Revista CENIC Ciencias Químicas, Vol. 41, No. 2, pp. 131-143, mayo-agosto, 2010.

Pierre-Antoine Favré

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105. E-mail: wisniak@bgumail.bgu.ac.il

Recibido: 18 de agosto de 2009. Aceptado: 27 de octubre de 2009.

Palabras clave: termoquímica, electroquímica, calor de combustión, calor de disolución, calor de adsorción, zinc.
Key words: thermochemistry, electrochemistry, heat of combustion, heat of solution, heat of adsorption, zinc.

RESUMEN. Pierre-Antoine Favre (1813-1880), un médico transformado en químico, realizó investigaciones extensas en las áreas de termoquímica, electrólisis, disolución de sales y adsorción y condensación de gases sobre sólidos. Entre sus muchos logros pueden mencionarse la determinación de la masa atómica del zinc, el hecho que la combustión del carbón en cualquier estado siempre produce una cierta cantidad de CO, y en la fijación del equivalente mecánico del calor.

ABSTRACT. Pierre-Antoine Favre (1813-1880), a physician turned chemist, carried on extensive research in the areas of thermochemistry, electrolysis, dissolution of salts, and adsorption and condensation of gases on solids. Among his many achievements we can mention the determination of the atomic mass of zinc, the fact that the combustion of carbon in any state always produces a certain amount of CO, and determination of the mechanical equivalent of heat.

LIFE AND CAREER

Very little information is available regarding the life of Pierre-Antoine Favre; most of what is known about him appeared in the eulogy published by Félix Le Blanc (1813-1886, at one time Vice President of the *Sociéte de Chimie de France*) in the bulletin of the Sociéte de Chimie de France.[1]

Pierre-Antoine Favre was born in Lyon, France, on 20 February 20, 1813 and passed away in Marseilles, on February 17, 1880. After taking the chemistry classes by Jean-Baptiste André Dumas (1800-1884), at *l'École de Médecine*, and receiving his degree of *Docteur en Médecine* (1835) he quitted medical studies and was admitted to the private laboratory of Eugène Melchior Péligot's (1811-1890), where he helped him in his researches about uranium. After Péligot's appointment as professor of general chemistry at the *Conservatoire des Arts et Métiers*, he became the official *préparateur* of his class.[1]

Favre's appointment by competition, as *agrégé* to the Faculty of Medicine of Paris (1843), allowed him to participate in the researches of Gabriel Andral's (1797-1876) in the area of physiology, as well as continue his important work in thermochemistry. In 1851 Favre was appointed *chef des travaux de chimie analytique* (head of the analytical laboratories) at the *École Centrale des Arts et Manufactures*, left vacant by Charles-Adolph Würtz (1817-1884) appointment to the chemistry chair at the *Institut Agronomique in Versailles*; while continuing his work as a fellow of the Faculty of Medicine. Towards the end of this appointment, he replaced Mateu Joseph Bonaventure Orfila (1787-1853) in his class on Medicinal chemistry at the Faculty of Medicine.[1]

Favre's doctoral theses for the degree of *docteur-és-sciences physiques*[2] (1853) contained original research and were very well received. The thesis on physics introduced a new element for the chemical theory of batteries, based on clever experiments in which the cell formed an integral part of the new mercury calorimeter. James Prescott Joule's (1818-1889) theories were still rather unknown, particularly to physicists, and received a consecration by Favre's precise experiments. Favre was able to explain with great simplicity the impossibility of decomposing water with the aid of only a Smee pile [**Note 1**], and to account for the energy effects of the cell composed of two liquids.[1]

Favre's thesis in chemistry[3] was related to the heat released during chemical reactions carried on in multiple proportions. For these researches, conducted by the wet procedure and using his mercury calorimeter, Favre made frequent use of hypochlorous acid as the oxidation

---

Note 1. *Some of the defects in the common battery of zinc and copper were significantly decreased by an ingenious modification made by Alfred Smee (1818-1877). Smee observed that if the copper plate of the battery was roughened by corrosive acids or by rubbing its surface with sand paper, its action become much more efficient, and the rough surface evolved the hydrogen much more freely. To take advantage of this finding he covered platinum foil with a finely divided black powder of platinum, deposited by electricity from a solution of that metal, and used it in place of the copper in the ordinary battery. In a later improvement Smee replaced the platinum foil by the cheaper silver foil.*

agent. He also studied the heat of combustion of the allotropes of phosphorus and sulfur and the thermal effects due to compounds called explosives or of negative work, according to the nomenclature of Marcelin Berthelot (1827-1907).[1]

In 1854, Henry Sainte-Claire Deville (1818-1881) was appointed maître de conferences at the *École Normale Supérieure* and Favre was appointed his successor as professor of chemistry at the *Faculté des Sciences de Besançon*. In 1856 he transferred to the newly created *Faculté des Science in Marseilles*, Favre became dean of the Faculty of Science in Marseille in 1872, retiring in 1878 because of ill health.[1]

Favre was twice a laureate of the *Académie des Science*; in 1864 he was elected correspondent member in the Chemistry section. He received the Cross of Honor at the beginning of his work at Marseilles. In 1868 the Physics section included his name in the list of possible replacements for Claude Pouillet (1790-1868), who had just passed away. In spite of not being a resident of Paris and being absent from the city at that time, he did get a certain number of votes in his favor. In 1868 he became a correspondent of the Physics section. Favre was also an associate member of the *Académie de Médecine*, corresponding member of the *Société Philomatique*, and non-resident member of the *Conseil de la Société Chimique*.[1]

Favre was a careful and skillful experimenter, who constructed many pieces of new, clever, and delicate instruments to obtain new and more precise information in the areas he was researching. His data were used by many to prove their hypothesis.

In 1878, his health deteriorated seriously, forcing him to abandon his classes and his work. He was appointed honorary professor and honorary dean, by decree of the Minister. After painful illness he passed away on February 17, at Saint-Barthélemy, near Marseilles, His wife, his widowed daughter, and his grandchildren survived him.[1]

Favre's first independent researches involved determination of the equivalent weight of zinc[4] and studies of cupric carbonate[5] and the ammonium carbonates of zinc and magnesium.[6] He also wrote several papers on such physiologically important compounds as lactic acid, mannitol,[7] and the constituents of human perspiration,[8] and studied procedures for desiccating gases.[9] At that time he begun in collaboration with Johan Theobald Silbermann (1829-1905) a long research on thermochemistry, which eventually became classic. The pertinent publications[10-12] were related to the heat of reaction and combustion, of simple and complex substances, mineral and organic, measured by the method of live combustion, using their own cleverly designed water calorimeter, which could be named a *calorie thermometer*. Among their many achievements on the subject, the author can mention in particular their demonstration of the fallacy of Pierre-Louis Dulong's (1785-1838) rule, which stated that the heat of combustion of a compound composed of carbon and hydrogen is the sum of the heats of combustion of the elements it contains, and the fact that the heat of combustion of carbon in oxygen is less than that of carbon in nitrous oxide.

In 1857, Favre provided important experimental measurement to prove Joule's ideas[13] about the conservation of energy by means of a voltaic battery operating an electric motor, which raised a weight. He showed that the total heat evolved in the battery and the circuit, when added to the equivalent in heat required to raise the weight, was equal to that evolved by the battery alone when it was short-circuited.[14-16]

Shortly before his retirement, Favre in cooperation with the mathematician Claude Alphonse Valson (1826-1901), a professor at the *Faculté des Sciences de Grenoble*, published a series of memoirs under the general title *Recherches sur la Dissociation Cristalline*.[17-25] These memoirs reported the thermal effects due to the dissociation of salts in water and the accompanying changes in volume.[1] Svante Arrhenius (1859-1927; 1903 Nobel Prize for Chemistry) cited this study in defense of the theory of electrolytic dissociation.[1]

In 1872, Favre was appointed dean of the Faculty of Medicine at Marseilles, and in 1875 the Minister of Finances appointed him as chief of the chemistry laboratory of the Customs Administration in Marseilles.[1]

Favre's most important memoirs in the period 1856 to 1865, were published collectively by the author under the title *Sur la Transformation et l'Equivalence des Forces Chimiques* and the *Académie* recommended it be published in the 1875 volume of *Recueil des Savants Étrangers* [**Note 2**]. This summary memoir led Favre to be awarded the 1875 Grand Prix Lacaze (*chimie*). The *Académie* had already awarded him the 1869 Prix Jecker (established in 1851 to accelerate the progress of organic chemistry).

Favre determined the equivalence of chemical work and the heat that replaced it, through the use of electrodynamic phenomena. The heat put into practice by this kind of phenomena was transmitted outside and employed to perform a given amount of work. According to his own words, his results were an experimental demonstration of the conversion of chemical work into electrodynamic work and vice-versa.[1] Some very elegant experiments allowed Favre to establish the *"equivalence between different transformations of heat, in such a way that starting from a phenomenon that generated a certain amount of motor work, expressed in calories, the amount of heat liberated was always the same when the motor work was destroyed, independently of the different transformations it had experienced"*.[26] Favre established that the mechanical equivalent of heat was 413 kg · m (which compares very well with the modern value of 426.9). The experiences were done with two calorimeters, one containing a voltaic battery, and the second, built *ad hoc*, an electromagnetic motor [built by Paul-Gustav Froment (1815-1865)] activated by the pile and capable of lifting an external weight.[1]

Favre did also some work of industrial importance. During the years 1845 to 1849, he was the administration chemist of the Salines de *l'Est*, where he was in charge of chemical analyses. In 1844 a larger manufacturer of food preserves [prepared by the Appert procedure [**Note 3**], asked him to find the cause of the alterations that took place in a series of products of large consumption. Favre discovered that the reason of the failure was not due to the defect in the packing process or to a lack of sealing of the walls, but to insufficiency of a temperature of 100 °C, in order to assure the conservation and destruction of the fermentation agents. To achieve the required sterilization temperature he recommended the use of

---

Note 2. *A journal issued by the Académie des Sciences for publishing important scientific contributions of non-members.*
Note 3. *The improvement of the technique of food preserves by boiling was discovered by Nicolas Appert (1749-1841) in 1810.*

saturated salt solutions in the bath or in the autoclaves. This was shown to solve the problem.[1]

While in Marseille he developed a method for eliminating the volatile fraction of crude petroleum, so as to employ the fuel for house and street illumination. He also made photometric experiences to determine the best lamps having a cylindrical wick, which was fed by heavy fractions of petroleum.[1]

SCIENTIFIC CONTRIBUTION

Favre published more than 50 papers on general chemistry, electrochemistry, thermochemistry, dissolution of salts, and the condensation and adsorption of gases. As was customary for a candidate for membership in the *Académie des Sciences*, he also published two booklets describing his main fields of research and findings.[27,28]

General chemistry

In order to determine the equivalent mass of zinc Favre analyzed very pure samples of zinc oxalate as well as the amount of water decomposed to oxidize a known weight of pure zinc. The gaseous products of the decomposition of the oxalate were passed through a column of cupric oxide heated red, followed by absorption of the CO_2 formed. The results indicated that the equivalent mass of zinc was 32.991 (H = 1.000), a result which compares very well with today's accepted atomic mass of 65.38.[4]

Copper carbonates were known to dissolve in ammonium sesquicarbonate, $(NH_4)_4[H_2(CO_3)_3]$, producing a blue liquid. Favre was interested in identifying the combination generated. To do so he concentrated the blue solution, saturated it with ammonium carbonate, and afterwards diluted it in alcohol. Initially no bicarbonate precipitated, but a few hours after the liquid was left to clarify, the walls were found to be covered by beautiful crystals of an intense blue color. Analysis of the crystals yielded the formula CuH_3NO,CO_2, corresponding to cuprammonium oxide carbonate, with ammonia playing the role of water. Heating the crystals to 200 °C in a stream of CO_2 caused sublimation of ammonium carbonate and partial reduction of the copper oxide. Heating the salt to a much higher temperature it decomposed with detonation. If the operation was carried in a stream of CO_2, the remaining residue was metallic copper. Favre also studied the thermal decomposition of copper hydrates and carbonates. The results indicated that the presence of water led to a lowering of the decomposition point of the salts and that the disengagement of the water was always accompanied by that of CO_2.[5]

Favre also studied the double carbonates of magnesium and ammonia and zinc and ammonium. These salts are easy to prepare, they produced neat brilliant and stable crystals, but their composition was found to be quite different.[6]

Mannitol and lactic acid are formed during the fermentation of sugar. Favre made an elemental analysis of mannitol and found 39.24 % carbon and 7.80 % hydrogen, figures very close to the theoretical ones.[7]

Favre and Maumené[29] found that copper oxide decomposed at a temperature near that of the fusion of copper to yield a new oxide, which they represented by Cu_5O_3, corresponding to the mixture $2Cu_2O.CuO$. According to Favre and Maumené, their finding could explain why the analyses of copper minerals were usually inconsistent. The metal was determined in the form of its oxide and the required heating probably was accompanied by decomposition into this new mixed oxide.

In 1853, Favre started, under the auspices of the physician Louis Jecker, researches, which were later published integrally in the *Archives de Médecine* of 1853 and in extract form, in the journal of the *Académie*.[8] According to Favre, the information available about the composition of human sweat was conflicting because the analysis had been conducted on very small amounts of the secretion and probably after fermentation had already begun. For this reason he collected a large volume of the material (40 liters!) and kept it all the time under controlled conditions to avoid its decomposition. Distillation of the liquid produced three fractions, the first one was always acid, the second neutral or alkaline, and the third always alkaline. The smell was very light, not unpleasant, and did not recall that of butyric acid, known to be present during the decomposition of sweat. The components were determined by analyzing the fractions of sweat, which were insoluble in absolute alcohol, and soluble in alcohol but insoluble in ether. The fraction insoluble in pure water and in acidified water was found to contain very small fragments of epidermis, the one soluble in acid water contained traces of earth phosphates, the part soluble in water contained a large amount of sodium chloride, a lesser amount of potassium chloride, and traces of alkaline albuminates, alkaline phosphates, calcium salts, and no magnesium. The fraction soluble in alcohol and insoluble in ether was shown to contain sodium lactate (analyzed through its zinc salt) and the sodium salt of a new nitrogen-containing acid, which Favre named *acide hydrotique* or *sudorique* (sudoric acid). In the free state, this new acid was syrupy, non crystallizable, soluble in absolute alcohol, and formed soluble salts with almost all the bases. It contained nitrogen and the elemental composition of its silver salt corresponded to the formula $C_{10}H_8NO_{13}$,AgO. The fraction soluble in ether was found to be constituted by urea and a bit of fatty material. Favre determined the main components of sweat were water (99.55 wt %), sodium chloride (0.22 wt %), and the hydrotates of sodium and potassium (0.156 wt %)[8] [The precise composition of sweat is still unknown, some known components are 2-methylphenol (*o*-cresol), 4-methylphenol (*p*-cresol), creatinine, and uric acid.].

Thermochemistry

Favre and Silbermann presented seventeen communications on experimental thermochemistry to the *Académie of Sciences*, in the period 1844 to 1849, covering more than 250 pages.[10-12] The subject was particularly important because since 1843 the *Académie des Sciences* had been proposing the subject "*Détermination des Quantités de Chaleur Dégagées dans les Réactions Chimiques*" for its *Grand Prix des Sciences Physiques*. In 1850 Favre and Silbermann were awarded 1 500 francs within the framework of the prize[30] [**Note 4**].

Note 4. *The report to the Académie, read by Regnault, in the name of the Commission assigned to judge the contributions to the prize, stated the following: "La Commission propose d'accorder à titre d'indemnité: 1. Une somme de quinze cents francs à l'auteur du Mémoire ayant pour épigraphe: Le travail est le fonds qui manqué les moins" (The contributions were presented anonymously, under an epigraph given by the authors).*
Two other contributions received 1 000 and 500 francs, respectively.[31]

In an important memoir[32] of Dumas (1800-1884) and Jean Servais Stas (1813-1891) about the atomic mass of carbon, they had corrected the numbers found by Jöns Jacob Berzelius (1779-1848) and Dulong, and proved that carbon, in any possible state, including diamond, burnt red in a stream of excess oxygen, always gave place to a certain amount of carbon monoxide, which had to be taken into account to obtain precise results. Favre and Silbermann thought that this circumstance could have altered Dulong's result about the heat of combustion of carbon. Having first determined the heat of combustion of carbon monoxide, and the proportion of the latter in the combustion of various carbons, they determined the heat of combustion of carbon when converted completely into CO_2. Their results yielded a very important result: the heat of combustion of carbon was different for each of its allotropic states. Afterwards, Favre alone used other experimental methods to prove that the same phenomenon occurred with the allotropic forms of phosphorus, sulfur, etc.[1]

Favre and Silbermann used a different experimental method than Dulong's to determine the heat of combustion of hydrogen, which turned out to be the same as that measured by Dulong. The combustion of different hydrocarbons of a homolog series proved that the law suggested by Dulong, that the heat of combustion of a hydrocarbon represented the weighed sum of the heats of combustion of the hydrogen and carbon in the compound, was wrong. Similarly, Velter's law that the amount of oxygen absorbed was proportional to the heat generated was also mistaken. It turned out that isomeric hydrocarbons and isomeric ternary organic compounds did not have the same heat of combustion. The consequence was obvious, it was necessary to drop the law according to which it was possible to calculate the heat of combustion of an oxygenated substance or a fuel, from knowledge of its elementary composition and the heat of combustion of hydrogen and carbon, after subtracting the hydrogen and oxygen corresponding to the composition of water. Favre and Silbermann provided the laws of increase of the heat of combustion corresponding to the different terms of a homolog series (fatty acids, compound ethers, and hydrocarbons), which showed that isomeric bodies were not isothermal, that is to say, did not have the same heat of combustion.[1]

In the second part of these researches, they reported the determination of the heat of decomposition of bodies called, consequently, explosive or endothermic, or with negative work, according to Marcelin Berthelot's (1827-1907) nomenclature; in other words, the report included a series of thermal effects corresponding to the modifications occurring in the molecular state of substances.[1]

A third part contains a large number of thermal measurements carried on with a new, quite cleverly designed, mercury calorimeter, which could be named a *calorie thermometer*. Favre and Silbermann used the wet method to determine a very large number of heats of reaction, with the help of equations, which contained, with their proper sign, the several heat effects known in advance. The set of these numerous results highlighted the intervention of the thermal factor, which little by little was replacing the vague concept of affinity.

In the two final papers of their joint research, published in 1852,[11,12] Favre and Silbermann divided their results as follows:

a) A large number of experiences done on the heat of combustion of several substances in oxygen: carbon in different allotropic states, hydrogen sulfide, carbon disulfide, different gaseous compounds of carbon, several well defined organic materials, a large number of compounds belonging to different series of homolog compounds, such as hydrocarbons of equation $C_{2n}H_{2n}$, esters, and the corresponding acids, as well as the oxidation of hydrogen by chlorine. A simple law was found to correlate the members of a given homolog series: the heat of combustion of the homolog series of hydrocarbons examined was seen to decrease as the chain was enlarged, and the differences were in arithmetic progression with their order C_2H_2, C_4H_4, C_6H_6, etc., the difference being 37.5 cal.
The results indicated the need to correct the heat of combustion of carbon determined by Dulong, because the latter did not consider the unavoidable formation of CO during combustion. The combustion of carbon in the form of diamond was always accompanied by the formation of CO and CO_2. For this reason, Favre and Silbermann performed careful measurements of the heat of combustion of CO in pure oxygen and found it to be 2.403 units/g CO.
They also proved that the heat of combustion of a given body varied according to its physical state and that except for ethylene, Dulong's rule relative to the heat of combustion of compounds of carbon, hydrogen, and oxygen, was only approximate. Favre and Silbermann also found that isomers belonging to the same homolog series had different heats of combustion. Thus, mixed ethers had a larger heat of combustion than the corresponding acids in the series; the two ethers burned (ethyl and amyl) gave a heat of combustion larger than that of the corresponding alcohol, and the many esters and acids burned did not show isothermicity.

b) A study of the combustion of carbon in NO confirmed Dulong's finding that carbon burning with NO released more heat that when burning in pure oxygen. Favre and Silbermann were intent in determining the heat accompanying the high temperature dissociation of the elements of NO. Their results indicated that the disintegration path was quite different from that assumed before by other investigators. NO_2 and hyponitric acid, which in many situations played the role of radicals, resisted decomposition at the temperature that destroyed NO. This result was undoubtedly true for NO_2; for hyponitric acid, which was not decomposed into nitrogen and oxygen, it was hard to decide if at the highest temperatures it tolerated it decomposed into nitrogen dioxide and oxygen since these substances would certainly recombine when the temperature was lowered.
Favre and Silbermann also measured the heat of decomposition of water peroxide, which Louis-Jacques Thenard (1777-1857) had indicated already that it decomposed when heated. Another measurement was the heat effect accompanying the transformation of aragonite into rhombohedral calcium carbonate.

c) Combinations carried on by the wet procedure. Here the authors studied the heat effect accompanying the hydration and dissolution of acids and salts, the reaction between acids and bases and salts with salts, in the formation of acid and basic salts, in double decompositions, and in the precipitation of metals from the salt solutions. They also determined the heat of oxidation, chlorination, bromination, iodination, and sulfurization of a series of metals, as well as the heat of formation of ammonia. All these experiments were conducted in the mercury calorimeter designed by the authors.

d) Investigation of the heat effects when using the chemical equivalent of different substances. These effects, which they named the thermal equivalent, were not related to the effect measured by Victor Regnault (1810-1878) under the same name, but which was really the chemical equivalents that satisfy the law of specific heats. Favre and Silbermann believed that their thermal equivalents reflected the affinity effect of thermal phenomena. Thus, the most stable compound, that is, the one in which the elements are joined by the largest affinity, seemed to be the one its formation was accompanied by the largest release of heat. The experiences of William Robert Grove (1811-1896) had shown that water was able to decompose at a temperature at which it resisted the action of Fe_3O_4 and ZnO. There was also a large difference between the thermal equivalent of silver chloride, a very stable compound, and the thermal equivalent of silver oxide, a very unstable substance. When the compounds formed by the combination of different non metals with metals took place in water, the amounts of heat released followed a very simple law. Hence, knowledge of the figures relative to the oxidation of a series of metals, and the chlorination, bromination, etc. of only one of them, allowed calculating the heat effect of bromination, chlorination, etc., of all the others. Implied in this result was a method for determining theoretically, the fictive heat of dissolution of an insoluble compound, and hence, the heat of formation of the compound.

Regarding saline combinations, the authors provided a new explanation about the composition of crystallized neutral salts.

e) Report of the heat effects accompanying the adsorption of HCl, SO_2, and CO_2, by carbon. One conclusion was that the heat of adsorption was larger than the heat of vaporization.

f) Determination of the specific and latent heat, using the mercury calorimeter.

g) The heat effect accompanying the compression or expansion of a gas. The results proved that the heat conductivity of hydrogen was much larger than that of other gases.

h) Chemical action of solar rays. During irradiation of chlorine with white light a true molecular transformation took place without change in volume, analogous to the one taking place in the rearrangement of the atoms that constitute butyric acid and ethyl acetate.

i) Thermal effects occurring during the chemical actions performed by the current of a pile. The results indicated that introduction in the circuit of a voltmeter having a resistance equal to that of a platinum wire of a given length, resulted in release of the same amount of heat released in both cases, as long as the heat required to decompose the water was taken into account.

Affinity was considered to be the force that led to the combination of substances, and afterwards maintained the stability of the compound formed. Favre first determined the heat effect that occurred during the formation and decomposition of hypochlorous acid (HClO) dissolved in the presence of diluted HCl, and afterwards the oxidation of large number of substances with the help of an excess of an aqueous solution of hypochlorous acid. Among them, were the combination of chlorine and oxygen to form chloric acid in diluted solution, the heat of transformation of phosphorus acid (H_3PO_3) into phosphoric acid, the heat of transformation of hypophosphorus acid (H_3PO_2) into phosphoric acid, the heat of formation of arsenic acid (H_3AsO_4), arsenous acid, $As(OH)_3$, phosphorus pentachloride, trichloride, arsenic trichloride, $AsCl_3$, NO, diluted nitric acid, nitrous acid, oxidation of SO_2 to SO_3, SeO_3, etc.[3]

All the above work constituted Favre's *Thèse Originale de Chimie*. His main conclusions were the following: (a) although the amount of heat released by the successive compounds resulting from the union of oxygen with a non metal increased as the degree of oxidation was augmented, these amounts were not proportional to the number of oxygen equivalents which had been fixed. The last equivalent of oxygen added released less heat than the previous one; (b) the compounds of oxygen and nitrogen did not exhibit the same phenomena, they could be accompanied by a release or absorption of heat, as the degree of oxidation increased; (c) the thermal effect measured increased as the affinity of the combining elements increased, and (d) in the case of phosphorus, the experiments were carried using the two allotropic form of the element. The heat of combustion of red phosphorus was substantially inferior to that of ordinary phosphorus.[3]

In a later paper Favre described his procedure to determine with the help of his mercury calorimeter, the value of the calorie expressed as a longitude of the expansion of the mercury in the calorimetric tube. The value was 0.141 5 mm when the calorimeter contained 498.700 g of water, and 0.165 7 mm when it contained 23.707 g of water.[26,33]

Favre had claimed for a long time that the only way of get an idea of the force called affinity, was to consider the thermal effects that took place. Favre and du Quillard used a mercury calorimeter for their experiments for measuring the heat of dilution in water of sulfuric acid, acetic acid, potassium acetate, potassium iodide.[34]

Favre measured the heat of solution in water for different concentrations of ethanol, glycerin, potassium carbonate, sodium carbonate, ammonium nitrate, potassium nitrate, sodium nitrate, barium nitrate, strontium nitrate, sodium acetate, barium acetate, potassium chloride, sodium chloride, sodium sulfate, potassium sulfate, ammonium chloride, barium chloride, calcium chloride, potassium bromide, and solution in ethanol of acetic acid, glycerin, potassium acetate, and calcium chloride.[35]

Two phenomena took place in the process, the reciprocal attraction between two different molecules, which is accompanied by a release of heat, and a diffusion process, which is accompanied by absorption of heat. The overall result was positive or negative depending on which effect predominated. When alcohol was the solvent, the diffusion process was seen to control. The dissolution of salts that crystallized in anhydrous form was always accompanied by absorption of heat.[35]

Favre concluded as follows: (a) When forming a new type or modifying a type by substitution, affinity appeared according to its well know characteristics; operating full equivalents, and when reacting successively equal fractions of equivalents, the reactions furnished equal amounts of heat; (b) The result was not the same when the type formed or modified reacted on a solvent, water for example, without formation of a crystalline product. In this situation the characters attached to affinity were not present, it was more a phenomenon of attraction, but not of the same order as the preceding one. This attraction did not count anymore, the equivalents that she activated; it seemed to operate over masses that did not obey anymore the law of multiple proportions, and this force did not seem to be limited more than the one that corresponds to the elastic force (vapor pressure) of water vapor at room temperature. Thus when letting act successive equal fractions, the amount of heat released were not the same; (c) in order to arrive to an equilibrium state, the substance which had been mixed released or absorbed thermal energy, independent of the amount of matter put into action; (d) Two orders of action seemed to be produced simultaneously; a reciprocal attraction of heterogeneous molecules brought into action, accompanied by a release of heat and a diffusion that produced a decrease in temperature; the net effect was positive or negative depending on whether the first or the second effect predominated. Thus when alcohol was used as the solvent, the diffusion effect seemed to govern the process, (e) Dissolution of salts that crystallized in anhydrous form, always yielded an endothermic effect when dissolved in water, (f) Solutions of salts that crystallize with water (hydrates), generated heat when dissolved in water. It seemed that the attraction effect, accompanied by release of heat, predominated when dissolved in an amount of water not too large; the diffusion effects predominated when the amount of water was increased substantially; (f) when mixing wine alcohol with one of its homologous, the amount of heat absorbed was the largest when the alcohol corresponded to a more condensed hydrocarbon, (g) the reaction of water with methanol and ethanol was exothermic.[35]

The solubility of the sulfates of sodium, potassium and zinc, and of sodium chloride was not influenced by pressure because their saturated solutions failed to crystallize as pressure was increased. The solubility of sodium sulfate in water increased substantially as the pressure increased, as proved by the fact that a saturated solution at 16.5 °C was able to dissolve more salt as the pressure was increased to 30 atm. Regarding the effect of pressure on the solubility of solid bodies, such as hydrated silica, and several salts, experience proved that the solubility was not affected by the pressure.[36,37]

Electrochemistry

The amount of heat developed in the voltaic circuit during the passage of electricity was known to depend on the conductivity of the same. Joule had already proved[13] that an electrical current flowing along a metallic conductor, developed an amount of heat proportional to the product of the resistance of the conductor and the square of the intensity of the current. In an electrolytic process, the amount of heat developed was proportional to the product of the square of the intensity of the galvanic current and the resistance to conductivity. Joule compared the voltaic heat results with those obtained by carrying on the direct combustion of substances by the dry method and concluded that the heat released by the combustion of equivalents of the substances was proportional to their affinity to oxygen. Joule believed that the heat released by chemical compounds, without transmission of electricity, originated from the resistance to electrical conductivity.

According to Favre,[2] some consequences of the above laws were: (1) the voltaic heat developed was proportional to the number of atoms of water or zinc employed to produce the current, (2) the total voltaic heat developed by the couple was proportional to its intensity and the number of atoms electrolyzed, (3) when the current produced by the voltaic pile, simple or complex, passed through a substance which was or was not an electrolyte, the voltaic heat developed in a given interval of time was proportional to the number of atoms which were electrolyzed in each trough,

Now, Favre was intent in finding if the amount of heat released by the resistance to the passage of a current in the conductor of the cell, was simply a loan done to the total heat effect, which corresponded only to the chemical action produced by the current. His results confirmed his opinion that the oxidation of zinc was not enough to explain the effects of the current; it was necessary to take into account all the chemical actions, which took place in the couple. According to Favre, a given mass of water molecules could react more independently than a single molecule from the entire mass that lost one of its elements. If the oxygen and hydrogen of any one molecule were separated, this effect would result in a known absorption of heat. The hydrogen that had been liberated did not belong necessarily to the same water molecules that had lost their oxygen, it might well belong to another water molecule. In an amalgamated couple (for example zinc and platinum) with the circuit open, there was a tendency for combination. Closing the circuit oxidized the zinc at the expense of the nearest water molecule and heat was released; because of the small conductivity of the liquid, this heat could be transferred without delay to the immediately neighboring hydrogen molecule. It would be gained by the molecules closest to the platinum, a conductor that allowed instantaneous passage, and it was from this metal that hydrogen disengaged. Therefore, the author had to admit that the current passed from the platinum to the zinc by the interconnecting metallic arch, that is, in the *opposite direction* on which it was admitted by convention.[2]

Thus, the explanation offered by Favre to the phenomena observed during the electrolysis of water in a voltaic pile, centered on the role played by a metallic good conductor, capable of transmitting, say, instantly to the hydrogen the heat that it required to become free. This heat would not be transferred with the same velocity from one elementary water molecule to another. In all the water molecules comprised between the two metals, evolutions of elementary molecules could occur that did not generate a current, because separations and combinations of hydrogen and oxygen would take place simultaneously, with a zero net thermal effect. Favre insisted that the only possible way to explain the phenomena was to consider simultaneously all the reactions taking place in a cell. In fact, independently of the tendency of zinc to oxidize, the oxidation could not take place without the intervention of an oxygen molecule from the water, previously decomposed, but this water molecule could not decompose without absorbing the 3 446 units of heat needed, which only the oxidation of zinc could provide. Hence, there was no reason for the reaction to begin. Interposition between the reacting elements of a metallic conductor (infinitely more conducting than the liquid in the cell) removed the obstacle opposing the reactions. Therefore, it had to be admitted that all the heat provided by the chemical reaction passed through the metallic arch in the direction indicated above.[2]

The effects produced by the currents of the cell seemed to belong to two modes of expression: (a) the currents of latent heat, (b) the currents of transmitted affinity. But both manifestations stemmed from the same source: the chemical action.[2]

Favre concluded as follows (1) the only source of thermal effects produced in the cell were the chemical actions generated by the active elements, (2) all the chemical actions that took place in the voltaic couple acted simultaneously in the production of the current, (c) the release of heat caused by the passage of voltaic electricity through metallic conductors was rigorously complementary to the heat confined in the elements of the cell, giving a total equal to the total heat effect corresponding only to the chemical reactions, independently of all the electricity transmitted, (d) the possible chemical decompositions caused by the passage of electricity through the circuit, always brought into play the same amounts of heat that accompanied the same chemical separation carried on by any other factor (Hess's law).[2]

Additional experiences carried on by Favre led him to the following results: (1) the amount of heat released by the conversion into sulfate of a given weight of a metal in a voltaic battery was always the same whenever the connecting metallic arc connecting the poles did not offer a sensible resistance, (2) the heat released by the passage of electricity through the conducting metallic arcs was strictly complementary to the heat confined in the voltaic cells, always yielding a total sum equal to the heat corresponding to all the chemical reactions that occurred in the battery, independently of the total electricity transmitted, (3) by placing a voltmeter in the circuit, in which the passage of electricity provoked a chemical decomposition, the heat confined in the couples was constantly diminished by the heat that would come into action in the act of this same chemical segregation taking place *without* the intervention of electricity, (4) coating with copper one of the platinum electrodes and then reversing the direction of current in the cupric sulfate voltmeter resulted in the coating with copper of the other electrode, while the first one lost an equal amount of the metal, which converted into sulfate. In this case, a double reaction took place in the voltmeter: the decomposition of cupric sulfate, and the formation of a new equal weight of the same salt. These two thermal identical actions were equal, although of opposite sign; they did not change the thermal balance of the operation.[38]

Favre proved that it was possible to apply to a voltaic battery the laws he had formulated before for a single couple,[2] as well as the following new ones: (a) when a voltmeter is connected within a voltaic circuit in order to determine any particular chemical decomposition, the heat confined within the couples is constantly decreased by the heat put into play by the chemical separation (without electricity); (b) a voltaic battery and its voltmeters may be considered as a system of couples where some can produce heat, and consequently electricity, and others, may or may not become spent. According to Favre, these three cases corresponded exactly to (1) the Smee couple, (2) a voltmeter with copper electrodes submerged in a solution of cupric sulfate, and (3) to a voltmeter with platinum electrodes submerged in water acidified with sulfuric acid.[38]

In another work, Favre studied the relation that exists between the mechanical work produced by electricity and the amount of chemical action generated. Favre believed that his results were an experimental proof that the mechanical work produced by a current carried always an expenditure of heat taken from the total heat disengaged by the chemical action of the pile. His equipment contained two calorimeters operating simultaneously; one contained the voltaic couples which reflected the total heat due to the chemical action in the absence of external work to the pile, the second, connected to a small electromagnetic engine attached to the pile, reflected the heat developed by the sum of the resistances in the operating engine. Favre proved that the latter derived from a heat loan to the total heat developed by the couples. When the engine operated to elevate a weight, the sum of the quantities of heat registered by the calorimeter was less than the heat corresponding to the chemical actions developed. Hence his conclusion that the amount of heat that had disappeared had been spent in developing an amount of work that he measured in kg · m . He was able to calculate the mechanical equivalent of heat by a novel method based on measuring the heat developed by an especially built brake, located inside a calorimeter and equilibrating the work done by the fall of a weight. His results gave 413.2 (kg · m)/kcal as the mechanical equivalent of heat. Favre believed that his results added new proofs supporting the idea of the existence of one unique force, capable of presenting itself in many ways without changing its essence (energy). He was thus stating the correlation and equivalence between the chemical thermal, electrical, and mechanical actions, as Joule had done previously.[13-15]

In another interesting work Favre investigated the possible effects of pressure on certain physical and chemical phenomena. For example, he wanted to know if changing the pressure at constant temperature electrolysis was slowed down or stopped completely, if certain reactions became possible or only facilitated, if the dissolving power of a liquid was modified, and lastly, if the reduction or oxidation properties of hydrogen or oxygen were modified. His equipment consisted basically of two glass ampoules capable of supporting 70 to 80 atm; one of them functioned as a gas generator. Hydrogen was produced by the reaction between zinc and sulfuric acid, and oxygen by a solution of cupric sulfate in contact with two platinum electrodes. When necessary, the two gases were obtained together with a voltaic cell containing water acidified with sulfuric acid. The reaction took place in the other ampoule were the gases acted by simple pressure or they reacted under the pressure they produced.[36,37]

Regarding the electrolysis phenomena, it was clear that pressure did not represent work that opposed the electrolytic one. But pressure could have an indirect action by modifying the properties of the medium in which the phenomenon took place. Thus the zinc sulfate formed during the electrolysis of the metal in the presence of sulfuric acid could become less soluble in compressed water, or it could crystallize on the surface of zinc and stop its attack. Jacques Babinet (1794-1872) and Nikolai Nikolaevitch Békétoff (1827-1911) had already put forward the idea that the pressure of the hydrogen liberated stopped the electrolysis of sulfuric acid by zinc, carried on in a hermetically closed space. Favre decided to test this theory experimentally. Using the apparatus described above, and working at three pressure levels (43, 50, and 86 atm) he was able to observe a decrease in the electrolytic work, even at the highest pressure he could attain. Favre did not observe any difference in the intensity of the current and the amount of gas produced during equal time intervals, even up to a pressure of 70 atm. All his results proved the absence of a direct influence of the pressure on the electrolysis of a liquid in which the conductibility remained the same. Hence he asked himself why in the first series of experiences the action of sulfuric acid on zinc diminishes as the pressure increases? The decrease was clearly not caused by the formation of zinc sulfate because the presence of this salt did not affect the electrolysis when the metal attacked formed a voltaic couple with platinum. It was more probable that the decrease in activity was due to the adherence of hydrogen on the surface of zinc, an adherence, which became stronger as the pressure was increased. It was adherence and not formation of an alloy.[36,37]

Now, Favre extended his research to the determination of the voltaic energy produced in couples with fuming nitric acid, permanganic acid and sulfuric acid mixed, and hypochlorous acid, as well as couples with cupric sulfate and occluded hydrogen in palladium.[39]

According to Favre's results, since the energy of a single Smee pile was equivalent to about 15 000 calories, the energy of a battery of five Smee piles being about 75 000 calories, should have been enough to electrolyze an aqueous solution of sulfuric acid, and of sulfates of copper, cadmium zinc, and others, but not of alkaline sulfates. Favre used a battery composed of four Bunsen piles and one Smee pile series. The purpose of the latter one was to measure the amount of chemical action produced in the voltmeter, as measured by the amount of hydrogen released. He was surprised to observe that the amount of energy required when using a partitioned voltmeter was larger than that with a voltmeter not having a partition. Favre concluded that the battery decomposed the alkalis and their salts because its energy was reinforced by that resulting from the oxidation of the metal itself. It also seemed probable that the metals, which decomposed water instantly or were liberated during the electrolysis of their salts, became oxidized and liberated variable amounts of energy, which was transmittable to the circuit. It proved that the borrowed quantity of heat from the battery could not be considered as the thermal expression of their formation.[40]

Favre examined the thermal effects observed during the electrolysis of hydrochloric, hydrobromic, and hydriodic acid. The diluted acids were placed in a voltmeter furnished with a partition, to keep the liberated halogen from contact with the hydrogen disengaged at the other pole. Under these circumstances, the heat absorbed in the voltmeter was the thermal equivalent of the analysis of the acid. He also examined the thermal effects produced by substituting the hydracids for sulfuric acid, in a Smee battery. Favre concluded that the numbers obtained were really the thermal equivalents of their analysis; whereas, as previously found, the heat absorbed by oxyacids during their decomposition was the thermal equivalent of the analysis of water, and not of that of the acid.[41]

Favre discussed the results of his experiments, which tended to confirm that a battery composed of five pairs of Smee's elements effected the decomposition of the alkalis and their salts only by virtue of the addition of energy, which it derived from the oxidation of the metal itself, this oxidation constituting a "synelectrolyte" phenomenon, taking place simultaneously with the electrolysis. From the experiments, it was concluded that the oxides and salts of the alkali-metals, when subjected to the action of the electric current, decomposed and gave up their metal. This metal being directly oxidized at the expense of the oxygen of the water set free a certain quantity of heat, which reinforced the voltaic energy of the battery.[42]

Additional experiments strengthened the conclusions that the heat borrowed from the battery for the electrolysis of sulfuric acid and nitric acid could not be considered as the true thermal expression of the heat of formation of these acids. Further, it appeared from these experiments that the secondary reactions, which accompany the electrolysis and produced heat not transmissible to the circuit, always tended to strengthen the energy of the battery whenever the current was weak and when the electrolysis offered great assistance. Quantities of heat borrowed from the battery in the electrolysis of certain zinc and copper salts were discussed. It was found that the change of poles produced no noticeable difference in the results, and obtained from the first set of experiment, as well as from the second, about 1 000 heat-units as the heat evolved during the electrolysis of one equivalent of cupric sulfate between copper plates.[42]

Dissolution of salts

Favre and Valson measured the heat effect accompanying the solution of salts in different states: non-hydrated (for example, magnesium sulfate), several of their hydrates (for example, magnesium mono and heptahydrate), and also of isomorphic double salts (for example magnesium sulfate pentahydrate and cupric sulfate heptahydrate). Their results indicated that the heats of solution of the anhydrous sulfates were mostly positive and very different one from the other and that this disparity disappeared with increased degree of hydration. The greater part of the heat evolved during the dissolution of an anhydrous salt, or of a salt in a state of hydration lower than its normal state, was due to the formation of the crystal containing the *normal* proportion of water. In the case of double salts, the amount of the heat liberated by the solution of one of the two salts remained sensibly the same. If two salts were dissolved in water, the total heat effect was the same as the sum of heats of solution of the two, determined separately.[17]

In a following work, Favre and Valson calculated the amount of work and its distribution during the solution of anhydrous sodium sulfate in water. The combination of anhydrous sodium sulfate and water to form crystalline sodium sulfate decahydrate diminished the total volume from 116.5 cm^3 to 110.0 cm^3, which measured in heat-equivalents is 49 244. The solution of one equivalent of anhydrous salt in one liter of water resulted in a contraction of 16.7 cm^3, measured by 126 519 heat-equivalents, while the solution of the decahydrate was accompanied by a contraction of 10.5 cm^3, measured by 79 548 heat-equivalents. Actual calorimetric measurement of the heat of solution of one equivalent of anhydrous and one equivalent of the decahydrate yielded the numbers +354 and –9 300 heat-equivalents, respectively, representing the difference in heat-equivalents between the opposing thermal effects accompanying the contraction of volume and the work of the internal force of association between the salt and the water. The results indicated that each saline radical produced a contraction of volume in the solvent peculiar to it, so that a given radical always absorbed the same amount of heat from the solvent, independently of the other radical with whom it was associated.[19]

Favre and Valson investigated in particular, the heat effect accompanying the solution of alums. These compounds represent a group of salts, which have many analogies between them. They are all represented by a chemical formula belonging to the same type, and are strongly similar from a crystalline viewpoint. As explained above, Favre and Valson had found that the solution of a crystalline salt was accompanied by a contraction in the total volume; the salts having the highest heat of solution usually had the largest volume contraction.[18] For a salt crystallizing as a hydrate, the largest part of the contraction took place during the formation of the crystal. It was possible to conclude that the largest part of the heat released came completely from the work of contraction. Two opposite phenomena took place during solution of a salt: First, there was a dissociation of the salt molecules that served as joints in the geometrical structure of the solid salt. Second, the salt exerted an opposite action on the solvent, which Favre and Valson named *coercive action*. The contractions of the total volume, the increase in the boiling point, and the lowering of vapor pressure at the same temperature, were different manifestations of the phenomena put into action by this effect. Favre and Valson studied six different alums: ammonium-potassium, aluminum-ammonium, chromium-potassium, chromium ammonium, iron-potassium, and iron ammonium. They first measured the heat of solution of one equivalent of alum in a large amount of water. For dissolved alums, the dissociating action of water was nearly the same for the potassium and ammonia alums of chromium and aluminum, but it was, however, much larger for ferric-potassium and ferric-ammonium alums. For alums previously dried at 85 °C, it could be regarded as the difference between the absorption of heat and the release of heat originating from the contraction of the total volume. Favre and Valson inferred that the two salts of each kind of alum were compounded in a solution. Moreover, in the case of ferric-alums, the constituents of the ferric-sulfate were also dissociated. They believed that the ferric chloride formed on precipitating a solution of ferric alum by barium chloride was in a less advanced state of dissociation than the ferric sulfate.[18]

The first work on alums was complemented by another one reporting the variation in volume accompanying the solution of the various alums in water.[20] The changes in volume were measured by two different methods: (a) comparing the density of the salts with that of their solutions, and (b) observing the increase of volume caused by the solution of a known weight of the salt in a given quantity of water. The numerical results indicated that the dehydrated alums could not be regarded as simple mixtures of their constituent salts, a conclusion confirmed by the fact that drying ammonia-alum did not result in the release of ammonia, even at a temperature high enough to volatilize ammonium sulfate completely. It seemed that in desiccated alums the constituent salts remained more or less combined, in spite of the fact that the density of dehydrated ammonium alum was essentially equal to that of a simple mixture of its constituent salts, and that the density of potassium alum was even less than the calculated one.

As mentioned above, Favre and Valson believed that in desiccated alum the constituent salts remained in a certain state of association. Adding water to calcined chrome-potassium alum resulted in the dissolution of the potassium sulfate, leaving the chromium sulfate undissolved. This result seemed to indicate that water was able to dissociate the saline elements, an action which heat was unable to do. The measured densities of crystallized alums indicated that their molecular volumes were essentially the same, so that they could be regarded as crystalline edifices composed of an equal number of molecular layers having the same structure and dimensions. It was also observed that the total contraction which took place in the union of the anhydrous salts with water to form the crystal was greater than that caused by the solution of the latter. This was the opposite of what occurred with sodium sulfate, the difference being produced by the influence of the crystalline form on the contraction phenomena. For alums, as for solutions of other salts, each substitution of a molecule of a base by another one, isomorphous with it, caused a variation in the density and capillary height of the solution, which depended only on the nature of the molecule and was independent of the actions of the same order exercised by the other molecules present.[21]

Favre and Valson had previously studied the coercive action of salts on water by measuring the densities of the saline solutions. Since this was a slow method, which did not allow observing the progress of the action, or the modifications due to the changes of temperature, they developed a special apparatus for this purpose, useful not only for determining the coefficient of contraction of liquids and saline solutions, but also of solid bodies. Favre and Valson employed it to observe the changes which took place during the precipitation of anhydrous sodium sulfate, which occurred when heating an aqueous solution saturated at 32.7 °C (below this temperature the salt exists as its decahydrate). Favre and Valson also reported some interesting effects that occurred when letting the saturated solution cool slowly in contact with room air at about 20 °C . The solution became supersaturated but introduction of small crystal initiated crystallization and caused a rapid increase in the temperature from 21.40 °C to 29.85 °C . A much longer time was required for the solution to return to the normal temperature than for a supersaturated solution owing to the fact that the crystals were bad conductors of heat. It would then seem that the supersaturated solution and the solution of the salt which had deposited the crystals, were in very different coercive states, the potential force stored up in the supersaturated solution presenting a striking analogy with that in explosive substances.[22]

Favre and Valson had already reported that the solution of a salt in water was usually accompanied by a contraction of the salt and the solvent, which could readily be determined by comparing the density of the solution with that of the salt and solvent. It was easy to calculate the mechanical value of this contraction since at 15 °C a contraction of 0.001 of the bulk of the water corresponded to 7 576 heat-units. In a previous publication[22] they had applied these considerations to determine the distribution of work in solutions of aqueous sodium sulfate. Now they applied them to a large number of salts, which exists either anhydrous or as different hydrates.[23] In their publication they reported the density of the anhydrous salt, its different hydrates, and of a solution containing one equivalent of anhydrous salt per liter. The results showed that the circumstances under which the hydrated salt assumed the crystalline state hardly changed its density, which could therefore be regarded as absolutely invariable (for example, if the salt was slowly crystallized, or was precipitated more or less rapidly in the bulk solution). The experimental results indicated that the contraction in volume increased in the order borates > carbonates > sulfates > chlorides > nitrates > bromides > iodides and that the contraction produced by dissolution of the anhydrous salt was always larger than that produced by the hydrated salt. The contraction due to the dissolution of the hydrated salt was usually smaller than the one produced during the formation of the crystal.[23]

Afterwards Favre and Valson repeated the calculation, this time for groups of anhydrous salts of a given acid with different metals. The results indicated that with the exception of the ammonium halides the solution of all other salts was accompanied by a contraction effect; aluminum sulfate and sodium carbonates presented the largest specific contraction. During the dissolution of a salt, two opposite effects took place, a contraction effect on the solvent caused by the solute, and an increase in the volume of the salt due to its dissociation, partial or total, into the constituent elements. The first effect was usually the strongest, so that the net final result was one of contraction.[23]

A comparison of the volumes of the normal solutions of salts containing the same metallic radicals (potassium and sodium, for example) showed that they were sensibly constant whatever the halide with which they are associated. It was also seen that the differences were sensibly constant when comparing salts containing the same halide associated with different metallic radicals, as with the chlorides and bromides of different metals. Hence, according to Favre, there exists a modulus of volume for normal saline solutions, analogous to those already established for the heat of formation, the capillary attraction, and the density. A remarkable results was that the modulus for a great number of the metallic radicals is the same, in spite of the large differences between their equivalent weights. Thus, magnesium, having an equivalent of 12, caused as great a variation of volume as cadmium, whose equivalent weight is 56. In general, dissolution of a substance was accompanied by a contraction of volume; a contraction generally smaller than the volume of the body dissolved, so that when an equivalent weight of a compound was dissolved in a liter of water, the volume of the solution is greater than a liter. One equivalent of KOH dissolved in one liter of water gave a solution measuring only 996 cm^3, while with NaOH the contraction was even greater, the volume being reduced to 987 cm^3.[24]

Favre and Valson also studied the dissociation of crystallized salts, particularly the chlorides of calcium, strontium, cobalt, nickel, and copper, the sulfates of sodium, magnesium, manganese, nickel, zinc, and copper, the nitrates of calcium, strontium, nickel, the acetates of sodium and zinc, and sodium carbonate. Solution of anhydrous salts gave place to a considerable contraction, especially in the case of sodium carbonate and the sulfates of magnesium, nickel, copper, and zinc. The contraction produced by the solution of successive portions of salt diminished as the solution became more concentrated until it finally became nearly constant. It was less considerable in the case of hydrated salts and in some circumstances it became equal to the volume of the solid salt after the addition of the first three or four molecules.[25]

Condensation and adsorption of gases

According to Favre[43] there was an intimate connection between the thermal phenomena accompanying chemical reactions and the chemical affinity or the degree of stability of the resulting combinations. Hence his interest in measuring the thermal effects that originated from the interaction between a gas and a solid, especially since their intensity was similar to that of chemical reactions. Pouillet had already proved that imbibition of quartz sand with distilled water was accompanied by a release of heat, in other words, that this process could be assimilated to a capillary one. According to Antoine Henri Becquerel (1852-1908; 1903 Nobel Prize for Physics), capillary actions were able to generate electrical current. In his study on the absorption of CO_2 by wood charcoal, Eilard Mitscherlich (1794-1863) had concluded that in the pores of the solid the gas must be present as a liquid. In this first study, Favre wanted to make a precise study of the thermal phenomena that take place when a gas *wets* a solid, in order to determine if in addition to the force necessary to cause the liquefaction of the gas trapped in the pores of charcoal, there was an additional special force, independent of the change in state. To answer this question properly it was first necessary to known the actual heat of liquefaction of some gases, in order to compare it with the thermal effect occurring during the condensation of the gas in the pores. For this purpose Favre used his mercury calorimeter, charcoal prepared from a variety of woods as adsorbent, and CO_2, SO_2, HCl, NO, and NH_3 as representative gases. The amount of gas adsorbed was referred to the unit weight of charcoal and the thermal effect to the unit weight of the gas. The heat released was measured up to saturation of the charcoal by the gas.[43]

His results indicated that for a given gas, the coefficient of absorption varied according to the origin of the charcoal; the denser charcoals absorbed less gas than the lighter ones. Due to their very different nature it was not possible to make a general comparison between the different gases, but based on the maximum absorption per unit weight of the same charcoal, they could be ranked as follows: $NH_3 > HCl > SO_2 > NO > CO_2$. The same order was kept for every one of the charcoals tested. The maximum amount of heat released by the absorption of one gram of HCl or NO was substantially larger than the heat of condensation of the same gas. For CO_2, the heat of absorption was much larger than the heat of solidification. For some of the gases, for example CO_2, the heat effect was the same for the same weight of gas absorbed, independently of the nature of the charcoal. This result was interesting because it seemed to indicate that the thermal effect was not due to the liquefaction of the gas but to a special action, because the introduction of a very small amount of gas, released more heat than that which accompanied its liquefaction.[43]

Favre did not believe that this special action was the result of ordinary affinity because experience proved that the same amount of a given gas was able to release, in the presence of charcoal, a variable amount of gas, a circumstance, which obliged the intervention of a surface action, which could not be the same in the different samples of charcoal. What seemed to relate this action to capillarity was the observation that the amount of heat released by the absorption of gas decreased as more gas became absorbed.[43]

Graham had reported extensively on the property of palladium of fixing hydrogen and forming an alloy with it,[44] Favre performed a series of thermal experiences that confirmed the metallic character of hydrogen and also contributed to explain the origin of the heat confined in a voltaic pile. His experiments were conducted using palladium as the negative electrode in a Smee cell.[45] This work was followed by another on the thermal phenomena taking place in a sulfuric acid voltmeter in which the palladium was juxtaposed with platinum, or palladium hydride was employed simultaneously with platinum or pure palladium. The two first arrangements resulted in the release of only one gas, while no gas was released in the third one (see below). These arrangements avoided the release of a mixture of hydrogen and oxygen, which resulted in secondary actions, which complicated the operation and its understanding. Thus, in a voltmeter having palladium as the negative electrode and platinum as the positive one, only oxygen gas was released and the amount of heat released exceeded by 4 154 units the amount released when both laminæ were made of platinum. These 4 154 units corresponded exactly to the fixation of hydrogen by the platinum. When palladium saturated with hydrogen was the positive electrode of the voltmeter and was juxtaposed with platinum, only hydrogen was released, and the amount of heat released was 4 154 units lower than the following series of experiments. When one electrode was palladium saturated with hydrogen and the other pure palladium, no gas was released because the palladium was already saturated with hydrogen. A circuit containing only one Smee pile was unable to decompose the sulfuric acid, although the latter nevertheless electrolyzed in the voltmeter. The voltmeter behaved as one made of two solid laminæ of hydrogen. The hydrogen released at one of the laminæ attached to the other and the hydrogen sulfate decomposed and regenerated simultaneously. The results were completely comparable to those taking place in a voltmeter composed of copper laminæ immersed in a solution of cupric sulfate. According to Favre, the hydrogen released from a combination and alloying with palladium, released about 8 800 cal; while ordinary hydrogen alloying with palladium released only about 4 200 cal. These results pointed to the metallic character of hydrogen because it participated in the voltaic phenomenon in the same as manner as zinc, cadmium copper, etc. do. Hydrogen burned (became oxidized) on the palladium lamina in the same manner as the metal because the total amount of heat released in this combustion was transmissible in the circuit. When a battery of five Smee cells was added to the circuit, the current produced was able of decomposing the sulfuric acid in the voltmeter. The intervention of the electrolysis of sulfuric acid was the fact that caused the discordance between successive experiences.[46]

Favre concluded that the amount of heat involved in the voltaic circuit originated only from the electrolytic reaction taking place in the circuit and was equal to the total heat involved in the reaction, and that the amount of heat that was confined in the couples originated from all the molecular actions that preceded or followed the electrolytic reaction, and which were not exerted along the circuit. This heat was equal to the algebraic sum of all the heat amounts involved in each of these actions.[46]

Favre performed additional experiments to prove that the hydrogen in palladium, where it replaced the active metal of a voltaic couple, constituted the active metal of a new couple. He achieved his purpose by replacing in a Daniell cell the amalgamated zinc lamina immersed in a bath of highly diluted sulfuric acid, by a palladium lamina charged with hydrogen. This new cell performed exactly as the primitive one, except that now it was the hydrogen, and not the zinc the one who played the role of active metal by being substituted by electrolytic copper from cupric sulfate. Similarly as in the Daniell cell, copper deposited over the platinum that was submerged over cupric sulfate contained in the external vase.[47]

In previous work Favre had endeavored to show that electrolytic hydrogen is an allotropic active modification of the element and that in changing into its ordinary form it disengaged 4 600 heat-units. He also proved that the absorption of hydrogen by palladium gave rise to a true alloy since the heat developed by the combination (9 000 units) was the same for the last as for the first portion of hydrogen added. On the other hand, the absorption of hydrogen by platinum (and of other gases by charcoal) were merely cases of capillary affinity, in which the gas may be supposed to form a layer whose density diminished with increased distance from the surface of the solid. This was indicated by the fact that the later portions of gas absorbed evolved less heat than the earlier. The complete saturation of platinum black with hydrogen (244 volumes) disengaged about 20 700 heat-units for one gram of hydrogen absorbed. When considering what takes place during the electrolysis of dilute sulfuric acid with a zinc-palladium couple, and with a zinc-platinum one, it was seen that in the first case the hydrogen entered into combination in the active state, since it was not been able to pass into the ordinary gaseous condition; but in the second case, the hydrogen liberated in the active state transformed itself immediately into the ordinary modification. In spite of the heat absorbed during its passage from the liquid into the gas state (which, as indicated by the absorption experiments with platinum-black, must be considerable) this change evolved 4 600 heat-units. The absorption of active hydrogen by platinum black ought therefore to develop about 25 300 heat-units, and this experiment the author proposes to make. These considerations and some former results were brought to bear upon the thermal relations of the formation of water.[48]

Favre had tried to prove that electrolytic hydrogen (nascent) is active, and that on changing to ordinary hydrogen it released about 4 600 cal . This amount of heat was not transmitted to the circuit and the allotropic transformation of hydrogen belonged to a class of phenomena, which he named meta electrolytic. In his researches on the absorption of hydrogen by palladium[45,46] Favre found that that about 9 000 cal corresponded to the alloying of hydrogenium[44] and palladium, and that the condensation of hydrogen by palladium and its condensation by charcoal were not exactly comparable. In fact, the fractional absorption of the gas by carbon was accompanied by decreasing heat effects. On the contrary, during the increasing fixation of hydrogen on palladium, identical heat effects accompanied the fixation of equal amounts of hydrogen. In addition, the condensation of hydrogen on palladium gave place to a defined alloy. Finally, Favre had investigated if the heat accompanying the formation of this alloy benefited the current, and found that the about 9 000 cal were released, which were not transmitted to the circuit.[48]

Now he proceeded to report the results of his study of the absorption of hydrogen by platinum black. Hydrogen condensed on palladium more or less uniformly to actually constitute a real alloy. It condensed on platinum black in the same manner as CO_2 or ammonia condensed on wood charcoal that is, forming more or less dense layers. The action of platinum black on hydrogen seemed to belong to the class of phenomenon due to capillary affinity. In addition, hydrogen condensed on substantially higher amounts on platinum black than on charcoal.[48]

Favre's resulted indicated that the amounts of heats released during the condensation of SO_2 or NO on wood charcoal were substantially larger than their heat of condensation.[48]

Consider now what happens when aqueous sulfuric acid is electrolyzed using a zinc-palladium cell or a zinc-platinum pile. In the first case the hydrogen is adsorbed by the palladium, while in the second it is liberated on the surface of the platinum. The hydrogen is liberated in a nascent (active) explosive state; it then experiences an allotropic transformation into ordinary *liquid* hydrogen. The amount of heat released during this transformation is such that in spite of the absorption of heat that takes place in the transformation of the liquid into a gas, the calorimeter accused a release of about 4 600 cal.[48]

In previous works on the electrolysis of acids, Favre had concluded that electrolytic hydrogen was active; in passing to the ordinary gaseous state it released 4 500 cal, an amount of heat, which was not transmitted to the circuit.[49] Work on the occlusion of hydrogen by palladium had shown that the amount of heat due to the condensation of electrolytic hydrogen on palladium was about 9 000 cal and that the mode of condensation was not comparable to the mode of condensation on wood carbon, where it resulted in an alloy having the nature of explosive compounds. In another work[48] Favre studied the absorption of ordinary hydrogen on platinum black and the thermal effects that accompanied the process.[50]

In this new paper he reported his experiences on the condensation on platinum black of active hydrogen, originating in an electrolytic process, such as the electrolysis of aqueous sulfuric acid. He also studied the condensation of ordinary hydrogen on palladium to determine if it resulted in converting ordinary hydrogen into active hydrogen. The results indicated that electrolytic hydrogen did not play the same role with platinum as it did with palladium. In fact, the fractional absorptions of hydrogen on platinum were reflected on the very weak heat effects that accompanied them. Nevertheless, hydrogen originating from an electrolytic process was fixed on platinum in an active state, not in an ordinary way. In the Smee pile, where the hydrogen from sulfuric acid replaced zinc, it was observed that hydrogen is in an active state and is not modified with a heat release of 4 500 cal, only after it is liberated.[50]

The experiments done on the condensation of electrolytic and ordinary hydrogen on palladium justified the existence of the two allotropic states of hydrogen and permitted to peep into the transformation phenomenon. The experiments on the condensation of electrolytic hydrogen on platinum indicated that the gas attached to the powder in the same way as ordinary gaseous hydrogen does, that is, forming more or less dense layers. Hydrogen fixed over platinum black, which constituted the negative electrode of the voltmeter, was attacked by the radical SO_4 with release of heat. In this manner, the voltaic energy of the couples was reinforced by the voltaic energy due to the combustion of hydrogen in the voltmeter. In addition, it was found that part of hydrogen condensed on the platinum black was in the state of ordinary hydrogen.[50]

Favre summarized his findings as follows: (a) the modes of fixation of hydrogen on palladium and on platinum black were not comparable. With platinum black the hydrogen condensed was not modified chemically; with palladium hydrogen suffered an allotropic modification before combining with the metal; (b) the platinum-palladium alloy was explosive: the metal saturated with hydrogen became incandescent in contact with air and water vapor was released. It was easy to account for the allotropic transformation of hydrogen. Considering that the adsorption of ordinary hydrogen on platinum black releases about 20 000 cal, we can find in the thermal phenomenon that accompanies the condensation of these compound and the thermal phenomenon that accompanies the combination of active hydrogen with palladium, we can find the expression of the amount of heat discharged during the allotropic transformation of ordinary hydrogen. The phenomena that occurred with ordinary hydrogen were analogous to the one taking place with oxygen under the influence of an electric discharge, and even more analogous to the one that occurred during the transformation of red phosphorus into ordinary phosphorus.[50]

Experiments were also undertaken to determine the amount of heat evolved during the absorption of gases by porous solids. To this end the latent heat of volatilization of several liquefied and solidified gases was calculated and compared with the heat evolved during the absorption of the same gases by charcoal. For the same gas the absorptive power of charcoal varied with the nature of the wood carbonized, as well as with the same fragment at different times. Different gases were absorbed by charcoal in very different quantities. The heat of solution in water did not appear to be connected in any way with that of absorption.[51]

BIBLIOGRAPHIC REFERENCES

1. Le Blanc F. Notice Nécrologique sur P.A. Favre, Membre du Conseil de la Société Chimique. Bull Soc Chim. 1880;33:392-400.
2. Favre PA. Recherches Chimiques sur les Courants Hydro-Électriques (première partie), Ann Chim Phys. 1854;40[3]:293-321. (This work is the summary of the Thèse Originale de Physique presented in 1853).
3. Favre PA. Recherches Thermo-Chimiques sur les Combinaisons Formées en Proportions Multiples. J Pharm. 1853;24:241-250;311-346;412-423. (This paper was presented as Thèse Original de Chimie, 1853).
4. Favre PA. Recherches sur l'Équivalent du Zinc, Compt Rendus. 1843;17:1196-1197. Ann Chim Phys. 1844;10:163-174.
5. Favre PA. Recherches sur les Carbonates de Cuivre, Ann Chim Phys. 1844;10[3]:116-120.
6. Favre PA. Analyse des Carbonates Ammoniacaux de Zinc et de Magnésie, et Observations sur le Carbonate de Magnésie, Ann Chim Phys. 1844;10[3];474-484.
7. Favre PA. Recherches sur la Mannite et l'Acide Lactique. Ann Chim Phys. 1844;11[3]:71-81.
8. Favre PA. Recherches sur la Composition Chimique de la Sueur Chez l'Homme. Compt Rendus. 1852;35:721-725. Arch Gén Méd. 1853;2:1-21. J Pharm. 1853;24:178-198.
9. Favre PA. Recherches sur la Dessiccation des Gaz. Ann Chim Phys. 1844;12[3]:223-228.
10. Favre PA, Silbermann JT. Recherches sur la Chaleur Dégagée Pendant les Combinaisons Chimiques, Compt Rendus. 1844;18:695; 1845;20:1565-1569; 1845;21,944-950; 1846;22:483-487,823-825;1846; 1846;23:199-206,411-413; 1847;24:1081-1090; 1848;26,595-600; 1848;27:56-58,111,158,362-366; 1849;28:627-632; 1849;29:449-451.
11. Favre PA., Silbermann JT. Recherches sur les Quantités de Chaleur Dégagées dans les Actions Chimiques et Moléculaires, Ann Chim Phys. 1852;34[3]:357-450.
12. Favre PA, Silbermann JT. Recherches sur les Quantités de Chaleur Dégagées dans les Actions Chimiques et Moléculaires, Ann Chim Phys. 1852;36[3]:5-47.
13. Joule JP. On the Heat Evolved by Metallic Conductors of Electricity and in the Cells of a Battery During Electrolysis, Phil Mag. 1841;19:260-277.
14. Favre PA. Recherches Chimiques sur les Courants Hydro-Électriques (troisième partie), Compt Rendus. 1857;45, 56-60.
15. Favre PA. Recherches sur l'Équivalent Mécanique de la Chaleur, Compt Rendus. 1858;46,337-340.
16. Favre PA. Recherches Thermo-Chimiques sur les Courants Hydro-Électriques: Des Résistances dans la Pile Voltaïque. Compt Rendus 1858;47:599-602.
17. Favre PA. Valson CA. Recherches Thermiques sur la Dissociation Cristalline. Compt Rendus. 1871;73:1144-1152.
18. Favre PA, Valson CA. Recherches sur la Dissociation Cristalline. Compt Rendus. 1872;74:1016-1025,1165-1173.
19. Favre PA, Valson CA. Recherches sur la Dissociation Cristalline; Évaluation et Répartition du Travail dans les Dissolutions Salines. Compt Rendus. 1872;75:330-336,385-388.

20. Favre PA, Valson CA. Recherches sur la Dissociation Cristalline. Aluns. Compt Rendus. 1872;75:798-803.
21. Favre PA, Valson CA. Recherches sur la Dissociation Cristalline: Aluns. Compt Rendus. 1872;75:925-930,1000-1005.
22. Favre PA, Valson CA. Recherches sur la Dissociation Cristalline. Nouvelle Méthode pour Étudier l'Action Coercitive des Sels sur l'Eau a Diverses Températures, Compt Rendus. 1872;75:1066-1071.
23. Favre PA, Valson CA. Recherches sur la Dissociation Cristalline: Évaluation et Répartition du Travail dans les Dissolutions Salines, Compt Rendus. 1873;77:577-584,802-808,907-915.
24. Favre PA, Valson CA. Recherches sur la Dissociation Cristalline. Compt Rendus. 1874;78:668-673.
25. Favre PA, Valson CA. Recherches sur la Dissociation des Sels Cristallisés. Compt Rendus. 1874;79:968-976,1036-1041.
26. Favre PA. Sur le Calorimètre a Mercure. Détermination de la Valeur de la Calorie. Ann Chim Phys. 1874;1[5]:438-444.
27. Favre PA. Recherches Thermochimiques sur les Mélanges, Arnaud, Marseille, 1862.
28. Favre PA. Notice sur les Travaux Scientifiques de P.A. Favre, Mallet Bachelier, Paris, 1862.
29. Favre PA. Maumené, Sur la Réduction Partielle du Bioxyde de Cuivre par la Chaleur et sur le Nouvel Oxyde qui on Résulte. Compt Rendus. 1844;18:658-659.
30. Tachoire H, Favre PA. (1813-1880). Actualité Chim. 1981;4:33-36.
31. Anonymous. Compt Rendus. 1851;31:753-754,810-811.
32. Dumas JB, Stas JS. Recherches sur le Véritable Poids Atomique du Carbone. Compt Rendus. 1840;11:991-1008.
33. Favre PA. Mémoire sur la Transformation et l'Équivalence des Forces Chimiques, Imprimerie Nationale, Paris, 1875.
34. Favre PE, du Quillard C. Recherches sur l'Affinité Chimique. Compt Rendus. 1860;50:1150-1154.
35. Favre PA. Recherches sur l'Affinité Chimique: Phénomènes Calorifiques Produits par la Réaction de l'Eau et de l'Alcool sur Diverses Substances. Compt Rendus. 1860;51:315-318.
36. Favre PA. Appareil pour l'Étude de l'Influence de la Pression sur Quelques Phénomènes Physiques et Chimiques. Compt Rendus. 1860;51:827-831.
37. Favre PA. Influence de la Pression sur Quelques Phénomènes Physiques et Chimiques. Compt Rendus. 1860;51:1027-1030.
38. Favre PA. Recherches Chimiques sur les Courants Hydro-Électriques (deuxième partie). Compt Rendus. 1854;39:1212-1215.
39. Favre PA. Recherches Thermiques sur l'Énergie Voltaïque. Compt Rendus. 1871;69:34-39;1869;73:890-896,936-943.
40. Favre PA. Recherches Thermiques sur l'Électrolyse des Bases Alcalines et des Sulfates Alcalins. Compt Rendus. 1871;73:767-780.
41. Favre PA. Recherches sur l'Électrolyse des Hydracides, Compt Rendus. 1871;73:971-979.
42. Favre PA. Recherches Thermiques sur l'Électrolyse des Bases Alcalines et des Sulfates Alcalins. Compt Rendus. 1871;73:1036-1040,1085-1090,1186-1191,1258-1262.
43. Favre PA. Sur la Condensation des Gaz par les Corps Solides et sur la Chaleur Dégagée dans l'Acte de Cette Absorption - Sur les Relations de ces Effets avec les Chaleurs de Liquéfaction ou de Solidification des Gaz. Compt Rendus. 1854;39:729-733.
44. Graham T. On the Occlusion of Hydrogen by Metals. Proc Roy Soc. 1868;16:422-427.
45. Favre PA. Recherches sur la Pile. De l'Origine de la Chaleur Mise en Jeu dans les Couples et qui n'est pas Transmissible au Circuit (suite). Compt Rendus. 1869;68:1306-1309.
46. Favre PA. Recherches sur la Pile. De l'Origine de la Chaleur Mise en Jeu dans les Couples et qui n'est pas Transmissible au Circuit. Compt Rendus. 1869;68:1520-1526.
47. Favre PA. Recherches Thermiques sur le Caractère Métallique de l'Hydrogène Associé au Palladium (suite): Sur un Couple Voltaïque dans lequel l'Hydrogène est le Métal Actif. Compt Rendus. 1870;71:214-215.
48. Favre PA. Recherches Thermiques sur la Condensation des Gaz par les Corps Solides: Absorption de l'Hydrogène par le Noir de Platine. Compt Rendus. 1873;77:649-656.
49. Favre PA. Étude sur les Réactions Chimiques à l'Aide de la Chaleur Emprunté à la Pile. Compt Rendus. 1866;63:369-374.
50. Favre PA. Recherches sur l'Hydrogène. Compt Rendus. 1874;78:1257-1265.
51. Favre PA. Recherches Thermiques sur la Condensation des Gaz par les Corps Solides et la Chaleur Dégagée dans l'Acte de Cette Absorption. Ann Chim Phys. 1874;1[5]:209-261.