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A HISTORY OF THERMOCHEMISTRY THROUGH THE TRIBULATIONS OF ITS DEVOTEES

Oddities, anecdotes, debates and accidents

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Abstract

The history and the evolution of thermochemistry are covered in a number of excellent books. In order not to repeat what has already been written, this paper will be concerned with thermochemists as persons through their odd stories and anecdotes, of hot, enduring and even fierce debates, of accidents in the laboratory.

Keywords: history, thermochemistry

Introduction

The history and the evolution of thermochemistry are covered in an excellent book by Medard and Tachoire [1]. In order not to repeat what has already been written, this paper will be concerned with thermochemists as persons through their odd stories and anecdotes, of hot, enduring and even fierce debates, of accidents in the laboratory.

Classical thermochemistry covers a period of about 150 years. But as I will obviously have to condense this history I have chosen the most representative thermochemists; so having to omit many others and many events that happened over this period. Many devotees of thermochemistry, mainly the pioneers, were also great chemists, contributors to the development of this science and a number of great chemists (T. Graham, T. Andrews, H. V. Regnault, H. Saint-Claire Deville, J. P. Joule, E. Frankland, F. Raoult, R. Bunsen and others) performed, albeit occasionally, thermochemical experiments.

The history of thermochemistry has accompanied the history of chemistry, at least since it was ascertained that a number of easy to be observed chemical reactions – such as combustions – were accompanied by the evolution of heat. Mankind learned very early on to control fire, and to understand the most common fuel materials. Later, the first alchemists understood that, by mixing liquids – e.g. water and alcohol – the mixture was warmer than the components. And, by mixing other sub-

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stances – like ice and salt – the resulting mixture was cooler. However, the study of the thermochemical phenomena became a science only after the understanding of the concept of heat, very different from the concept of temperature.

The early development of the concepts of temperature and heat

The concept of temperature developed from the sensorial perceptions of hot and cold. These perceptions were immediately connected by using the reading from rudimentary equipment (thermometers), based on the variations of gas and liquid volume. The invention of the thermometer provided the means for developing not only thermometric measurements but an entirely new science – that of heat measurements with the invention of a new type of thermal instrument – the calorimeter.

Nevertheless, although the physicists of the mid-eighteenth century had good thermometers, they persisted in a wholly mistaken idea concerning their function [2]. They regarded the instrument as a device for measuring the amount of heat in a body, and not its temperature in the modern sense of that word (in old writings the graduations of a thermometer are commonly referred to as marking ‘degrees of heat’ and not ‘degrees of temperature’).

Most of the early philosophers held that heat was a material substance, weightless, indestructible, that could enter into or leave the pores of a body. A body became hot by absorbing some of this ‘matter of heat’, ‘heat substance’, ‘igneous fluid’ or, as it was finally called, ‘caloric’, and the more it absorbed the hotter it became. Some physicists believed that cold was a separate substance or fluid which they called ‘particles of frost’ or ‘frigoric’. Luckily, this view did not become widely adopted.

In conclusion, the thermal state of a body depended upon the extent to which the matter composing it had absorbed or was mixed with caloric.

Even the term ‘temperature’, at least at the beginning, had a different meaning. To the old-time physicists and chemistry the word ‘temperature’ was the equivalent of ‘mixture’, ‘proportion’ or ‘compound’, a usage completely justified by its ancient derivation. Thus, for example, bronze would be described as ‘a temperature of copper and tin’, that is, copper mixed or ‘tempered’ with tin. Before the role of carbon was discovered, steel was commonly held to be a temperature or mixture of iron and phlogiston, and hence the process of controlling the strength of the mixture was called ‘tempering’. The tempered zones of the earth were those regions where the tropical heat and the polar cold were mixed in agreeable proportion. Applied to thermal phenomena the word ‘temperature’ thus meant simply the mixture of the matter of a body with caloric, and the degree of the temperature meant the strength of the mixture.

The pioneers

It was Joseph Black (Fig. 1) who, in the middle of the eighteenth century, was the first to conceive that heat was a measurable physical quantity, distinct from, although related to, the quantity indicated by a thermometer and called temperature. Black never published his great discoveries on heat, although he taught them in his academic lectures. These lectures, which also incorporated his chemical researches, were published after his death by John Robison in the book Lectures on the elements of chemistry, dedicated to Watt [3]. In chemistry his major contribution was the investigation of the role of carbon dioxide (or fixed air) in the reactions of the carbonate, especially magnesium carbonate or magnesia alba. This study was discussed in his dissertation for the degree of Doctor of Medicine at the University of Edinburgh in 1754 entitled De humore acido a cibis orto, et magnesia alba which we can translate On the acid humour arising from food, and magnesia alba.

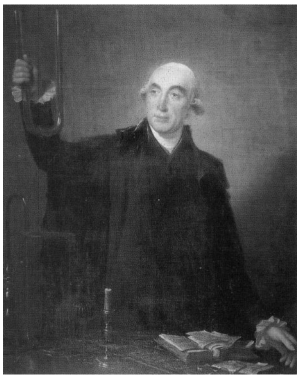

Fig. 1 Joseph Black (1728–1799)

Until Black had made his discovery, there was no clear distinction in people's minds between the concepts of 'quantity of heat' and 'degree of hotness' or 'temperature'. Black studied the subject experimentally heating bodies of different substance (quicksilver and water) and noting the times required by them to reach the same thermometric reading. He found that equal masses of different material needed different times to attain the same 'degree of heat'. Black explained the new facts by stating that different substances had different 'capacities for the matter of heat'. Because of this difference of 'capacity' two bodies of unlike substance contained at the same thermometer reading unequal amounts of heat.

Another Black's important discovery was (during the years 1761–64) about the capacity of a body to absorb heat when there is a change of state.

Among the first thermochemists, the Swede Johan Carl Wilcke has to be remembered for his determination of the heat required for the melting of ice in 1772, obtaining a value 10% lower than today's. Lavoisier and La Place cited Wilcke's contribution in a footnote in their Mémoire sur la chaleur [4].

The research on heat carried out by Lavoisier and Laplace made great steps forward, especially from the theoretical point of view, but even for the improvements made in the experimental field (the use of ice calorimeter). All the experts in Calorimetric Science will have seen the drawing of this famous equipment (Fig. 2), just as we all know who Lavoisier was in the history of chemistry.

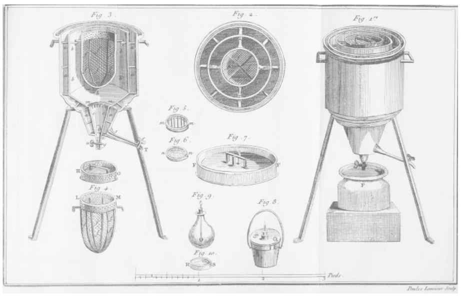

Fig. 2 Ice calorimeter

One of the most important pioneer in thermochemistry is Adair Crawford that in 1778 published the book Experiments and observations on animal heat and the inflammation of combustible bodies [5], where he described his experiences on heat and the origin of animal heat, which was his principle interest. In this book Crawford gives his own values of measurements on specific heat of different gases (air, oxygen, carbon dioxide, hydrogen) and on the heat of combustion of different solid bodies (his values are higher than today's by 10–30%).

About twenty years later, Crawford's data, together with Lavoisier's, were elaborated and calculated by the Count Rumford (Table 1) [1]. From this comparison Rumford concluded as follows:

It is rare to find experiments made by different persons at distant periods, and with very different apparatus, which agree better together.

Fig. 3 Benjamin Thompson, Count Rumford (1753–1814)

Benjamin Thompson, Count Rumford (Fig. 3) was born near Boston, in New England. He had a very adventurous life that we cannot go into detail. The Count Rumford's best known experiments were those concerning the heat production created during the boring of cannons. He refused the idea, which up to then had been accepted, that heat was a kind of fluid material, thin and weightless, able to go from one body to another. He hypothesised that heat was motion [6].

Table 1 Heat of combustion (J g^{-1}) of solid or liquid bodies according to Crawford, Lavoisier and Rumford (*)

	Crawford	Lavoisier	Rumford
Wax	34.108	46.685	39.614
Tallow	33.823	31.949	35.016
Rapeseed oil	31.681	–	38.940
Charcoal	24.104	32.162	–
Olive oil	–	49.647	37.840
Phosphorus	–	33.346	–

(*) re-elaborated by Medard and Tachoire [1]

At this point I would like to go back and talk about Marie-Anne Pierrette Paulze. Who was she?

Most chemists probably have no idea who she was. However this was her maiden name: she was better known as Lavoisier's wife. Even fewer known that, after she became a widow, she married again to the Count Rumford.

Marie Anne Pierrette Paulze was the daughter of Jacques Paulze, member of the Ferme Générale, which was a company of financiers who collected the King's taxes for him. As is known, Antoine Lavoisier was a member of this body; therefore he visited the home of his older colleague and met his daughter. Immediately he appreciated her intelligence, liveliness and her inborn refinement.

They were married in 1771 (Antoine was 28 and Marie-Anne 14). They were happily married, with no children, until Lavoisier died.

She translated Kirwan's book 'Essay on phlogiston' [7] but the best known of Marie's activities in collaboration with her famous husband is undoubtedly the production of the 13 copperplate illustrations for his famous Traité de chimie (1789). These plates, signed Paulze Lavoisier Sculpsit, were all drawn and engraved by the hand of Marie.

Fig. 4 Marie Anne Pierrette Paulze (1758–1836)

Physically Marie was a very attractive person; of petite build, she possessed fine blue eyes, a small mouth, a distinctly turned-up nose, a clear complexion, and pretty auburn hair (Fig. 4).

That she retained these attractions in later years is borne out by the variety of distinguished suitors who proposed marriage to her, subsequent to Lavoisier's execution. Among many suitors, the luckiest one was, at least at the beginning, Count Rumford. During his wanderings he had settled in Paris, and started to go to Mme Lavoisier's home. The Count was immediately fascinated by her. Their courtship is well documented in the correspondence between the Count and Sarah, his daughter from a previous marriage. Here is a short excerpt from a letter in which Rumford speaks about Madame Lavoisier [8]:

I made the acquaintance of this very amiable woman in Paris, who, I believe, would have no objection to having me for a husband, and who in all respects would be a proper match for me. She is a widow, without children, never having had any; is about my own age, enjoys good health, is very pleasant in society, has a handsome fortune at her own disposal, enjoys a most respectable reputation, keeps a good house, which is frequented by all the first philosophers and men of eminence in the science and literature of the age, or rather, of Paris. […] She is very clever […] She has been very handsome in her day, and even now, at forty-six or forty-eight, is not bad-looking; of a middling size, but rather 'en bon point' that thin. She has a great deal of vivacity and writes incomparably well.

They married in 1805, but it lasted only 4 years, ending with not very elegant accusations. When his marriage started to get worse and worse, Rumford unburdened himself to his daughter [8]:

I have the misfortune to be married to one of the most imperious, tyrannical, unfeeling women that ever existed, and whose perseverance in pursuing an object is equal to her profound cunning and wickedness in framing it. It is impossible to continue in this way, and we shall separate […] A separation is unavoidable, for it would be highly improper for me to continue with a person who has given me so many proofs of her implacable hatred and malice. […].

Rumford concluded this letter that after another quarrel in public 'she goes and pours boiling water on some of my beautiful flowers'. From what Rumford says it would seem that he was talking about another woman; unfortunately we don't know the side of Mme Lavoisier de Rumford (as she liked to be called), since she decided to keep silent!

M. A. Delahante, grand son of one of Lavoisier's colleagues at the time of the Ferme Générale, has given us an interesting yet irreverent picture of the last years of Mme Lavoisier [9]. As a boy together with his brother, often visited the elderly lady, a friend of his grand father:

I remember her with this feeling of great respect mixed with a little fear […]. We went towards a fireplace and arrived in front of a sofa, on which, a kind of old Turk reclined. This old Turk was all that was left of the young beautiful woman painted by David; this was Mme Rumford, looking very masculine, with her hair dressed in a very bizarre way. She welcomed us rather brusquely, she made us sit down and questioned us about our studies, but the conversation was obviously not interesting for her. After talking for few minutes, she often stood up very abruptly, placing herself with her back to the fireplace, like a man. She lifted up her skirt from behind, up to her garters and calmly warmed her immense calves. After a little while, she kindly let us go, and we didn't need to be told twice.

Marie died at the age of 78 in 1836, alone with her memories.

Pierre-Louis Dulong

Now let's go back to the story of thermochemistry. Following the pioneers, there was a fertile period in thermochemistry, thanks especially to the works of Favre and Silbermann, Hess, Dulong, Graham and Andrews who opened the door for the consequent research made by Thomsen and Berthelot.

Fig. 5 Pierre-Louis Dulong (1785–1838)

Pierre-Louis Dulong (Fig. 5) is famous mainly for the law of the atomic heats: 'The atoms of all simple bodies have exactly the same capacity for heat' (the law of Dulong and Petit, 1819). Dulong was interested in thermochemistry, but his results were not published until after his death. His family asked Jean François Arago to publish them. Thanks to Arago, Dulong's vast work on specific heat of gas was known, these results being discovered in Dulong's laboratory note book. He devised a respiration calorimeter in which the heat was absorbed by water instead of ice as in Lavoisier's ice calorimeter.

It is worth remembering here an accident with Dulong as protagonist [10]. Dulong in the October of 1811 was completing his researches on the possibility of synthesising a compound of nitrogen and chlorine. Unfortunately the product, nitrogen trichloride, was highly explosive and Dulong was seriously injured, losing a finger and the sight of an eye. He resumed his study in the following October, but after only one experiment he was again seriously wounded. He decided that he had had enough! Dulong also realised that nitrogen trichloride was an endothermic compound (a concept at that time unknown).

During that period Davy had great rivals in Thenard, Gay-Lussac and other French scientists in many fields of chemistry, and, in repeating the experiments of Dulong, had the same accident. Davy was wounded by a splinter of glass striking the cornea of his eye [11]. Even Faraday (who in that period was Davy's assistant) was the victim of an explosion with nitrogen trichloride.

Some historical explosions

By reading old books of chemistry and history of chemistry we learn that also some of other greatest chemists of the past, the fathers of chemistry, were sometimes involved in accidental explosions, some of which serious [12]. Already in 1703 Johann Joachim Becher, the forerunner of the phlogiston theory, asserted:

> The chemists are a strange class of mortals who seek their pleasures among soot and flame, poisons and poverty, yet among all these evils I seem to live so sweetly that may I die if I would change places with the Persian King.

The chemists of the past were content with very modest laboratories: sometimes the back-shop of a pharmacy, more often the kitchen of their own house. It was enough to have good light and equipment to obtain water and heat. Also in 1800, the idea of danger was already present in the image of the chemistry activity; however, chemists showed the wounds that they had obtained with their activity with pride. A chemist was easily recognisable by his wounds: generally some fingers were missing and sometimes even an eye!

Even the great Justus Liebig was not immune from accidents, as can be seen in the following cases. When Liebig was a student about 16 years old at high school, he already enjoyed making chemical experiments. Unfortunately 'he played' with silver fulminate that one day exploded in the classroom causing considerable damage. He was expelled with the verdict that he was 'hopelessly useless'. Several years later (when he was interested in the isomorphism of cyanate and silver fulminate) he was victim of another explosion. On that occasion Liebig almost lost his eyesight when a sample of fulminic acid exploded under his nose and he was sent to hospital to ponder over its dangers.

In April 1853, during a lecture by Liebig before a selected audience in Munich (Queen Therese and Prince regent), he exhibited the strikingly beautiful combustion of carbon bisulfide in nitric oxide. The delight of the onlookers led him to repeat the demonstration. This time, to the great horror of all present, there was a terrific explosion, the flask was shattered into bits. Queen Therese, Prince regent and Liebig himself were seriously wounded by the flying glass. The accident would have been fatal for Liebig if his snuffbox had not prevented a large splinter of glass from penetrating his femoral artery [13].

Robert Bunsen, another great chemist and sometime thermochemist, was also in an accident which is well documented. Around 1839, Bunsen began some researches on organic compounds of arsenic. Many years before, a French chemist Cadet had distilled arsenious oxide with potassium acetate obtaining a liquid with a terrible smell which was not only intensely poisonous but also spontaneously inflammable. Bunsen found that the chief component of this dreadful liquid was an organic compound of arsenic. On account of the terrific odour, Bunsen gave this compound the name of cacodyl.

In 1843 he was the victim of a very serious accident in the laboratory during the preparation of cacodyl cyanide. The explosion cost him the sight of one eye and caused weeks of illness from the breathing of poisonous fumes [14]. After this experience, Bunsen devoted himself exclusively to work in the inorganic field!

Hess's law

Germain Henri Hess (Fig. 6) was born in Geneva (Switzerland), but at the age of three he was taken to St. Petersburg, where his father was a teacher. All his early work was done in the field of mineral chemistry and chemical analysis. In 1838, Hess began the series of studies on which his fame chiefly rests. In a paper 'The evolution of heat in multiple proportions' he showed that the various hydrates of sulphuric acid could be detected by the heat evolved in their formation.

Fig. 6 Germain Henri Hess (1802–1850)

Hess introduced the term thermochemistry, for the first time, in a paper in the French language Recherches thermo-chimiques, read in front of Imperial Academy of Science of Saint Pitersbourgh in 1840. The word thermo-chimie is also found in the conclusions of a letter written by Hess to Arago in the same year [15].

When Hess began his career in thermochemistry, the concept of chemical affinity had been at the centre of chemical enquiry for more than a century. In spite of many suggestions, preferably to explain affinity in terms of electrical or gravitational forces, almost nothing was known about the cause and nature of affinity. In this state of puzzling uncertainty some chemists felt it more advantageous to establish an adequate experimental measure of affinity, whatever its nature was. One way of providing affinity with a quantitative description was by means of the heats evolved in chemical reactions. Hess believed that the proper measure of chemical affinity was given by heats of dilution.

In the same letter to Arago, Hess enunciated the fundamental law of thermochemistry, now known as the law of Hess [15]:

A combination having taken place, the quantity of heat evolved is always constant whether the combination is performed directly or whether it takes place indirectly and in different steps.

Continuing his studies, Hess was led in 1842 to his second major law, the 'law of thermoneutrality'. This states that in exchange reactions of neutral salts in water solution, no heat effect is observed.

After Hess's death, his excellent work was not continued in Russia, and thermochemistry was disregarded for over ten years Hess's contribution being slowly forgotten.The work of Hess was once more brought to light by Wilhelm Ostwald. In his 'Textbook of General Chemistry', published in 1887, Ostwald began the section on thermochemistry with a full account of the contributions of Hess in this field, and later he reprinted the most important papers of Hess.

Favre and Silbermann

The first large-scale series of calorimetric determinations of heats involved in chemical reactions were carried out by P. A. Favre (Fig. 7) and J. Th. Silbermann. They collected a large amount of thermochemical data, reporting hundreds of accurate measurements which in the two decades to follow constituted the main body of data for thermochemistry. In general, Favre and Silbermann obtained very precise results, even if they are compared with today's. It should be remembered that each determination required a particular and different procedure according to the type of sample being tested. There was certainly no standard method!

Fig. 7 Pierre-Antoine Favre (1813–1880)

However, some of the measurements made with the mercury calorimeter, were criticised. For example Thomsen revealed differences, even up to 30%, between his results and those of the two Frenchmen, concerning the case of the neutralisation heat of the bases with acids and the dissolution heat of salts in water. There was a slight outcry, which however never reached serious proportions.

Favre had some quarrels even with Berthelot over the mercury calorimeter, and the two protagonists continued their differences in papers published simultaneously in Annales de Chimie et de Physique and in Bulletin de la Société Chimique. This was a real quarrel at personal level as demonstrated by their heated and sometimes offensive tones, even if it was disguised by good manners [1].

Thomsen *vs.* Berthelot: a long controversy

Hans Peter Julius Thomsen (Fig. 8) was a Danish physicist, one of the most important thermochemists. Thomsen, personally carried out over four hundred chemical measurements. It seems he never accepted students. His ambition was to determine the absolute values of chemical forces by means of thermochemical measurements and thus supply the vague concept of affinity with a new quantitative and operational meaning. Thomsen adopted as a fundamental assumption that the heat of combination of a compound has to equal the difference between the thermal affinities of the compound and those of its constituents; that is, the thermal affinity of energy is conserved:

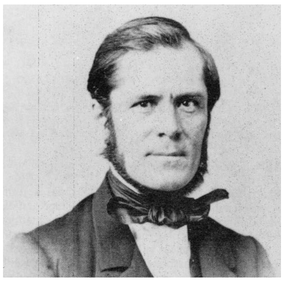

Fig. 8 Hans Peter Julius Thomsen (1826–1909)

The force which unites the component parts of a chemical compound is called affinity […] In order to split up a compound, to overcome the affinities, a force is necessary the quantity of which can be measured as the amount of heat evolved in the formation of the compound from its constituents in question.

From 1866 to about 1886 Thomsen performed an extensive research programme in experimental and theoretical thermochemistry, publishing a steady flow of papers to Danish and German journals. The bulk of Thomsen's results was collected in the book Thermochemische Untersuchungen [16].

Ten years after Thomsen had completed his system Marcelin Berthelot (Fig. 9) in France began his extensive research in thermochemistry. The whole work, experimental and theoretical, was collected in his Essai de mécanique chimique fondée sur la thermochimie [17]. In these and later publications Berthelot represented the science of thermochemistry as a French invention with himself as the chief inventor, an account

Fig. 9 Marcelin Berthelot (1827–1907)

which was bound to cause a collision with Thomsen. This collision is well documented [1] in numerous publications by both contenders: neither of the two chemists wasted an occasion to point out the bad methods, illegitimate conclusions and inaccurate measurements of the other; or conversely, to claim their own priority and competence. Instead of applying the results and methods of the other they jealously stuck to their own works and referred to the other mainly for the purpose of criticism.

Enunciating in its final form the principle of maximum work, Berthelot didn't cite Thomsen and he presented himself as the founder of thermochemistry. Thomsen felt however obliged to assert his own priority and to protest against Berthelot's claim of being the founder of the laws of thermochemistry. He subjected Berthelot's work to a devastating criticism, bluntly characterising it as 'fraud' based on 'uncritical armchair works'. The result of Berthelot's efforts was, Thomsen said, merely to have 'loaded the scientific journals with a countless number of false and totally unusable numerical values'. Though not directly accusing Berthelot of plagiarism, he concluded that Berthelot had done no more than restate the results found by himself twenty years earlier.

Thomsen's attack resulted in a vehement response from Berthelot. Berthelot maintained that his thermochemical principles were quite different from those stated by Thomsen and refused Thomsen's statement that he was the first to elaborate a fundamental law and declared that Thomsen's principle (every purely chemical action is usually accompanied by an evolution of heat) was a banality known for a century. The controversy between the two chemists lasted for more than twenty years. The real subject of the controversy concerned which of the two scientists should be credited as the founder and doyen of thermochemistry. This quarrel went on even on the occasion of the ceremony when the London Royal Society awarded both scientists with the Davy medal in 1883.

In France Thomsen's case was supported by Pierre Duhem (Fig. 10) who had his own reasons for doing so. Duhem felt that his career was blocked by the repressive authority associated with Berthelot's principle of which he always was a fervent critic. Even when Duhem was young, in his doctoral thesis, he had dared to contradict

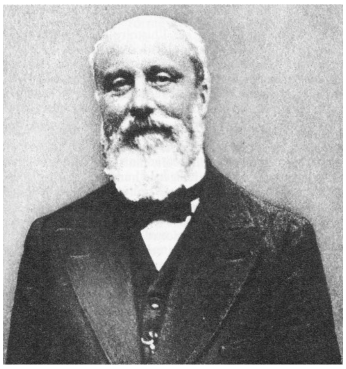

Fig. 10 Pierre Duhem (1861–1916)

Berthelot's conclusions concerning the principle of maximum work. Duhem was the best student of his course and his thesis was refused, a fact unheard of at that time: the reasons being: Duhem's work cannot be considered important enough to be put forward as a thesis in front of Science Faculty of Paris [18]. Following this Duhem was continually distanced from the Academic world and was only able to work in provincial universities.

According to Duhem, Berthelot's position and the influence he had, greatly slowed down the development of thermodynamic and physical chemistry in France.

One example of what Duhem thought of Berthelot is shown in a letter dated 16 January 1893, written to the czechoslovakian physicist Wald [18]. The Journal de physique had refused Wald's publication of a paper contradicting the principle of maximum work of Berthelot:

Dear Sir,
without doubt you cannot ignore why Berthelot is so powerful in the French scientific world and therefore it cannot be allowed to go against the principle of maximum work. The editor of Journal du Physique declares that he cannot publish your work. I don't know who I can turn to, a scientific journal independent from Berthelot cannot be found in France.

It seems that Duhem and Berthelot never actually met. Whereas Duhem wrote to state his case, Berthelot, in his untouchable position, completely ignored him. There was only one direct communication between the two that we know of. A letter written by the illustrious academic Berthelot on fifth February 1903, refusing to publish Duhem's work, with the excuse of the Academy's reduced budget [18].

Berthelot was a very fertile and inexhaustible writer; it seems he published over his long career more than 1600 articles, besides 25 monographs.

Berthelot's own experiments in thermochemistry started in 1870. At that time, he had already formulated the basic principles of thermochemistry, using as experimental evidence the investigation of Dulong, Andrews, Favre and Silbermann and others. The number and formulations of Berthelot's principle were subject to changes in his various publications but in their essence they affected two statements both of which were shown to be consequences of the mechanical theory of heat. According to Berthelot's 'principle of molecular work' the measure of chemical affinity was given by the quantity of heat evolved. The second principle which Berthelot considered the proper foundation of rational thermochemistry, was first stated in 1864. The 'principle of maximum work' states that 'Every chemical change accomplished without the intervention of external energy tends to the production of that body, or system of bodies, which disengages most heat'.

Starting from this date, Berthelot's publications on thermochemistry followed at an incredible rate, both in Comptes Rendus of Accademie and in Annales (the same articles were sometimes published in both Journals). We must not forget either that Berthelot continually published other articles on other subjects (organic chemistry, history of chemistry, scientific philosophy).

For example, in the index of the Annales of 1891 there are six articles on thermochemistry making a total of over 70 pages and 3 articles on the history of chemistry with other 90 pages. But here there is a surprise. The first article in the Annales of 110 pages entitled Recherches sur les conductibilités électriques des acides organiques et de leurs sels was by his son Daniel Berthelot. There is another example in the Comptes Rendus in 1895, the year in which argon and neon were discovered by Rayleigh and Ramsay. Eight of the 13 papers in the index are by Berthelot.

When Berthelot published this first compendium of his thermochemical research, J. W. Gibbs's fundamental theories on thermodynamic were already known, Favre had demonstrated the endothermicity of numerous reactions for some time, Saint-Claire Deville had also shown the spontaneous and endothermic dissociation of compounds at a high temperature. At this point Berthelot should have realised that his model didn't respond to a general law, nevertheless he carried on with his ideas, forever going against the new theories of thermodynamics. As he held a high official position his ideas had some negative consequences in many sectors from teaching to research and to industry.

The legend of calorimetric bomb

Paul Vieille (Fig. 11) and Émile Sarrau were among the first to measure the heat of explosion under oxygen pressure, to be sure of measuring the heat of complete combustion. The calorimetric bomb was therefore born to determine the heat of combustion under oxygen pressure.

Concerning this bomb, very soon a legend was diffused that it had been thought of by Berthelot. Even today in many small or encyclopaedic papers or books, the creation of the calorimetric bomb is wrongly attributed to Berthelot (as Medard and Tachoire correctly noticed [1]).

Some publications by A. Scheurer-Kestner, by P. Mahler and the same Berthelot contributed to the birth of this legend. This misunderstanding may have been caused because of an ambiguous sentence in a note by Berthelot and Vieille, who worked together on writing various papers published in 1884 [19]:

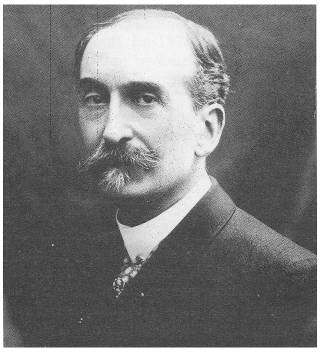

Fig. 11 Paul Vieille (1854–1934)

The determination of the heat of combustion of coal and organic compounds is very difficult for two reasons: combustion with oxygen requires a lot of time; furthermore, such combustion is never completed, constantly forming a certain amount of carbon oxide and unburnt hydrocarbons.

To find a remedy to these problems that one of us imagined as the calorimetric bomb, in which combustion is made by detonation…

Near this sentence, there was a bibliographic note on Sur la force des matières explosives, by just Berthelot. A not so careful reader could easily have made a mistake, thinking that one of us was Berthelot himself, who actually didn't do much to clarify the misunderstanding. In the first publication with Vieille on solid hydrocarbons heat combustion, Berthelot wrote our bomb, whereas some months later, he wrote my bomb.

Medard and Tachoire carefully collecting some facts and some witnesses proved that the inventor of the bomb was Vieille [1].

Conclusions

With Berthelot and Thomsen we can consider as ended the period of the classic thermochemistry. After begins that of the thermodynamics. But that is another story.

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