

La química en la historia,
para la enseñanza.

The significance of applied research

Henry-Louis Le Châtelier

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Resumen

Henry-Louis Le Châtelier (1850-1936) es un nombre conocido por todos los estudiantes de fisicoquímica. Él fue un científico teórico y experimental que dejó su marca en muchas actividades. Su cuidadoso estudio y análisis del desplazamiento del equilibrio químico nos dio el principio que lleva su nombre. La interpretación correcta de las condiciones para realizar la síntesis del amoníaco lo llevaron a tratar de realizar el proceso. Aun cuando el proyecto fracasó por razones mecánicas, sus experiencias proveyeron la base para el éxito de Bosch y Haber. Su trabajo en metalurgia nos dio el termopar platino-rodio, uno de los actuales estándares internacionales de medición de la temperatura. Le Châtelier realizó la investigación básica que estableció el mecanismo de curado del cemento hidráulico, así como el papel que juegan sus componentes.

Abstract

Henry-Louis Le Châtelier (1850-1936) is a well-known name to all students of physical chemistry. He was a multifaceted theoretician and experimentalist who left his mark in several fields. His extensive and careful analysis of the displacement of chemical equilibrium gave us the principle that carries his name. Correct interpretation of the conditions for the synthesis of ammonia led him to try its realization. Although the intent failed due to mechanical problems, he prepared the ground for Bosch and Haber. His work on metallurgy gave us the platinum-rhodium thermocouple, one of today's accepted standards for measuring temperature. He did also the basic work that established the mechanism of setting of hydraulic cements and established the role played by all its major components.

Chemists and chemical engineers are familiar with

Le Châtelier through the principle that carries his name, a rule stating the effect of operating variables on the coordinates of chemical equilibrium. They are generally unaware of his rich contributions in other scientific areas such as cement, metallurgy, pyrometry, flame temperature and explosions, and combustion. Here we describe his personal life and career, his scientific achievements, and, in particular, the significance of his contribution to chemical equilibrium.

Life and career

Henry-Louis Le Châtelier was born in Paris, on September 8, 1850. His parents came from families with famous ancestors that included Guillaume Delisle (1675-1726), Philippe (1700-1773) and Jean-Nicolas Buache (1741-1825), royal geographers; Charles François Beautemps-Baupré (1766-1854) and Louis-Isidore Duperrey (1786-1865), explorers; the Durand brothers; and the three Deseine brothers, architects and sculptors. His mother, Elisabeth Durand, was an ardent Catholic of the school of Lamartine and was responsible for her children growing and being educated in an orthodox religious atmosphere, in spite her husband's strong republican ideas [Desch, 1938]. Henri told later she had had a critical influence in his personality: "Ma mère, catholique ardente, enthousiaste de la poésie, mettant au dessus de tout le sentiment du devoir et de l'honneur, renonça de bonne heure à toute relation mondaine pour se consacrer entièrement à l'éducation de ses enfants. Je fus habitué à une discipline très stricte L'ordre est pour moi une des formes le plus parfaits de la civilisation." (My mother, an ardent Catholic and poetry enthusiast, put above all the sense of duty and honor and resigned happily to all mundane relation to dedicate herself completely to the education of her children, I was accustomed to a very strict discipline. For me, order is one of the most perfect forms of civilization) [Oesper, 1931; Laffite, 1962].

Henry's father, Louis Le Châtelier (1815-1873), had been trained in the *École Polytechnique* and the *École des Mines* and between 1855 and 1868 served as consulting engineer to the financial society *Crédit*

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Mobilier.¹ One of the projects financed by the bank was the railways system, not only of France, but also of Spain, Austria, and Russia.² 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 aluminium was first successfully manufactured on a commercial scale. He was an ardent republican who exiled voluntarily after Napoleon III came into power, after the plebiscite.³ He went to Spain, Austria, and Hungary to collaborate in constructing their steel industry.

Louis Le Châtelier had a profound influence on the scientific formation of his son. According to Henry a very young age he had him read at Louis Poinso's (1777-1859) "Treatise on Statics" and later his memoir about the rotation of bodies. "Mon père aimait passionnément la géométrie, mais avait peu de considération pour l'analyse" (my father loved geometry but had a distrust of mathematical methods). He repeated constantly to him Poinso's saying that "a calculation can never yield more than was put into it at the beginning".

Henry's grandfather had collaborated with Louis Vicat (1786-1861) and had a profound interest in problems related to cements [Bouvier, 1936].

Henry was the oldest of six children, five brothers and one sister. His brother Louis (1853-1928) was a bridge and railway engineer who constructed steel plants, played an important role in improving the steam locomotive, in coal mining and utilization,

in the manufacture of open-hearth steel and of aluminium, in the organization of the Bordeaux pine forest, and headed the French department of Bridges and Roads. He also established the blast furnace at Caen and played a leading part in the crusade against syphilis [Guillet, 1937].

Alfred (1855-1929), the second brother, graduated as an army officer from Saint-Cyr and participated in several missions in Africa. Eventually he became professor of Muslim Sociology at the *Collège de France* and was one of the inspirers of French colonial policy. The third brother, George (1857-1935), was an architect and the youngest brother, André (1861-1929), was a maritime engineer who worked with Henry in creating the autogenous welding industry and devised methods for the safe storing of liquid acetylene. He studied the resistance of metals to high temperatures, invented the metal lath (a wood substitute) and also worked on high temperature enamels.

Henry's sister, Marie, married Dr. Leroux, a pediatrician.

Henry Le Châtelier entered the *Collège Rollin* from where he received his diploma of Bachelor of Letters in 1867 and of Bachelor of Sciences in 1868. After graduation he entered the *École Polytechnique* (1869) at the top of the admission list and remained until graduation as the best student of his class. While at the *École des Mines* he voluntarily attended other lectures, including those of Henri Saint-Claire Deville (1818-1881) at the Sorbonne and of Étienne Jules Marey (1830-1904) at the Collège de France, while pursuing literary studies under George Charpentier (1846-1905). On September 11, 1870, Henry and all the student body at the *École* had to suspend their studies after being appointed sub-lieutenants by the government of National Defence, and ordered to take part in the defence of Paris during the siege by the Prussian Army. The next year he transferred to the *École Nationale Supérieure des Mines* and after graduation (1873) he took a study trip to Belgium that provided the material for his first publication (about manganese castings) [Le Châtelier, 1874]. Afterwards, he joined the *Corps des Mines*, a government engineering service, where he took part in the Rondaire government mission to Algeria to report on the possibility of constructing an inland sea in that region.

After his return to France (1875) he served for two years as a mining engineer in the *Corps des Mines* at Besançon [Desch, 1938] and during this period he

¹ *Crédit Mobilier* was also involved in the financing of American Railroads. Their operations were very shoddy and the scandal culminated in a Congressional investigation in 1878 (See; Dobbin, F., *Forging Industrial Policy*, Cambridge University press, Cambridge, 1994; p 54-56).

² Benoit-Pierre-Émile Clapeyron (1799-1864) built the first French railroad that was an economical success. Clapeyron was also responsible also for the design of the locomotive of the same [See: Wisniak, J., Benoit Paul Emile Clapeyron: A Short Bibliographical Sketch, *Chem. Educator* [Online] 5(2), 83-87; S1430-4171 02370-0 (2000)].

³ In 1848 the King of France, Louis-Philippe, was overthrown, the Republic reinstalled, and after the brief bloody war in Paris (the so-called June days), Louis Napoléon Bonaparte was installed as President. On December 1852, Bonaparte made a coup d'état that installed him as Emperor Napoleon III of France. Ardent republicans like Louis Le Châtelier reacted by going into exile, others, like the famous chemist Théophile Pelouze, who was a member of the city council of Paris, resigned their public office.

published another short scientific note, which dealt with a metallurgical problem [Le Châtelier, 1876]. Henri Eduard Tresca (1814-1885) had shown that the fibrous character of wrought iron made by the puddling process was due to the presence of inclusions of slag, or as it is generally called, cinder. To isolate these inclusions Le Châtelier adopted the method used by Jean-Jacques Théophile Schloessing (1824-1919) to analyse cast iron, namely, the removal of metallic iron by distillation in a stream of dry chlorine at a dull red heat. In this manner the slag was left forming a skeleton of the original specimen.

Le Châtelier served many in academic positions: In 1877 he became professor of general chemistry in the *École des Mines*; in 1882 he was first appointed *répétiteur auxiliaire* and then *répétiteur adjoint* at the *École Polytechnique*; in 1883 professor in the *Collège de France* where in 1898 he succeeded Paul Schutzenberger (1829-1897) in the chair of Mineral Chemistry. He held this chair for ten years. In 1907 he became professor at the Sorbonne, replacing Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry), the discoverer of fluorine. He got his doctorate of Physical and Chemical Sciences in 1887, when he became professor of Industrial Chemistry and Metallurgy in the *École des Mines*. In 1907 he was appointed professor of General Chemistry at the Faculty of Science of Paris. This title he retained until he became honorary professor in 1925 [Silverman, 1937]. In 1887 he exchanged his chair for that of Industrial Chemistry in the same College and retained this post until his retirement in 1919.

During his several teaching positions he introduced important reforms into the teaching of chemistry in Paris. At that time chemistry was considered a descriptive science. Preparation methods and properties of the different substances were taught methodically in a certain order but without general concepts. A chemistry course looked like a dictionary and a list of tables of constants. Le Châtelier courses were built around general laws and principles and he presented facts only as applications of these. All his lectures were illustrated by real examples. He stressed the value of these laws in predicting new facts and emphasized the necessity of precise measurements since these alone could lead to valid general conclusions. He used to say to his students "that the essence of my teaching was to make them think, I want to implant in your spirits the fertile germs of certain ideas, with the hope that you will develop them and make them fructify by the action

of your own effort" [Laffite, 1962].

According to Bouvier [Bouvier, 1936] Le Châtelier was first and foremost a physical chemist, in his researches and in teaching chemistry. The combination of chemistry and physics marked his works. Pure chemistry provided him with the methods

and their precision and applied chemistry the subjects to study. He had become acquainted with cements in his grandfather home and learned the theory of the Portlands and the modifications produced by fire. After a firedamp explosion in Saint-Étienne he studied the combustion of gaseous mixtures. Using the laws of mechanical chemistry he established the material balance of industrial ovens. After a series of very good studies he explained the complex composition of alloys. The use of a double galvanometer allowed him to follow the cooling of samples of metals, the thermoelectric pyrometer and the platinum-rhodium thermocouple to evaluate high temperatures [Le Châtelier, 1887b; Kayser and Patterson, 1998], etc., without considering his practical procedures for evaluating dilation, electric resistance, etc.

Le Châtelier coupled chemical phenomena with the laws of thermodynamics and established various principles that have become classic, among them we can mention the laws of displacement of chemical equilibrium that permit predicting the results that will be obtained if the pressure or the temperature are changed. This law permitted Le Châtelier to take a patent on ammonia synthesis well ahead of Fritz Haber (1868-1934; 1919 Nobel Prize in Chemistry).

According to Bouvier [Bouvier, 1936] what Le Châtelier appreciated the most in a person was his character: "Dans les Sciences comme dans toutes les circonstances de la vie, une persévérance inlassable, une vigueur inflexible dans la lutte contre les obstacles et une affabilité non démentia avec les collaborateurs sont les éléments essentiels du succès" (The essential elements for success in science like in all other circumstances of life, are a relentless perseverance, an inflexible vigour in the fight against the

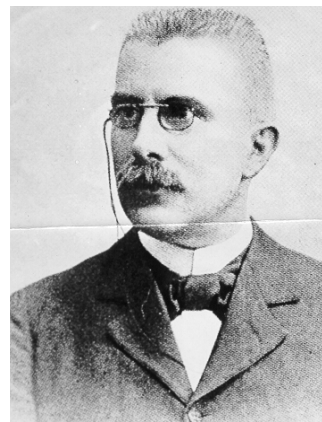


Figure 1. Henry Le Châtelier

obstacles, and an extreme affability towards your collaborators). The extraordinary influence that Le Châtelier had in industry was illustrated when in 1922, on the occasion of becoming 50 years old, about 300 industrial firms attended the ceremony on his honor.

Le Châtelier believed strongly that research must be practical and mission oriented. He expressed this very strongly in the following words: “La fusion de la théorie et de la pratique doit aujourd’hui être la préoccupation dominante de tous ceux que s’intéressent tant au progrès de la science qu’à celui de l’industrie. Faute d’une telle collaboration, la Science privée de tout contrôle effectif, se perd en vaines imaginations, et l’industrie, privée d’une direction précise, s’immobilise dans des tâtonnements empiriques sans issue” (The fusion of theory and practice must be always the preoccupation of those interested in the progress of science and industry. Without such collaboration, science, lacking an effective control, gets lost in vain imagination, and industry deprived of a precise direction, freezes without issue).

Another proof of his strong ideas regarding applied research can be found in a money gift that he gave in 1922 to the *Académie des Sciences* with the specific condition that the income is given to “persons possessed of such scientific aptitude and facilities for work involving precise measurements which would sooner or later be applicable to industry.”

Some mention should be made regarding his literary activities. 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* where he expounded his ideas regarding applied research, his political ideas and expressed his deep patriotism. He illustrated his ideas with funny remarks about friends, teachers, and scientific principles. For example, 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. He compared the chemical affinity that exists between sulphuric acid and potassium hydroxide as being similar to that existing between a dog and a bone; the dog has an affinity for the bone but it may be equally claimed that the bone has an affinity for the dog and the two absorb each other to form one single entity. The only diffe-

rence lies in the fact that the dog has personal feelings, which are absent in the bone; but how one can say which is nobler, the acid or the alkali? [Pope, 1937].

In 1876 Henri Le Châtelier married, Geneviève Nicolas, and their descendants comprised seven children, thirty-four grandchildren, and six great-grandchildren.

His health was excellent but deafness troubled him in his later years. When well over 80 he travelled to Morocco. Henry Le Châtelier died on September 17, 1936, at the age of 86, at Miribel-les Échelles (Isère).

Honors

Le Châtelier received many honors for his contribution to science and industry. He was made Chevalier de la *Legion d’Honneur* in 1887, promoted to Officier in 1908, Commandeur in 1919, and finally to Grand Officier in 1927. In 1895 he received the Lacaze Prize. He was appointed Inspecteur Général des Mines in 1907 and kept this position until 1919 when he reached the mandatory retirement age. In 1892 the *Académie des Sciences* awarded him the Jérôme Ponti Prize and in 1907 elected him to the Chemistry Section, succeeding Edmé Frémy (1814-1894) who had passed away.

Le Châtelier was six times candidate to the Académie des Sciences (1894, 1897, 1898, 1899, 1900, and 1907). He was finally elected member on May 6, 1907, running against Joseph Achille Le Bel (1847-1930), Charles Moreu (1863-1929), Louis Bouveault (1864-1909), Clément Colson (1853-1939), Emile Clément Jungleich, Haurior, and August Béhol. He received 40 of the 58 votes cast.

According to Lette [Lette, 1996] the reason for his rejection were being a strong Catholic holding conservative ideas and injecting anti Parliament expressions in many of his speeches. At that time the French society was highly anticlerical so that Le Châtelier ideas were politically incorrect. Opposition to his political ideas reflected also in the long time it took him to get the *Legion d’Honneur* and the opposition he faced in the *École Polytechnique* and in the Sorbonne. He himself told: “Cela m’a valu des fiches dans les trois ministères don’t j’ai dépendu, Guerre, Travaux Public, et Instruction Publique” (My attitude has resulted in having a dossier in each of the three Ministries where I worked: War, Public Works, and Public Education) [Laffitte, 1962].

Around 1880 the Republicans regained control of the Legislature of the Third Republic and stood

for a strong centralized regime, intransigent anticlericalism, an assertive nationalism in foreign policy, and revision of the constitution to prune out its monarchical aspects, social reforms as labor laws and a graduated income tax. Eventually primary education became free, compulsory, and secular, with religious teaching in the public schools replaced by civic education; a strong anticlerical bias thenceforth marked French public education. A new extreme moral and political low was reached in 1894 with the Dreyfus affair. The new left majority that arose afterwards retaliated by bringing the army under more rigorous civilian control and by embarking on a new wave of anticlerical legislation. Most religious orders were dissolved and exiled and in 1905 a new law separated church and state, thus liquidating the Concordat of 1801. During this event Le Châtelier, consistent with his strong religious belief, probably sided with the Army and against Dreyfus.

Le Châtelier became a foreign member of the Royal Society in 1913 and received the Davy Metal in 1916. He was made a foreign member of the Chemical Society in 1908 and an honorary member of the Institute of Metals in 1913; an associate member of the *Académie Royale* de Belgique in 1913, a foreign member of the *Accademia dei Lincei* in 1918, and an *Ehrenmitglied* of the German Chemical Society in 1931. He was a *Président d'Honneur* of the French Chemical Society. The Iron and Steel Institute awarded him the Bessemer medal in 1910 and he received honorary degrees from Aix la Chapelle (1910), the University of Manchester (1920), the Polytechnic Institute of Copenhagen (1921), the University of Louvain (1927), and Universidad de Madrid (1934). In 1906 he was made a knight of the Order of St. Anne of Russia and in 1928 a Chevalier of the Order of the New Republic of Poland. In 1922 his scientific jubilee was celebrated at the Sorbonne, a medal being struck in his honour and a small volume was issued, containing the addresses delivered on that occasion.

Le Châtelier was very prolific, he published a total of 635 (!) works in the form of books, papers, memoirs, notes and reports. A complete listing of his works appeared in a special issue of *Revue de Metallurgie* (January 1937), the journal he helped publishing.

As a suitable final remark we can mention that when Gustave Eiffel (1832-1923) built his famous tower in 1889, he decided to honor 72 distinguished French scientists and engineers by putting their names in the structure. This "invocation of science",

as Eiffel called it, reflected his worry over accusations that the tower was useless and waste less. There are eighteen names per side of the tower, all positioned just below the first platform of the structure, on the outside. The letters in the names are 60 cm high. Le Châtelier's name is located on the second façade, opposite the Point du Jour Quay. He was one of the three scientists that were alive at the time the tower was inaugurated on March 31, 1889.

Scientific activities

Le Châtelier was a multifaceted researcher that left his mark in many scientific and industrial areas. Here we will discuss a few of them.

Cement

This subject is of interest not only because Le Châtelier's significant contributions to it but because he came into it by a twist of destiny and it also signals the beginning of his scientific career.

In 1877, only two years after graduating from the *École des Mines*, Auguste Daubrée (1814-1896) the director of the institution, asked him to become professor of general chemistry. According to Le Châtelier, his only qualification was a good report on his work in chemistry in the *École* examinations and that there was no engineer in the Mining Corps that was better qualified [Desch, 1938].

Vicat, his grandfather's friend, had done his research on synthetic hydraulic cements at the *École des Mines* and left there a large set of samples. This led Le Châtelier to look into the subject and to find that very little had been published on the constitution of this class of materials. Originally it was thought that the hydraulic properties of cements were due to the presence of manganese but this explanation was discarded after Hippolyte Victor Collet-Descotils (1773-1815) proved that the burning converted silica into a soluble form [Frémy, 1865] and after Vicat showed that the silica of the clay was the essential agent in the hardening process [Vicat, 1818].

His first paper on the setting of cements appeared in 1882, after he had worked in the subject two years [Le Châtelier, 1882]. This work led eventually to his doctoral thesis, published in 1887 first as a memoir and then as a book [Le Châtelier, 1887a].

In order to become familiar with the problem, Le Châtelier decided to start his research with a simpler case, the curing of plaster of Paris. Antoine Laurent de Lavoisier (1743-1794) had already shown

that the burning of plaster was accompanied by a loss of water and that during the setting process the solid became again hydrated, so that the final product was gypsum, with the crystals entangled with one another. Anselme Payen (1795-1871) had found that the dehydration of gypsum took place at the constant temperature of 300°C. Le Châtelier repeated Payen's experiment but with the thermometer immersed in the reacting mass and observed that there were two temperature arrests, a long one at 135°C and a short one at 170°C. He understood immediately that the difference of his results with those of Payen was due to the latter having measured the temperature of the furnace and not that of the reacting mass. The second temperature arrest was initially assumed to be an experimental error but after repeating the experiments several times Le Châtelier understood that the two arrests reflected the fact that the water loss occurred in two steps, one at 135°C where three quarters of the water were lost, and the other at 170°C, where the rest of the water was lost. There was thus a lower hydrate of calcium sulfate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, which proved to be the substance present in normal plaster, and not, the anhydrous salt, as Lavoisier has supposed. The hemihydrate was obtained in crystal form by heating gypsum in water in a sealed tube at 150°C.

The dehydration results did not explain why addition of water hardened the mass, particularly since the amount of water added was incapable of dissolving more than one thousand of the calcium sulfate present. Previous experiences by Jean Charles Marignac (1817-1894) provided to Le Châtelier the answer of the question. Marignac had observed that if burnt plaster was shaken with water and quickly filtered, a much more concentrated solution was obtained than if the hydrated salt had been taken. If this solution was left to rest it deposited gypsum crystals and returned to the normal concentration, that is, the original solution was supersaturated. The process of setting was thus explained not by the conversion of each particle of the solid hemihydrate into gypsum but by the production of a highly concentrated solution around each particle, from which the new crystals of gypsum separated, forming an interlocking mass. A series of crystallization and supersaturation stages allowed complete hydration of gypsum from a limited amount of water.

Le Châtelier understood that the process was rapid and involved very small crystals that were hard to observe. To test his ideas he performed a brilliant

experiment: he added alcohol to slow down the hydration process and thus he was actually able to observe the crystallization.

In the next step he extended this work to calcareous cements by studying the properties of the hydrates of barium and metasilicates, barium and calcium ortosilicates, several aluminates of calcium, etc. Their crystallization gave a clue to the probable mechanism of setting of the calcium compounds. Le Châtelier prepared the compounds of lime, silica, and alumina in pure form and then studied their properties. He found that the orthosilicate $2\text{CaO} \cdot \text{SiO}_2$ had a very interesting property; it could only be prepared at very high temperature and upon solidification formed a very hard mass that turned into a loose powder on further cooling. Le Châtelier explained these results as a polymorphic change involving a large change in volume.

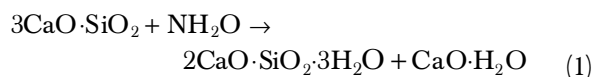
Le Châtelier found that the reaction between barium oxide and silicon oxide yielded two well-defined anhydrous silicates, one having one mole of BaO ($\text{BaO} \cdot \text{SiO}_2$) and the other having two moles ($2\text{BaO} \cdot \text{SiO}_2$). The monobarium silicate could be hydrated with six molecules of water, the same as calcium sulfate. The dibarium silicate reacted with water in a more complicated form, it decomposed into barium hydroxide and monobarium silicate hydrated. These processes were completely different from the one presented by the corresponding calcium compounds.

Further experimental work included the study of several aluminates such as $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3$. The first three hydrolyzed in the presence of a large amount of water and the fourth one yielded the stable hydrate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$. On the other hand, iron sesquioxide, Fe_2O_3 , furnished stable compounds such as $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, which were found not to take part in the setting process. In the presence of water they only expanded and did not react.

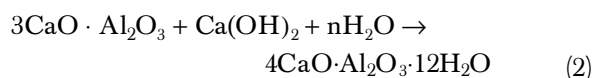
A microscopic analysis of thin sections of cement clinkers allowed Le Châtelier to observe four different kinds of crystals, which were later named by Alfred Elis Törnebohm (1838-1911) *alite*, *belite*, *celite* (brown), and *felite*. In well-burnt clinker celite formed the filling material and magma from which the alite had separated. Le Châtelier made the interesting observations that the *grappiers*, or hard nodular masses which resisted slaking, yielded a cement, which when ground, consisted almost entirely of

alite, with a minimum quantity of inter-crystalline material [Detsch, 1938]. He also deduced that the alite crystals, the elements of a first consolidation, were formed during the cooking by precipitation in a medium of the fusible celite. Celite was the result of a second consolidation and after serving as flux and making possible the chemical reactions, solidified and filled all the voids present in the mass.

All this information allowed Le Châtelier to develop a theory applicable to the setting of all hydraulic cements. In contact with water, a super-saturated solution was formed which deposited a less soluble hydrated material; this constant solution and deposition of material resulted in the production of an interlaced and coherent mass of minute crystals. By the shrewd use of Henri Clifton Sorby's (1826-1908) microscopic petrographic methods he found that all cements contained a common constituent, $3\text{CaO}\cdot\text{SiO}_2$, whose composition he established. The basic reaction that described the hardening process was



Dibarium silicate reacted similarly but the hydration of the aluminate was only an accessory reaction



Le Châtelier's view that tricalcium silicate was the main constituent of Portland cement did not meet with general acceptance, and many investigators considered alite as a solid solution of calcium aluminates and silicates.

Le Châtelier explained the hardening processes of hydraulic cement as follows:

(a) Each hydraulic cement is constituted by a compound or a mixture of compounds, able to combine with water and form a stable hydrated system.

(b) The anhydrous system is unstable in relation to water and hence it must be soluble. In contact with water it forms a supersaturated solution, which deposits hydrated crystals spontaneously. The initiation of crystallization constitutes the setting process.

(c) This mechanism repeats itself indefinitely. The initial cement paste transforms slowly into an interlocking mass of crystals. Since these crystals originated from a saturated solution, they are shaped long and fine needles. The numerous points of contact of the latter generate their packing.

In other words, the properties of hydraulic cements are the result of three phenomena: (1) the chemical one of hydration, (2) the physical one of crystallization and, (3) the mechanical one of hardening.

Le Châtelier's also concluded that there must be an upper limit to the content of calcium oxide, corresponding to the formation of triacalcium silicates and aluminate. An excess of this compound results in expansion and disintegration on setting. Insufficient lime would lead to the formation of the bicalcium silicate, unable to hydrate. Although the theoretical limit is three moles of calcium oxide per mole of acid elements, the practical limit is about 2.5 because actual fusion does not occur in the kiln and the reactions do not go to completion. The limit fixed by Le Châtelier constitutes the first theoretical hydraulic modulus and has developed into other modules depending on the specification for the cement [Le Châtelier, 1887].

Le Châtelier's thesis forms the basis of our present knowledge on cements and mortars, and in all significant matters it has proved to be correct.

Le Châtelier returned on several occasions to the study of cement, concerning himself especially with the improvement of methods of analysis and testing, with the control of manufacture, and with the conditions bringing about the disruption of masses of cement and concrete in air, water, or seawater. The damaging action of seawater was caused by the reaction between free calcium hydroxide and magnesium salts, with the resulting flocculent magnesium hydroxide destroying the cohesion between the particles.

He also carried out many researches on the allied subjects of ceramics and glass. The eventual construction of the phase diagram of the system $\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2$ gave a solid validation of Le Châtelier's work: the domain of existence of the Portland cement corresponds exactly to the reduced ternary system $\text{SiO}_2, 3\text{CaO}\cdot\text{SiO}_2, 2\text{CaO}\cdot\text{Al}_2\text{O}_3, 3\text{CaO}$. The liquidus of tricalcium silicate is perfectly delimited between the liquidus of calcium oxide, bicalcium silicate, and tricalcium aluminate [Rengade, 1937].

As a final remark, we can mention that during his research about cements Le Châtelier had the need to measure the temperature of firing of lime and different hydraulic pastes. There was no current procedure capable of making accurate measurements in the high temperature zone. After testing several methods Le Châtelier selected the thermoelectric method.

Flame temperature and explosions

Increased industrialization of the French economy had led to a substantial increase in the production of coal, from less than four million tons in the first part of the nineteenth century, to more than seventeen million tons afterwards. Increase in the tonnage produced was accompanied by an increase of the depth at which the coal was extracted. Between 1867 and 1877 a series of explosions caused by *grisou* (firedamp gas) left hundreds of workers dead. The public clamour led the French government to appoint in March 26, 1877 a Commission to establish the best means of guarding against explosions in the mines. The Commission promptly found itself lacking information about *grisou* and its properties. It was known that methane was the chief component of the gas; Humphry Davy (1778-1819) had found that the combustion of *grisou* with air was highly dependent of the temperature of the mixture, it could occur in a slow progressive manner, or suddenly, with substantial increase in volume and development of light. No information was available on the flammability limits, the combustion process itself, the speed of flame propagation, as well as reliable methods for determining the proportion of firedamp in a mine atmosphere. There was no parameter that could be used to determine the detonation of mixtures of air and methane. The concept of lower flammability limit was hardly established and a rapid method to study the atmosphere in mines was to observe the way the flame of Davy's safety lamp blazed. The length of its bluish aureole was used as a qualitative indication of the danger of explosion.

In March 1878, Le Châtelier and François Ernest Mallard (1833-1894) were asked to participate in the work of the commission and to study the problem experimentally.

Mallard and Le Chatelier decided to make a scientific study of the combustion process of gaseous mixtures in order to clarify the following points: (a) How was the explosion related to the composition of the mixture and at what temperature did the phenomenon initiate, and (b) what was the velocity of flame propagation. By answering these questions they expected to generate safety rules for the mines [Pascal, 1937].

Their first work was to determine the temperature of inflammation of mixtures of hydrogen, methane, and carbon monoxide in various proportions with air. They enclosed the gas in a 200-mL measuring flask, added increasing quantities of a flamma-

ble, such as hydrogen or illuminating gas, and observed at what concentration an alcohol flame originated the inflammation of the mixture. Their results indicated that the inflammation temperature depended more on the nature of the fuel than on its concentration. Not only that, the combustion process at different temperatures showed a discontinuity in the temperature, which Le Châtelier and Mallard believed occurred at the inflammation temperature. Their results indicated that the actual value of this temperature was much lower than that assumed before [Le Châtelier and Mallard, 1880].

In order to measure the velocity of flame propagation Le Châtelier and Mallard had need to know several thermodynamic parameters, such as the specific heat of gases at very high temperatures, which were unavailable at the time. The only data were those of Regnault had determined these up to 200°C [Regnault, 1862], which could not be extrapolated safely. Mallard and Le Chatelier succeeded in measuring these heats using Bunsen's method of explosion in a closed vessel to measure the temperature and pressure of explosion and a calorimeter to determine the heats of reaction. Le Châtelier and Mallard studied about one hundred mixtures by these procedures and obtained the maximum pressure they achieved upon explosion. Some of their results were as follows [Le Châtelier, and Mallard, 1881a,b]:

Mixture	Maximum pressure (atm)
CO + 0.5 O ₂	9.9
H ₂ + 0.5 O ₂	9.0
C ₂ N ₂ + O ₂	16.4
Cl ₂ + H ₂	8.0

They also developed the following differential equation that described the cooling of the gas inside a spherical vessel

$$\frac{d\Delta T}{dt} = a\Delta T + \left(b + \frac{c}{P_0} \right) (\Delta T)^2 \tag{3}$$

where ΔT was the difference in temperature between the gas and the surroundings at time t , and P_0 the pressure of the mixture at 0°C. Any anomaly with respect this equation meant that gaseous dissociation was present, as for example, with carbon dioxide at temperatures below 2000 K [Châtelier and Mallard, 1881c].

Simple relations were developed to correlate the change of the specific heats with temperature, inclu-

ding the practical equality of the specific heat of the perfect gases (oxygen, nitrogen, hydrogen, an carbon dioxide) up to the highest temperature. Le Chatelier and Mallard measurements showed unequivocally that the specific heat increased with temperature. Their results allowed, for the first time, to calculate rather precisely the temperature of combustion and thus perform adequate heat balances of a furnace.

Flame propagation was studied by passing mixtures of gases through a gas tube having an appropriate diameter so that the cooling that took place near its walls did not affect the velocity of propagation. In this situation the velocity of advance of the flame achieved a characteristic limit. Mallard and Le Chatelier found that the velocity of the stream, initially uniform, would become irregular and that at the same time strong vibrations would take place inside the tube. Eventually the inflammation was transmitted at such a high velocity that it resulted in an explosion that destroyed the tube. The passage of the flame through the tube was registered photographically and this register allowed calculated the velocity of propagation. Mallard and Le Chatelier found, for example, that the highest velocity (about 3000 m/s) took place with equimolar mixtures of acetylene and oxygen. Their results showed that there were two types of flames propagation, one very slow that led to a deflagration, and another, very fast, that led to an explosion [Le Chatelier and Ballard, 1881b].

In the course of their studies it became evident that the means of estimating the concentration of firedamp in the atmosphere of a mine were not sufficiently accurate. This parameter was usually measured by examining the change in appearance of the flame in a safety lamp. Mallard and Le Chatelier improved the method by using a non-luminous flame of alcohol in place of an oil or paraffin flame, and simplifying the apparatus for the analysis of mine gases. The first work determined the influence of the velocity of the streams on the safety of mine lamps. Their conclusions are today employed in the two most used indicators of gas: the alcohol lamp of Chesneau and the hydrogen lamp of Francis Clowes [Le Chatelier and Mallard, 1881d].

Mallard and Le Chatelier used the results of their studies to recommend addition of a large amount of ammonium nitrate to a nitro explosive, to lower the detonation temperature of the explosive. This recommendation became eventually the basis of the called *safe explosives* [Le Chatelier and Ballard, 1881d].

Le Chatelier and Mallard's results on firedamp in mines were published in a lengthy memoir [Le Chatelier and Mallard, 1882; Audiart, 1937].

Solubility laws

In a paper written in 1884 [Le Chatelier, 1885] Le Chatelier pointed out that the nature of the conditions he had established for the stability of chemical equilibrium was the same as those for mechanical equilibrium. The principle of action-reaction made possible to know the *sign* relation that existed between two opposing phenomena, but taught nothing about its size. Nevertheless, in specific cases it was possible to learn about the intensity of the effect by using the mechanical theory of heat.

The two laws of thermodynamics allowed deriving the following differential equation for an adiabatic curve

$$\frac{dP}{dT} = \frac{E \cdot L}{T(u' - u)} \quad (4)$$

where E was the factor for converting thermal to mechanical units, L the heat of phase transfer, and u' and u the specific volumes of the new and the original phase. Equation 4 could be applied to the evaporation of water in the pure state and from a saturated saline solution, to yield

$$\frac{d\bar{w}}{dT} = \frac{E\lambda}{T(u' - u)} \quad (5)$$

$$\frac{dP}{dT} = \frac{E \left(\frac{xQ}{1 - mx} + \lambda \right)}{T(u' - u)} \quad (6)$$

where \bar{w} and λ were the vapor pressure and heat of vaporization of pure water, x the salt solubility coefficient expressed as the number anhydrous salt equivalents dissolved in one equivalent of water, m the number of water equivalents that abandoned one equivalent of salt that crystallized, and Q the heat of solution at saturation of one equivalent of crystallized salt. Assuming that the gas phase behaved as an ideal gas and that the specific volume of the gas (u') was much larger than that of the liquid (u) gave

$$\frac{d\bar{w}}{w} - \frac{dP}{P} = -k \frac{xQ}{1 - mx} \frac{dT}{T^2} \quad (7)$$

where $k = E/R$. Combination of eq (6) with Adolph Wüllner's law of for the decrease in vapor pressure in a saline solution

$$\frac{\bar{w} - P}{P} = \delta x \quad (8)$$

led to

$$\frac{d\bar{w}}{w} - \frac{dP}{P} = -\frac{\delta x}{1 - \delta x} \quad (9)$$

Equating eqs (7) and (9) yielded the differential equation that described the solubility of the salt in question, as a function of the temperature

$$\frac{\delta(1 - mx)}{1 - \delta x} \frac{dx}{x} = kQ \frac{dT}{T^2} \quad (10)$$

According to Le Châtelier, eq (10) represented an approximate law of solubility because of the approximations introduced by use of the laws of the ideal gas and that of Wüllner. Nevertheless, it was expected to become more and more accurate as the absolute value of Q increased.

The differential eq (10) could be simplified by considering that the two factors $(1+mx)$ and $(1+\delta x)$ were generally small in comparison to unit, so that

$$\frac{dx}{x} = \frac{k}{\delta} Q \frac{dT}{T^2} \quad (11)$$

Equation (11) showed that each state of a given substance had a different solubility curve.

Le Châtelier used the last statement frequently to study and interpret phenomena based on supersaturation. A result of one such study was the opportunity to prepare a series of new borates, in particular, the salt $B_2O_3 \cdot Li_2O \cdot 16H_2O$, the most hydrated salt known at that time that contained 75 percent of its weight in water.

In addition, he was able to prove that the slope of each of the branches of the solubility curve depended on the heat of solution Q at infinite dilution of the particular species. Thus, at the intersection of the curves the ration of the tangents was equal to the ratio of the latent heats of solution.

Chemical equilibrium

Within Le Châtelier's work his studies about chemical equilibrium, or in a more general way, his studies about chemical mechanics, hold a place of first importance. Chemical mechanics oriented most of his work and gave unity to the total.

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 [Le Châtelier, 1888] he enounced 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, was later elaborated further by Wilhelm Ostwald (1853-1932) and became the basis of modern theories of catalysis.

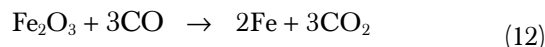
Le Châtelier established the general law of equilibrium in chemical systems. The equation he derived was later modified only in its form and continues to be used extensively. It is known that this equation permits, using only one experimental result, to calculate the equilibrium conditions, without any relation to the temperature and pressure. He also showed that knowledge of the emf of a cell permitted calculating the dissociation of steam at high temperatures; a very surprising result at the time it was formulated.

Le Châtelier was the first to express in almost general way, a law, that in a way has contributed to make his name known to chemistry students all over the world: the law of displacement of the equilibrium. He presented this law as a purely experimental result. It enclosed within its generality, partial results that had already been obtained by Moutier, van't Hoff and Robin. It was a very useful law because it permitted the experimenter to predict at which temperature and pressure it was necessary to operate to realize a given reaction. It also allowed explaining a series of previously unexplained results. It was now possible to understand why endothermic compounds were stable at high temperatures while exothermic were at low temperatures. One of the most important results of this work was related to the synthesis of ammonia. The reaction occurred with a contraction in volume, fact that indicated that production of ammonia would have to be conducted at high pressures. Based on using previous experiences made by Louis-Jacques Thénard (1777-1857) Le Châtelier predicted that the reaction would be catalyzed by iron. Experiments performed at 600°C, and 200 atmospheres, in the presence of metallic iron, resulted in an explosion. As a result of this accident Le Châtelier abandoned the project but, nevertheless, he was so convinced that ammonia synthesis had taken place that he took out a patent to assure

his priority to the process. Le Châtelier's results were implemented by Karl Bosch (1874-1940; 1931 Nobel Prize in Chemistry) and Haber to achieve the industrial synthesis of ammonia. Both recognized their debt to Le Châtelier's early results.

In 1876 and 1878 Gibbs published two papers in which he developed a number of basic relations related to chemical equilibrium [Gibbs, 1876, 1878]. Like other Gibbs' works this paper went almost unnoticed because of its heavy mathematical content. At that time mathematicians were not interested in chemistry the same as chemists were not interested in mathematics. But Le Châtelier was among those chemists who were interested; he saw immediately its importance and had the work translated into French. He recognized that the laws of chemical mechanics were potentially present in Gibbs' work. He wrote: "It is clear that Gibbs has played the most important part in developing the laws of chemical mechanics" [Oesper, 1931; Lafitte, 1962].

Another example cited by Le Châtelier's to justify his results was the case of the blast-furnace reactions. The overall reaction taking place in the furnace is



In practice the gas, which leaves the furnace contains a large concentration of carbon monoxide. In those times it was assumed that the partial oxidation of the gas was due to its poor contact with the ore. For this reason, one of the first solutions tried was to increase the height of the furnace to increase the residence time. This and other solutions failed and the real explanation had to wait for the development of the laws of reversible equilibrium to understand the phenomenon.

In 1884 Jacobus Henricus van't Hoff (1852-1911) had reported on the effects of temperature upon chemical equilibrium, stating that "toute équilibre entre deux états différents de la matière (systèmes) se déplace par un abaissement de la température vers celui des deux systèmes don't la formation développe de la chaleur" (All equilibria between two different states of matter—systems—are displaced by a lowering of temperature toward that of the two systems whose formation develops the heat) [van't Hoff, 1884]. In the same year Le Châtelier published a memoir in which he extended Van't Hoff's conclusions to cover all the variables of the reaction. This memoir was the first of a series of papers on the laws of chemical equilibrium, which culminated up in a

memoir of 126 pages in the *Annales des Mines* for 1888 [Le Châtelier, 1888].

Le Châtelier succeeded in integrating the equations in which the free energy (Gibbs energy) was expressed in terms of the heat of reaction and the specific heats: "the integration constant was, however, unknown, and his comment was" It is highly probable that the constant of integration is a determinate function of certain physical properties of the substances in question. The determination of the nature of this function would lead to a complete knowledge of the laws of equilibrium. It would permit us to determine a priori, independently of any new experimental data, the full conditions of equilibrium to a given chemical reaction".

Ironically, and for a different reason, Le Châtelier's theories also went unnoticed: the journal *Annales des Mines* was not widely read by chemists. His work would have to wait until 1909 when Walter Nernst (1864-1941) took them further.

Le Châtelier's great generalization of the phenomena of chemical equilibrium, now known as the principle of mobile equilibrium states, was originally in a very unclear manner [Le Châtelier, 1884]: "Tout système en équilibre chimique stable soumis à l'influence d'une cause extérieure qui tend à faire varier soit la température, soit sa condensation (pression, concentration, nombre de molécules dans l'unité de volume) dans sa totalité ou seulement dans quelques-unes des ses parties, ne peut éprouver que des modifications intérieures, qui, si elles se produisaient seules, amèneraient un changement de la température ou de condensation, de signe contraire à celui résultant de la cause extérieur" (Every system in stable chemical equilibrium submitted to the influence of an exterior force, which tends to cause the variation either in its temperature or its condensation—pressure, concentration, number of molecules in the unit of volume—in its totality or only in some of its parts can undergo only those interior modifications which, if they occur alone, would produce a change of temperature, or of condensation, of a sign contrary to that resulting from the exterior force). In 1888 he proposed a much more simplified form of the law [Le Châtelier, 1888]: "Tout système en équilibre chimique éprouve du fait de la variation d'un seul des facteurs de l'équilibre une transformation dans un sens tel, que, si elle se produisait seule, elle amènerait une variation de signe contraire du facteur considéré" (Every change in one of the factors of a system in chemical equilibrium occasions a rear-

rangement of the system in such a direction that the factor in question experiences a change in sense opposite of the original change).

The thermodynamic derivation and consequences of Le Châtelier's principle appear in many publications and books and will not be repeated here [Hillert, 1995; Solaz-Portolés, 1995; Wisniak, 1999].

Taylorism

Le Châtelier received in 1904 like a revelation the theories of the American engineer Frederick Winslow Taylor (1856-1925). For him they were a perfect illustration of the precepts of industrial science, perfectly fitting the domain of social economy and being an extension of the scientific spirit and its methods, in all the aspects of moral and intellectual life. Le Châtelier proceeded to import these concepts into the area of scientific organization of work, rationalization of production and industrial research, as can be seen in his thoughts about technical education. In this question, Le Châtelier revealed himself as a non-compromising defender of a type of scientism. Taylor sent to Le Chatelier a pamphlet outlining the methods by which he had attacked industrial problems, and the latter was delighted to find here examples of the application of the scientific method, which might well serve as a model to even professional scientists. The essential features of *Taylor's procedure* were: (a) change one variable at a time, (b) make precise measurements of each single factor and (c) define exactly the objective of each step [Lette, 1996].

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