

*The Le Chatelier Memorial Lecture.*HENRY LE CHATELIER,
1850—1936.

A MEMORIAL LECTURE DELIVERED ON OCTOBER 28TH, 1937.

By CECIL H. DESCH, D.Sc., Ph.D., F.R.S.

IN accordance with the custom of this Society on the death of one of its distinguished Foreign Members, we commemorate to-day a great French chemist whose career, singularly clear and consistent in the principles by which it was guided, covered a very wide range, so that the student of chemistry meets with his name in what might at first appear as very different fields. A great physical chemist, Le Chatelier applied the principles of the science to a variety of problems, many of which were presented to him by industry. As a teacher and for many years an acknowledged leader, he exercised a profound influence on the academic and industrial life of France, whilst his character and achievements were held in honour by men of science of many nations and schools.

Henry Louis Le Chatelier (the second name is not used in his publications) was born in Paris on the 8th of October, 1850. His father and mother came from families which numbered among them men of distinction in science, in exploration, and in art. His father, Louis Le Chatelier, had been trained in the *École Polytechnique* and the *École des Mines*. Holding a position in the *Crédit Mobilier*, he was actively associated with many industrial advances, notably with the construction of railways in France, Northern Spain, and Austria; with the establishment of the Siemens–Martin process of steel smelting; and with the development of the Deville process by means of which aluminium was first successfully manufactured on a commercial scale. Having a small private laboratory, he conducted experiments in chemistry, and kept up a close friendship with men of science, including Dumas, Chevreul, Tresca, and Siemens, and above all with Henri Sainte-Claire Deville, whose laboratory at the *École Normale* he often visited with his son on Sundays. Louis Le Chatelier seems to have had clearly defined ideas of scientific method. He had a love of geometry, but a distrust of mathematical methods when extended beyond what he regarded as their legitimate sphere, an attitude which is reflected throughout in the writings of his son, on whom he sought to impress the need for the clear statement of a problem before attempting its solution, and the avoidance of all superfluous hypotheses.

Henry was the eldest of six children. One of his brothers, Louis, became the technical director of engineering and metallurgical works, another, André, made a reputation as a naval engineer and was a pioneer of autogenous welding, and a third, Alfred, after several missions in Africa, became professor of Mussulman Sociology in the *Collège de France*, and was one of the inspirers of French colonial policy. The mother, née Durand, was an ardent catholic of the school of Lamartine, who devoted herself entirely to the upbringing of her family. It was she who mainly influenced him in his earlier years, impressing on him, as he says, a love of order, both in society and in scientific thought, producing in him a strong distaste for revolutionary ideas of every kind, whether in the domain of politics or in that of atomic physics.

After his schooling at the *Collège Rollin*, of which he always spoke with affection, he entered the *École Polytechnique* in 1869. The standard of teaching does not seem to have been high, but he was at least encouraged in the study of geometry. Moreover, some of the students showed independence of thought, and inspired by the ideas of Auguste Comte, Le Chatelier and a friend, Pistor, attempted to re-write the official course in physics, eliminating all metaphysical ideas, such as that of force. His studies were interrupted by the necessity of serving as a sub-lieutenant during the siege of Paris, but in 1871 he passed into the *École des Mines*, in order to be trained for the engineering service of the State. Here, besides taking the professional courses, he voluntarily attended other lectures, including those of Sainte-Claire Deville at the Sorbonne and of Étienne Marey at the *Collège de France*, while pursuing literary studies under a professor named Charpentier.

On graduating from the *École des Mines*, he took part in a government mission to Algeria to report on the possibility of constructing an inland sea in that region, and on returning served for two years as a mining engineer in the *Corps des Mines* at Besançon. He had, as he tells us, at that time no intention of teaching, but looked forward to a career in administration.

During this period he published one short scientific note—his first communication to the Academy of Sciences—and in view of his later fame as a metallurgist it is interesting to find that it dealt with a metallurgical problem. Tresca 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." In order to isolate these inclusions, Le Chatelier adopted a method which had been used by Schloesing for the analysis of cast iron, namely, removal of metallic iron by distillation in a stream of dry chlorine at a dull red heat. A skeleton of the original specimen remained, consisting of these non-metallic inclusions. This method has been revived during the last few years for the study of inclusions in cast irons and in alloy steels.

In 1877, only two years after graduating from the *École des Mines*, Le Chatelier was recalled to the same institution by its director, the famous geologist, Daubrée, to become professor of general chemistry. He tells us that his only qualification was a good report of his work in chemistry in the College examinations, but that there was no engineer in the Mining Corps who was better qualified. However, he entered seriously on the duties of the post, and determined to undertake research. His father had died some years before, and he was at a loss to know how to choose a subject for investigation. He approached Sainte-Claire Deville, who told him, rather scornfully, that the question was absurd; that one had only to begin work in a laboratory to find oneself surrounded by problems, the only difficulty being to select from among them. This counsel not being very helpful, he remembered that his maternal grandfather, Pierre Durand, had been a friend of Vicat, the first investigator of synthetic hydraulic cements, and that when examining the specimens left by Vicat at the *École des Mines* he had consulted the literature of the subject, and had found that a scientific knowledge of the constitution of this class of materials was completely lacking. This decided his choice of a thesis for his doctorate. Even before starting this work, however, he began, in collaboration with his senior colleague F. E. Mallard, the studies of fire-damp in mines to which reference will be made later.

His first paper on the setting of cements appeared in 1882, after he had been working on the subject for two years, but for an account of the work it is better to turn to its full presentation in his thesis, submitted in 1887, and republished in 1904 with further additions under the title "*Recherches expérimentales sur la constitution des mortiers hydrauliques.*" The views as to the constitution and setting properties of cements here set forth have been extended and supplemented by later workers, but they remain unchanged in essentials. Being well aware of the complex nature of Portland and similar calcareous cements, and having the classical work of Vicat on pozzolanic materials as a guide, Le Chatelier decided to begin with a simple example, that of plaster of Paris. Lavoisier had shown that in the process of "burning" gypsum water was lost, and that in the course of setting the solid was again hydrated, so that the final product was gypsum, with the crystals closely entangled with one another. The dehydration of gypsum had been found by Payen to occur at 300°. Repeating the experiment, and adopting Regnault's plan of immersing a thermometer in the mass and observing the temperature at which an arrest occurred on heating, Le Chatelier found that water was lost at 135°. Payen had recorded the temperature of the furnace in which the mass was enclosed, and not that of the gypsum itself. A small arrest was also noted at 170°, but this was for some time attributed to experimental error. Later (1883), as the same point reappeared in every experiment, the loss of weight was determined, and it proved that only three-fourths of the water was driven off at 135°, the remainder being lost at 170°. There was thus a lower hydrate of calcium sulphate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and this proved to be the substance present in normal plaster and not, as Lavoisier had supposed, the anhydrous salt. The hemihydrate was obtained in crystals by heating gypsum in water in a sealed tube at 150°, and was also recognised



[To face p. 140.]

in the incrustations found in marine boilers. It was not clear, however, why the mass should become hard as the result of re-hydration. The solubility of calcium sulphate in water is too low to allow of the whole going into solution and crystallising in the new form, when only sufficient water is present to make the mass pasty. Marignac had observed that if burnt plaster were shaken with water and quickly filtered, a much more concentrated solution was obtained than if the hydrated salt had been taken. The process of setting was thus to be 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. The crystals are too small for their form to be observed, but by mixing with dilute alcohol in place of water, the process was so retarded that the actual crystallisation could be watched. The formation of hydrated crystals out of contact with the original solid could be seen still more easily by dissolving plaster in a solution of potassium sulphate and then filtering. The solution obtained is so highly supersaturated that the filtered liquid becomes a pasty mass of hydrated crystals.

The next step was to extend this work to calcareous cements, but some experiments were first made with the silicates of barium. The metasilicate, BaO,SiO_2 ,* was prepared in a hydrated form with $6\text{H}_2\text{O}$, and proved to be identical with crystals previously recorded by Pisani as being formed inside glass bottles containing baryta water. The anhydrous salt, prepared by fusion, set with water like plaster, forming the hexahydrate. An orthosilicate, $2\text{BaO},\text{SiO}_2$, was also prepared by fusion, and this reacted with water, giving the same hydrated metasilicate, together with crystals of barium hydroxide. This behaviour gave a clue to the probable mechanism of setting of the calcium compounds. Cement clinker was known to be a complex substance, so the problem was approached synthetically, the compounds of lime, silica, and alumina being first isolated in a pure state and their properties examined. One calcium silicate was already known, CaO,SiO_2 , and this proved to be inert. The orthosilicate, $2\text{CaO},\text{SiO}_2$, required a very high temperature for its preparation, and whilst forming a hard mass on solidification, fell into a loose powder on further cooling. This behaviour had already been observed in certain slags and cements, and the property was now explained as being due to a polymorphic change involving a large expansion of volume. As the disintegrated silicate had no hydraulic properties, but merely formed a mud with water, it was concluded that it played no part in the setting of cement. The analysis of "grappiers" (hard nodular masses often found in hydraulic limes, and resisting slaking with water) suggested that a compound $3\text{CaO},\text{SiO}_2$ might exist, but for some time all attempts to prepare it synthetically failed. Calcium chloride was added as a flux, but the product was a new compound, $2\text{CaO},\text{SiO}_2,\text{CaCl}_2$. However, by decomposing this by superheated steam the tribasic compound was obtained in a nearly pure state. Since it set hard with water without expansion, it was concluded to be the essential constituent of Portland cement. It was identified in cement clinker by the appearance of its crystals in thin sections under the microscope, the mineral constituents surrounding it being considered to have served as a flux during its formation at a high temperature.

Alumina is, however, also present in cement, and as aluminates of several metals were already known, it was probable that this oxide was combined with lime. Three such compounds were prepared synthetically: $\text{CaO},\text{Al}_2\text{O}_3$; $3\text{CaO},2\text{Al}_2\text{O}_3$; and $3\text{CaO},\text{Al}_2\text{O}_3$. All of these set rapidly with water, but formed a less stable mass than the silicates. The next stage was the study of the products of hydrolysis, and it was shown that the final product of the setting of the silicate was $\text{CaO},\text{SiO}_2,2.5\text{H}_2\text{O}$, whilst the far more easily soluble aluminates yielded a product which was given as $4\text{CaO},\text{Al}_2\text{O}_3,12\text{H}_2\text{O}$, but was later shown by Candlot to contain only three molecules of lime, and its formula was altered accordingly. Iron oxide, although a stable compound $3\text{CaO},\text{Al}_2\text{O}_3,\text{Fe}_2\text{O}_3$ was prepared, was found to take no part in the setting. The hydrolysis of the silicate liberated two molecules of lime, which could be recognised as crystals of calcium hydroxide in the cement after setting. The mechanism of setting and hardening was worked out in detail, based on results obtained with plaster and on the formation of an unstable supersaturated

* It is convenient to represent compounds of this kind as being composed of simple oxides.

solution which then deposits the stable products in the form of very fine interlocking crystals. The process was studied in the synthetic compounds and in commercial cements and hydraulic limes, and its identity proved. The thesis contained other important conclusions. For instance, since any excess of uncombined lime in the clinker was found to cause expansion and disintegration on setting, a limit was set to the ratio of bases (lime and magnesia) to acids (silica and alumina), the fact being also indicated that as actual fusion does not occur in the kiln, the reactions are always incomplete, so that the practical limit of lime is below the theoretical. This limit was the first "hydraulic modulus," various values for which have been given by later writers and embodied in specifications. Lastly, the causes of the disintegration of cements after setting are discussed, and it is shown why the presence of free lime causes an increase of volume, whilst the liberation of calcium hydroxide during setting has no such effect.

This memoir, which contains excellent drawings of the several substances, as examined by Sorby's petrological methods, forms the basis of our knowledge of cements, and in all substantial matters it has proved to be correct. The very accurate thermal analysis of the component systems at the Geophysical Laboratory in Washington, which has added greatly to our knowledge, has confirmed the existence of Le Chatelier's three calcium silicates, and the only alteration in regard to the aluminates is the substitution of a 5 : 3 molecular ratio for the 3 : 2 originally given. When it is considered how simple were the experimental means employed, and how complete the results, the investigation must be regarded as one of the classics of inorganic chemistry.

The picture of hardening presented in this work met with some objections. In 1893 W. Michaëlis put forward the view that setting and hardening are colloidal processes, the gradual desiccation of the colloid giving the mechanical strength. This view was never accepted by Le Chatelier, and when a general discussion of the problem was arranged by the Faraday Society in 1919, he maintained his original position, admitting, however, that the crystals might be so minute as to be indistinguishable as such. The difference between the two views then became little more than one of terminology, since *X*-ray experiments show that the colloidal silicates are largely made up of very minute crystals.

Le Chatelier returned on several occasions to the study of cements, 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 sea water. His simple apparatus for determining the liability of a cement to disruption, consisting of a split cylinder having two pointers attached, the divergence between which measures the expansion of the cement enclosed in it when immersed in water at 100° for three hours, has been generally adopted. He also carried out many researches on the allied subjects of ceramics and glass.

The research on cements illustrates very clearly Le Chatelier's attitude towards science. Having the social importance of scientific discovery always in view, he refused to recognise any distinction between pure and applied science. His most interesting themes were suggested to him by the needs of industry, whilst he insisted constantly on the importance of the reaction between the two, instancing the origin of the rare-gas industry from the academic investigation by Rayleigh of the anomalies in the density of nitrogen, and on the other hand of the creation of thermodynamics by Sadi Carnot as the result of an attempt to improve steam engines in order to meet English competition.

The research on cements opened up several other lines of work having important results. It became necessary to devise some means of measuring high temperatures, such as that of the fusion of silicates, with much greater accuracy than could be obtained with such crude instruments as those of Wedgwood and Siemens. Antoine Becquerel had proposed in 1830 to make use of the thermoelectric effect originally discovered by Seebeck, and platinum-iron and platinum-palladium couples had been used by Pouillet and by Edmond Becquerel. Regnault, however, made a careful study of these couples and found such irregularities in their behaviour that he condemned the method as being inherently inaccurate. Le Chatelier took up the subject, and found that the irregularities were due to contamination of the one wire by diffusion of the other metal, producing a varying *E.M.F.*, and to the lack of uniformity of the wires themselves, it being possible to produce an

effect even by heating locally a single wire. In 1887, therefore, he proposed the use of a couple composed of one wire of pure platinum and another of an alloy of platinum containing 10% of rhodium. This proved satisfactory, and although many other combinations have been used, this couple remains to-day the international standard. It is interesting to note that, only two days after the reading of the paper describing the new pyrometer, Dr. Ludwig Mond ordered two such couples by telegram, and these, introduced into his works, were the first to be used in industry. In 1890 the couple was introduced into the steel industry by Sir Robert Hadfield. It was, however, not enough to devise a couple of constant properties; the best conditions for use had to be found. The readings were made much more accurate by using an aperiodic galvanometer of the Desprez-d'Arsonval type, whilst the method of calibration by using a number of fixed points, such as the melting points of pure metals and the boiling point of sulphur, was introduced at the same time, making the troublesome comparison of each couple with the air thermometer unnecessary. With these inventions thermoelectric pyrometry became at once a standard method, the applications of which have continually increased. He also concerned himself with optical pyrometry, for the purpose of measuring the temperatures reached in open-hearth steel furnaces. Modifying Cornu's photometer for the purpose, and comparing the radiation from a standard amyl acetate lamp with that to be measured, interposing a red filter, he was able to measure temperatures with greater accuracy than before, giving 1500—1600°, for instance, as the working temperature of the Siemens furnace, whilst previous estimates had been as high as 2000°. Although the instrument itself has been superseded, valuable work was done with it, especially in the determination of the emissive powers of various heated solids, the great variation in which is the principal source of error in industrial measurements with the optical pyrometer when strict black-body conditions are not attained.

Simultaneously with the research on cements, research was being carried on in another field. Work on the explosion of gaseous mixtures was undertaken at the request of a commission appointed in 1877 to examine the best means of guarding against explosions of fire-damp in mines, public opinion having been aroused by a succession of mining disasters. In May 1878, F. E. Mallard and Le Chatelier were asked to study the problem experimentally, and this was the beginning of a long series of researches. That a certain temperature was needed to bring about an explosion was known from the work of Humphrey Davy, but the conditions of propagation of a flame were unknown, and there were no satisfactory methods of determining the proportion of fire-damp in a mine atmosphere. The two collaborators first determined the temperature of inflammation of mixtures of hydrogen, methane, and carbon monoxide in various proportions with air, and found these to be lower than had been suspected. From this they passed to measurements of the velocity of propagation of flame, a subject on which research is even now being conducted. In the course of these studies, they found it necessary to determine certain physical constants for which, at the time, no figures were available. The only values of the specific heats of gases were those of Regnault, determined at atmospheric pressures and at temperatures not over 200°. Extrapolation of such values to high temperatures gave quite misleading results. By using Bunsen's method of explosion in a closed vessel provided with a pressure gauge, and so obtaining the temperature of combustion, the heat of combustion being determined calorimetrically, the specific heat could be calculated. Simple relations were found, including the practical equality of the molecular heats of the "perfect" gases (oxygen, nitrogen, hydrogen, and carbon monoxide) up to the highest temperatures, while increasing slowly with the temperature, and the effects of dissociation on other gases, such as chlorine, water vapour, and carbon dioxide. These data became of importance for the study of combustion in industrial furnaces as well as in their immediate application to explosions of mine gas, although certain sources of error were later discovered which necessitated numerical corrections in some instances.

In the course of these experiments it became evident that the means of estimating the quantity of fire-damp in the atmosphere of a mine were not sufficiently accurate, and the usual method of examining the change in appearance of the flame in a safety lamp was improved by using the non-luminous flame of alcohol in place of an oil or paraffin

flame. The apparatus for the analysis of mine gases was also simplified. Further, the same collaborators undertook a study of mining explosives, and succeeded in establishing general principles governing the choice of safe explosives, with results of considerable value to the mining industry.

The work on cements and that on gases at high temperatures had this in common, that both investigations involved a study of chemical equilibria. Le Chatelier was never tired of expressing his indebtedness to Sainte-Claire Deville, and it was his studies of dissociation that brought home to him the importance of reversible reactions. The dissociation of calcium carbonate by heat, examined experimentally by Debray, is one of the primary reactions in the production of quicklime and of cement clinker. A study of the temperature of dissociation of this compound and of several others led him to consider the general problem of chemical and physical equilibrium. Le Chatelier's interest in thermodynamics, which led him to occupy a great part of his life in such studies, came in great measure from his sense of its importance for practice. As an example, he quotes the case of the blast-furnace reactions. The gross reaction may be expressed by the equation $\text{Fe}_2\text{O}_3 + 3\text{CO} = 2\text{Fe} + 3\text{CO}_2$, but the gas which leaves the furnace actually contains a considerable proportion of carbon monoxide. This was thought by some practical men to be due to insufficient contact between the ascending gases and the ore, and furnaces were in some places increased in height in order to obtain longer contact. No benefit was derived from the change, as was explained by Sir Lowthian Bell, and a knowledge of the laws of reversible equilibrium would have shown that the reversibility of the reactions made the presence of carbon monoxide inevitable. The knowledge actually existed at the time that the practical experiment was tried, but it had not been utilised by industry.

A note published in 1884 contains a generalisation of a principle enunciated by van 'tHoff for the effects of temperature only, extended to cover all variations of conditions. This, which is now known as the Le Chatelier principle, was at first rather cumbrously expressed. "Any system in stable chemical equilibrium, subjected to the influence of an external cause which tends to change either its temperature or its condensation (pressure, concentration, number of molecules in unit volume), either as a whole or in some of its parts, can only undergo such internal modifications as would, if produced alone, bring about a change of temperature or of condensation of opposite sign to that resulting from the external cause." This was the first of a series of papers on the laws of chemical equilibrium, summed up in a memoir of 126 pages in the *Annales des Mines* for 1888. The principle mentioned above is here stated in a form which is at once simpler and more comprehensive: "Every change of one of the factors of an equilibrium occasions a rearrangement of the system in such a direction that the factor in question experiences a change in a sense opposite to the original change." Changes of electromotive force are included as well as those of pressure and temperature. The memoir contains a large number of applications of the principle, based on experiments which are partly original and partly taken from the work of others. Stress is laid on the empirical nature of the generalisation, but it has proved of great service in co-ordinating the facts of physical chemistry. Some later writers have even sought to represent the laws of biological and social evolution as special applications of this general principle.

While engaged in the preparation of this memoir, Le Chatelier met with the work of Willard Gibbs, and found that his main results had been anticipated, so far as their mathematical form was concerned. He considered, however, that the highly abstract presentation by Gibbs, having no reference to chemical data, could have been of little value to chemists. He was the means of presenting the work of Gibbs to the French public in a translation, and later of applying the doctrine of phases to solid systems in his studies of metallurgy. Much of this work was parallel with, but independent of, that of van 'tHoff, whom he frequently quoted in his later writings.

The same paper contains an interesting anticipation of later ideas. Le Chatelier succeeded in integrating the equations in which the free energy is expressed in terms of the heats of reaction and of the specific heats. The integration constant was, however, unknown, and the comment is made that "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 corresponding to a given chemical reaction." It was further shown that if a chemical reaction is equivalent to the sum of two other reactions its constant of integration is the sum of their integration constants. Several other predictions followed, among them that for homogeneous gas reactions of similar character, such as that between hydrogen and the several halogens, the constants would be found to be nearly equal, as later experiments have shown them to be.

The *Annales des Mines* was not widely read by chemists, and these predictions appear to have been overlooked until the methods were revived by Nernst in 1909. Full justice was done to Le Chatelier by Nernst and by G. N. Lewis, but the work has passed unnoticed by many writers on physical chemistry. The teaching of such general ideas made slow progress in France, and as late as 1905 Henri Moissan refused to admit an article on chemical equilibria into his "Traité de Chimie Minérale," although Le Chatelier succeeded in, to use his own expression, "smuggling" six pages on the subject into his section dealing with cements.

True to his general principles, he sought to apply the knowledge gained in these studies to practical ends. One of the reversible reactions in blast furnaces is the decomposition of carbon monoxide into carbon dioxide and solid carbon, and under his direction this reaction was examined experimentally by O. Boudouard, resulting in the curve which is familiar to all metallurgists, the necessity of the presence of iron oxide as a catalyst if equilibrium is to be attained at the lower temperatures being also demonstrated. With another student, G. Chaudron, the equilibria between iron and its oxides, hydrogen, and water vapour were similarly determined. Although some of these data have since needed revision, they formed a model for later researches in this field. The work extended over many years. One such investigation calls for notice. The synthesis of ammonia from nitrogen and hydrogen presented special interest as a study in chemical equilibrium. That it would be of practical value seemed unlikely, as it was to be expected that the conditions would be difficult to realise. The fact that the union of the two gases is accompanied by a contraction showed that increased pressure would favour synthesis, whilst a catalyst would probably be essential. The notes of Thenard were at hand, in which it was stated that the dissociation of ammonia was complete at 600° in presence of metallic iron. This temperature was adopted, with a pressure of 200 atmospheres. The mixture of gases was forced by an air compressor into a steel Berthelot bomb, the reduced iron in the interior being heated by a platinum spiral. The result was an explosion which blew fragments of the heavy bomb through the floor and the ceiling. In the belief that combination of the gases had occurred, a patent was taken out as a means of securing priority. On examining the compressor later, however, it was found that a tap had been accidentally left open during the experiment, and that air as well as nitrogen and hydrogen had been forced into the bomb, thus accounting for the explosion. The work was abandoned, but the right conditions (of temperature, pressure, and catalyst) for the synthesis had in fact been attained in 1900, and both Haber and Claude acknowledged their indebtedness to this early record when they successfully achieved the industrial production of ammonia.

A paper published in 1906 indicates for the first time the method of drawing up the "thermal balance sheet" of an industrial furnace.

From 1883 onwards, Le Chatelier made a number of observations of polymorphic changes in solids. The first solid studied was boracite, and shortly afterwards, in collaboration with Mallard, he examined the dimorphism of silver iodide and the effect of pressure on the change, thus giving a further example of the principle which had been derived from the study of dissociation. The most interesting discovery, made by means of his modification of Fizeau's dilatometer, which could be used at temperatures up to 1000°, was the transformation of quartz at 570°. The other forms of silica were also studied, and the results were applied to the processes of manufacture of refractory materials and

to the examination of slags. A systematic work "La silice et les silicates," was published in 1914.

In 1887 he had exchanged his chair for that of Industrial Chemistry in the same College, and this post he retained until his retirement in 1919. In 1898 he succeeded Schutzenberger in the chair of Mineral Chemistry in the Collège de France, which he held for ten years, and in 1907 he succeeded Moissan at the Sorbonne. In these several teaching posts he had the opportunity of influencing a large number of students, and of introducing important reforms into the teaching of chemistry in Paris. Courses of lectures in inorganic chemistry had been largely catalogues of compounds, their preparation and properties. In Le Chatelier's lectures, the general principles of chemistry were taught and illustrated by concrete examples. The lectures were prepared with the utmost care, and the fine delivery of the speaker and the perfect clarity of his discourse made him an outstanding teacher. Widely read and with an excellent memory, he could advise his students as to their reading as well as guide their experimental work. His method may be seen in the volume published in 1908, "Leçons sur le carbone." This is described in the preface as the literal text of the lectures which he delivered at the Sorbonne in the session 1907—8. After a discussion of the meaning of science and of a scientific law, the work of his predecessor, Moissan, is related as illustrating the importance of studies of simple substances in a purely chemical manner. An account of the several forms of carbon and of their properties leads up to the subject of fuels. After a chapter on metallic carbides and their industrial importance, a survey of the oxides of carbon and the carbonates introduces the subject of the laws of chemical equilibrium, which are discussed on the lines of the author's previous work. A final section deals with the determination of atomic and molecular weights, but throughout the book, atomic conceptions are ignored, formulæ being used merely as a representation of combining proportions. The applications to industry are constantly introduced, and several of the chapters contain interesting sketches of the history of a discovery or of an idea. It is certain that the lectures made a great impression on their hearers, and left their mark on French chemistry. A somewhat similar treatment is found in "Le chauffage industriel," first published in 1912, and again reproducing a course of lectures. Starting from the general principles of combustion, the work treats of the nature of fuels and the determination of their value, passing to accounts of the production of gaseous fuels and the design of furnaces, stress being laid on principles rather than on technical details, which should, in the author's opinion, be learned in industrial practice.

The professor of metallurgy at the École des Mines, Lan, having become Director, invited Le Chatelier to undertake the lectures in that subject. He declined, on the ground that the field was quite strange to him, but he was persuaded to include a few lectures on metallurgy in his course on industrial chemistry. He gradually became more interested, and it is as a metallurgist that his name has been chiefly known to the later generation of scientific workers, his contributions to that branch of science having been numerous and outstanding. The accounts of metals, and especially of alloys, in chemical literature were unsatisfactory. Brilliant work on the structure of certain alloys had been done by isolated workers, especially by Sorby, but their investigations had been little noticed by chemists, who commonly looked on alloys as indefinite mixtures, somewhat resembling the glasses. As far back as 1863, Mathiessen had shown that alloys might be regarded as solidified solutions, but this idea had not been brought into relation with the phase rule or with other general principles, and such researches as those of Ramsay and of Heycock and Neville were little known in France. Le Chatelier undertook the improvement of methods of determining the temperatures at which alloys underwent changes on heating and cooling, employing thermal, dilatometric, and electrical resistance measurements for the purpose; and carrying these to higher temperatures than previous workers had used. In 1895 he pointed out that the study of the constitution of alloys comprised two distinct parts, (a) the chemical constitution, including the formation of intermetallic compounds and solid solutions and of allotropic modifications; and (b) the physical structure, or arrangement of the several kinds of crystal within the solid alloy. He showed that the widely used method of extraction with solvents and analysis of the residue

as a means of discovering definite chemical compounds between metals often led to misleading results, and that much more trustworthy information could be obtained by studying the variation of some physical property with composition and with treatment. The form of the freezing point-composition curve, often presenting maxima at simple atomic ratios, was particularly useful.

Sorby's method of polishing a flat surface of a metal and developing the structure by etching, and then examining it by reflected light, was taken up by Floris Osmond, then engaged in the steel works at Le Creusot, whose first paper on steel was published in 1885. Osmond discovered the allotropic changes in iron, and explained the hardness of quenched steels by the retention of a hard variety of iron, stable at high temperatures, on rapid cooling. Osmond's method of preparation of the specimens was cumbersome, more so than that of Sorby twenty-five years earlier, and Le Chatelier, wishing to learn his technique, succeeded in making a number of improvements, including the use of alumina, prepared by igniting ammonium alum, as a polishing powder in place of rouge. The consultations between these two workers led to a clarification of their ideas, and Le Chatelier's paper in the *Revue générale des Sciences* in 1897 placed the whole subject of the hardening of steel in a new light. The laminated structure discovered by Sorby and known as pearlite was noticed to be very similar to that of a eutectic, and was to be regarded as formed by the breaking up of a solid solution, stable at high temperatures, into two phases, in this instance iron and iron carbide (ferrite and cementite), a process quite parallel with the simultaneous crystallisation of two phases from a liquid solution. Quenching suppressed this resolution of the solid solution, but not the allotropic change in the iron, so that the hard constituent, known as martensite, was to be considered as a solid solution of carbon in the low-temperature modification of iron (α -iron). The behaviour of certain alloys of iron with nickel and with manganese, which were not hardened by quenching, was used to confirm this view, the high-temperature, non-magnetic form of iron being preserved in them unchanged. The idea of an intrinsically hard modification of iron (β -iron) was only slowly abandoned by some metallurgists, and controversy continued for many years, but the essentials of the modern view are to be found in the paper of 1897. In 1899 Roberts-Austen published the first freezing-point curve of the iron-carbon system, noting at the same time many of the thermal arrests at lower temperatures. These data, which Le Chatelier's paper made it possible to interpret, were used by Bakhuis Roozeboom to construct the first equilibrium diagram for the series, which, although since modified in many respects, has the general form of the diagram used to-day, the form of the curves having been determined with great care by Carpenter and Keeling in 1904, and since modified in detail by many workers. The paper by Roozeboom, the first application of the phase rule in detail to a metallic system, gave a new impetus to the study of the metallography of steel, and thence to that of alloys in general. A committee was formed in France, at the instigation of Le Chatelier, and in 1901 a volume appeared, "Contribution à l'étude des alliages," containing papers by the leading French metallurgists, and this, in the absence of formal text-books, was long used as a work of reference. It contained important papers by Osmond, Charpy, and others, and reprinted several contributions of Le Chatelier. These described the methods of investigating the constitution of alloys by determining their physical properties, with the aid of improved instruments which he had devised for the purpose. The most interesting of these was an improved form of microscope, designed specially for work with metals. Hitherto, microscopes of the biological type had been used, with the addition of devices for illuminating opaque objects by vertical or inclined rays. Although the photo-micrographs of the copper-tin alloys, made at this time by Heycock and Neville, which have hardly been surpassed by later workers, were made with such a microscope of the simplest type, most investigators had much difficulty in placing the specimens under the best conditions for illumination, the levelling on the stage being particularly troublesome. Le Chatelier departed entirely from the ordinary construction, and placed the specimen face downwards, without mounting, over the opening of a stage, the objective being below, and the direction of the rays changed by means of prisms. This inverted instrument proved to be exceedingly convenient in practice, and the principle was later adopted by most makers of metallographic micro-

scopes, including the most elaborate of modern instruments. It has the disadvantage of adding to the number of reflections, and for this reason some makers are reverting to the older type, taking advantage of improved methods of lighting, but most photographic work is done with the inverted form of instrument.

He made several minor improvements in metallographic technique, as in the preparation of polishing powders of regulated fineness and in the use of electrolytic methods of etching.

With increasing teaching responsibilities, Le Chatelier's experimental work naturally became more restricted, but he continued to supervise the work of students, and frequently published notes on metallurgical questions. In order that French metallurgy might have an organ of its own, he founded in 1904 the *Revue de Métallurgie*, having the support of the Société d'Encouragement and of the Comité des Forges in the undertaking. The new journal, under his active direction, at once took a leading place, which it has since retained. One paper, contained in the first volume, may be mentioned, as it represented an attempt to study the effect of different cooling liquids on the quenching of steel, cooling curves being taken by means of a thermocouple attached to the specimen. The spot of light from the galvanometer was received on a moving plate, a pendulum being arranged to interrupt the beam every second to facilitate counting. The galvanometer, of very low resistance, was not sensitive enough for high accuracy, and Le Chatelier pointed out that for a more refined study a thread galvanometer or an oscillograph should be used. This was actually done by later workers, and in the hands of German metallographers the method has been developed in a remarkable way, so as to include exceedingly high rates of cooling, but the pioneer work constituted a valuable step.

An article in the *Revue de Métallurgie* on the high-speed tool steels developed in America by F. W. Taylor and his collaborators led to a correspondence with Taylor, who wrote that since completing the investigation he had devoted himself to a larger problem, that of the organisation of factories. Le Chatelier became a fervent advocate of Taylor's principles, which were fully in accordance with his own ideas of the need for introducing scientific method into the conduct of industry. In his view, Taylor's methods consisted essentially in planning a technical operation by the study of each of the factors concerned in it, human as well as mechanical, as one would plan the determination of the velocity constant of a chemical reaction. The details of the system as applied to a factory have been much criticised, but the plan of setting apart a special staff for the planning of the operations required for a given product has proved its value, however difficult the application may be in a given case. Le Chatelier returned again and again to the subject, and collected several of his memoirs, with a new preface, in a volume entitled "Le taylorisme," first published in 1928.

The European war brought new duties. Routine teaching was suspended for a time, and Le Chatelier turned to matters connected with national defence, including an important metallurgical problem, the heat treatment of shells. After the close of the war, he continued his work of writing and of pressing forward the reform of the teaching of science and of the conduct of those industries which depend for their success on the application of scientific knowledge, while returning from time to time to the special problems of metallurgy in which he had so long been interested. In 1925 he published a little volume, "Science et industrie," and in 1936, only a short time before his death, this was revised so as to represent his considered opinion in the light of later experience, and re-issued under the title "De la méthode dans les sciences expérimentales." After reviewing the general principles of science, and making use of the classical essay of Descartes, he discusses methods of observation and the way in which discoveries are made, passing on to questions of apparatus and of experimental errors. His illustrations are largely drawn from his own work or from that of such teachers and friends as Deville and Osmond. The later chapters deal with plans of teaching, especially of chemistry and technology, with the application of science to industry, and with the Taylor system.

This small work throws an interesting light on the attitude of its author towards science. Laying stress on the need for accurate observation and experiment, he constantly warns against the misuse of hypotheses. Recognising fully the need of working

hypotheses as a means of progress, he insists on the possibility of experimental verification as a test of their value, and regards those which are not accessible to experiment as exceedingly dangerous. In his own work, he avoided as far as possible even the conception of atoms, using formulæ as expressions of chemical composition merely. His work was confined to inorganic chemistry, so that he never had to concern himself with questions of structure, which would inevitably have called for atomic conceptions, but it is instructive to follow his work, and to observe how independent the results obtained are of any ideas of the constitution of matter. For modern physical theories of the atom he had no taste, and he became more conservative with advancing age. For the inorganic chemist, however, at a time when students are often encouraged to build up their knowledge of chemistry on a basis of theories of the structure of the atom, there are lessons to be learned from

such a purely chemical treatment of the reactions between substances, including the quantitative thermodynamical study of chemical change. There is much that is suggestive in these chapters, and the author's aim of bringing together pure and applied science is clearly brought out. He shows how chemistry arose from the practical needs of mankind, and how the constant reciprocal action of pure science and industry has helped and stimulated both. This thesis is illustrated by a wealth of examples, almost entirely French. One of the objects of the book, indeed, is to insist on the supremacy of French science, although he holds, somewhat unexpectedly, that French industrialists have lagged behind other countries in the application of the discoveries of their compatriots. His teaching and influence, exerted especially during the years following his official retirement, must have done much to remedy this. His zeal for the advancement of industry was quite disinterested, as he never sought monetary reward. Intensely patriotic Frenchman as he was, he had many friends in other countries, some of whom had worked in his laboratory, whilst others had made his acquaintance through his writings. The memorial issue of the *Revue de Métallurgie* contains eloquent tributes from metallurgists of many countries, which are sufficient evidence of the respect and esteem in which he was held. He was a familiar and welcome figure at international congresses, to which he often contributed.

Le Chatelier received many honours in the course of his long life. He was admitted to the Académie des Sciences in 1907, succeeding Henry Moissan. He became a Foreign Member of the Royal Society in 1913, received the Davy Medal in 1916, and was elected a Foreign Member of our own Society in 1908. The Iron and Steel Institute awarded him the Bessemer Medal in 1910, and he received honorary doctorates from Aachen, Manchester, Copenhagen, Louvain and Madrid. 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. As late as October 1936, as Honorary President, he gave an eloquent address to the International Congress of Mines, Metallurgy and Geology in Paris, receiving an enthusiastic welcome. His health was excellent, but deafness troubled him in his later years, although he kept up his personal friendships to the last. When well over 80 he travelled to Morocco. His death came on the 17th September, 1936, at Miribel-les-Échelles (Isère). Only three days before, when the Institute of Metals was meeting in Paris, a cordial letter of greeting from him was read, but when the meeting of the Iron and Steel Institute opened a few days later in Düsseldorf, the news of his death was the first announcement made by the chairman.

Henry Le Chatelier married, in 1876, Mlle. Geneviève Nicolas, and their descendants comprised seven children, thirty-four grandchildren, and six great-grandchildren. A family photograph taken on the occasion of the sixtieth anniversary of his wedding includes forty-four persons. His widow and many of his family were present at the commemoration at the Sorbonne on 24th April, 1937, presided over by the President of the Republic, M. Albert Lebrun, who as a mining engineer had been one of his students and spoke in his address of the impressions produced by his teaching. Addresses were given by representatives of the several branches of chemistry and industry with which he had been associated, and Prof. Carl Benedicks spoke on behalf of the many representatives of foreign societies present.

All who knew Le Chatelier recognised his high character and lofty ideals. Anxious

as he was for the progress of industry and for the improvement of material conditions, he had always in mind the moral as well as the material welfare of mankind. In the address to the Mining Congress already referred to, after an eloquent passage on the relations of science and morals, he added :

“ Let us hope, without deceiving ourselves too much, that if the 19th century remains celebrated in the records of humanity for the progress of the experimental sciences and for the creation of industry on the large scale, the 20th may distinguish itself by its understanding of social problems and by its love of justice,”

and in an article which he was revising on the day of his death, he urged that the vital problems of industry to-day are essentially moral problems. This conclusion is consistent with the whole of his life work. With Latin clarity of thought, and in the best traditions of French philosophy, he looked on human thought and activity as a whole, and in his interest in special problems never lost sight of their bearing on human welfare.

I am indebted for much information to the memorial number of the *Revue de Métallurgie*, and especially to the article by Prof. Léon Guillet. M. François Le Chatelier, of Ugine (Savoie), has kindly supplied me with further notes about his father's work, and with the excellent photograph, taken a few years ago by M. Louis Lumière. A survey of Le Chatelier's work on thermodynamics and chemical equilibria is contained in the full obituary notice by Prof. P. Pascal (*Bull. Soc. chim.*, October, 1937).
