of Diamonds, Z. Elektrochem., 56, 480-483, 1953.
- Fremy, E., Recherches sur les Fluorures, Ann. Chim. Phys. [3], 5-50, 1856.
- Gautier, H., Centenaire de l'École Supérieure de Pharmacie, Volume Commémoratif, A. Joanin, Paris, 1904, p. 249-257.
- Gautier, H., Moissan, H., Détermination de la Chaleur Spécifique du Bore, *Compt. Rend.*, **116**, 924-928, 1893.
- Lebeau, P., Henri Moissan, *Bull. Soc. Chimique* [4], 3, I-XXXVIII, 1908.
- Moissan, H., Étude sur les Oxydes de Fer, Compt. Rend., 84, 1296-1299, 1877.
- Moissan, H., Sur les Volumes d'Oxygéne Absorbé et d'Acide Carbonique Émis dans la Respiration Végétale, *Ann. Agronom.*, **5**, 56-67, 1879.
- Moissan, H., Sur Deux Variétés Allotropiques d'-Oxyde de Fer Magnetique, *Compt. Rend.*, 86, 600-603, 1879.
- Moissan, H., Sur les Oxydes Métalliques de la Famille du Fer, Thèse de Doctorat ès Sciences Physiques, Paris, 1880.
- Moissan, H., Sur les Sulfures et Séléniures de Chrome, Compt. Rend., 90, 817-819, 1880.
- Moissan, H., Sur le Trifluorure de Phosphore, *Compt. Rend.*, **99**, 655-658, 1884.
- Moissan, H., Sur la Préparation et les Propriétés Physiques de Pentafluorure de Phosphore, *Compt. Rend.*, **101**, 1490-1495, 1885.
- Moissan, H., Sur un Noveau Corps Gaseux: l'Oxyfluorure PF<sub>3</sub>O<sub>2</sub>, *Compt. Rend.*, **102**, 1245-1248, 1886a.
- Moissan, H., Action d'un Courant Electrique sur l'Acide Fluorhydrique Anhydre, *Compt. Rend.*, 102, 1543-1544, 1886b.
- Moissan, H., Sur la Décomposition de l'Acide Fluorhydrique par un Courant Électrique, *Compt. Rend.*, 103, 202-205, 1886c.
- Moissan, H., Nouvelles Expériences Sur la Décomposition de l'Acide Fluorhydrique par un Courant Électrique, *Compt. Rend.*, **103**, 256-258, 1886d.
- Moissan, H. Berthelot, M., Compt. Rend., Chaleur de Combinaison du Fluor avec l'Hydrogène, Compt. Rend., 109, 209-213, 1889.
- Moissan, H., Préparation et Propriétés des Phosphures de Bore, *Compt. Rend.*, **113**, 726-730, 1891.

- Moissan, H, Préparation du Bore Amorphe, *Compt. Rend.*, **114**, 392-395, 1892a.
- Moissan, H., Sur la Préparation de l'Iodure de Bore, *Compt. Rend.*, **114**, 622-625, 1892b.
- Moissan, H., Préparation et Propriétés de Pentasulfure de Bore, *Compt. Rend.*, **115**, 271-275, 1892c.
- Moissan, H., Étude de la Météorite de Canon Diablo, Compt. Rend., 116, 288-292, 1893a.
- Moissan, H., Sur la Présence du Graphite, du Carbonado et de Diamants Microscopiques dans la Terre Blue du Cap, *Compt. Rend.*, **116**, 292-295, 1893b.
- Moissan, H., Analyse des Cendres du Diamant, Compt. Rend., 116, 458-463, 1893c.
- Moissan, H., Le Four Électrique, G. Stenneil, Paris, 1897.
- Moissan, H., Préparation et Proprietés de l'Hydrure de Calcium, Compt. Rend., 127, 29-34, 1898a.
- Moissan, H., Préparation et Proprietés de l'Azoture de Calcium, Compt. Rend., 127, 497-501, 1898b.
- Moissan, H., Préparation du Calcium Crystallisé, Compt. Rend., 126, 1753-1758, 1898c.
- Moissan, H., Le Fluor et ses Composés, G. Steinhel, Paris, 1900.
- Moissan, H., *Traité de Chimie Minérale*, Masson, Paris, 1904.
- Moissan, H., Sur Quelques Réactions Fourniers par les Hydrures Alcalins et Alcalino-Terreux, *Ann. Chim. Phys.* [8], 6, 289-322, 1905a.
- Moissan, H., Action d'une Trace d'Eau sur la Décomposition des Hydrures Alcalins par 'Anhydride Carbonique et l'Acétylène, Ann. Chim. Phys. [8], 6, 323-333, 1905b.
- Moissan. H., Recherches sur l'Ammonium, *Compt. Rend.*, **144**, 790-797, 1907.
- Parsons, C. A., Some Notes on Carbon at High Temperatures and Pressures, *Proc. Roy. Soc. London* [A], **79**, 532-535, 1907.
- Ramsay, W., Moissan Memorial Lecture, J. Chem. Soc., 101, 477-488, 1912.
- Royère, C., Le Four Électrique d'Henri Moissan a Cent Ans: Une Filiation Four à Arc, Four Solaire, Four à Plasma? Ann. Pharm. Fr., 57, 116-130, 1999.
- Sidgwick, N. V., Chemical Elements and Their Compounds, 1, 491-493, Clarendon Press, Oxford, 1950.
- Stock, A., Henri Moissan, Ber. Deut. Chemis. Gessel., 40, 5099-5130, 1907.
- Verne, J., Le Secret de Wilhelm Storitz, Societé Jules Verne, Paris, 1985. (The manuscript was written in 1901).
- Viel, C., Henri Moissan, Premier Français Prix Nobel de Chimie: l'Homme, le Collectionneur de Tableaux, Ann. Pharm. Fr., 57, 94-100, 1999.