

Phlogiston: The rise and fall of a theory

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

The phlogiston theory was born around 1700 and lasted for about one hundred years. It provided for the first time a unifying approach to widely different chemical and physical phenomena and as such was adopted by the most famous European scientists, particularly the French ones. Its demise came with Lavoisier's new insights into the phenomena of chemical reactions in general and combustion in particular, as well as about the composition of air. Lavoisier's results disproved the phlogiston theory and established the applicability of the principle of mass conservation to chemical reactions.

Keywords: Phlogiston, Lavoisier theory, mass conservation

The phlogiston theory originated around 1700 from the ideas and experiences of Joachim Becher (1635-1682) and consolidated with the teachings of George Ernst Stahl (1660-1734)¹. According to Becher, material substances were composed of the three elements, air, water and earth. Air was only an agent that agitated water and earth and allowed them to form mixtures (compounds). The relative ratio of earth and water varied from compound to compound, and this explained the large number of substances that constituted the Earth. There were two classes of principles of substances, essential and accidental. For the animal and vegetable kingdoms the essential principles were oily spirit, fixed salt, and volatile salt and the accidental ones *phlegm* and *terra in capite mortuo*. In the mineral kingdom, they were sulphur and salt, and vinegar and mineral salt, respectively. Sulphur and salt with mercury constituted qualities; if the substance contained sulphur and salt in a volatile condition it was of mercurial quality but if they were present in an intermediate state (not volatile nor fixed) it was of *sulphurous* quality. If sulphur and salt were in a fixed state, then the substance was of a salty quality. In addition, Becher believed that there were three types of earth principle. The first one, *terra lapidea*, corresponded to a molten fluid and vitreous earth; the second one, *terra pinguis*, was a greasy, oily, combustible, and sulphurous earth that was present in all combustible substances of the animal and vegetable kingdom and in fossils or minerals in so far as they were capable of combustion. The third principle was *terra mercurialis*, a fluid, subtle, volatile and

mercuric kind of earth. A simple body was incapable of burning; a body, to be combustible, had to contain *terra pinguis*, which was expelled during combustion. Metals and metallic substances were composed of the three earths in different proportions and the residue left after combustion was *terra lapidea*. The addition of weight that occurred during the calcination of lead, tin, and antimony was due to the addition of *fire matter*².

Stahl was a student of Becher who expanded his ideas about the nature of substances and fire and founded the phlogiston theory. Its basic tenets were based on the fact that a large number of chemical substances were combustible; some like carbon and sulphur burned with a flame and released a large amount of heat, while others, like the metals, suffered a deep transformation and became calxes. According to Stahl these common features were due to a component, which was present in all bodies and carried the property of combustibility. It was the *inflammable principle*, which Stahl named *phlogiston* (from the Greek $\phi\lambda\omicron\xi$, flame)³. In one of his books⁴ he gave a very detailed account of phlogiston and its properties. The easier a body burned, the more phlogiston it contained. Thus, wood, charcoal, phosphorus, and sulphur contained large amounts of phlogiston. Metals contained phlogiston but calx oxides were deprived (or almost) of it. It was also liberated during the calcinations of metals where it constituted a common principle. After combustion there remained a *terre*, or a *chaux* (calx), that was believed to be a simple body. It was then possible to write

Metal (or combustible) \rightarrow calx + phlogiston

The differences between the different metals arose from the differences in their calxes (the residue of

combustion). The same feature characterized sulphuric, nitric, and phosphoric acids. Phlogiston constituted the motive power of fire, it could never be destroyed and did not escape from the atmosphere and for the production of flame both phlogiston and free air were necessary.

According to Stahl, phlogiston, in its simple and pure form, never lent itself readily to union or condensation and, therefore, it was readily liberated from compounds, particularly by chemical reactions. During combustion phlogiston was released in the form of fire and dissipated in the air. The phlogiston thus liberated passed into the atmosphere where it occurred in a free state; there its presence caused lighting and the consequent collapse of the dispersed excited air (thunder). Phlogiston was one of the most permanent of terrestrial matters, it was found in winds, in clouds, in lightning, and in showers. Phlogiston passed from air to plants and from the latter to animals; there was a phlogiston cycle in nature, common to the three kingdoms. It was present in all combustible bodies such as carbon, oils, and fats, and hence it was liberated in all combustions. A large amount of air was needed for combustion because it had a low capacity for absorbing phlogiston. The flame contained the heat in pure and free forms, while phlogiston constituted combined heat. Hence, combustion was simply the transformation of combined fire to free fire. Stahl believed that flaming, burning, and violent fire was a very effective instrument for the fusion of a mixture and entered as a part of the total composition.

An important property of phlogiston was that it could be transferred from one body to another by means of a chemical reaction. Stahl showed that it was possible to recover from a metallic calx the starting metal by heating it with a body rich in phlogiston, such as carbon. This result was proof that the flammability principle could be transferred from one body to another. Equally, he showed that combustion and calcinations were two transformations essentially similar. Bodies that had phlogiston in abundance could communicate it to bodies that did not have it. Thus, for example, when lead was heated it lost part of its phlogiston and become litharge, further heating led to the loss of the remaining phlogiston, the final product being minium. Contrary to this, it was enough to heat litharge with a body rich in the inflammable principle, like wood charcoal, to regenerate the metal. Sulphur behaved in a similar manner; it was composed of vitriolic acid

and phlogiston. During combustion it freed its phlogiston while sulphuric acid subsisted. But it did not lose its phlogiston completely. In addition to sulphuric acid, sulphurous acid was also formed. The latter was simply sulphuric acid containing a very small amount of phlogiston, which gave it its odour. Phlogiston had the peculiar property of not combining with water or highly watery bodies².

The initial success of the phlogiston theory was its being the first consistent general theory that tried to explain chemical reactions in general and combustion in particular, as well as being a broad conceptual scheme into which could be fitted most of the chemical phenomena known in the eighteenth century. For these reasons during the fifty years following Stahl's death it was adopted by the most respected European chemists: Johann Henckel (1679-1744), Johann Juncker (1679-1759), Johann Heinrich Pott (1692-1777), Andreas Sigmund Marggraff (1709-1782), Jeremias-Balthazar Richter (1762-1807) and Martin-Heinrich Klaproth (1743-1817) in Germany; Torbern Olof Bergman (1735-1784) and Carl Wilhelm Scheele (1742-1786) in Sweden; René-Antoine Ferchault de Réaumur (1683-1757), Jean Hellot (1685-1766), Guillaume François Rouelle (1703-1770), Jean Darcet (1725-1801), Antoine Baumé (1728-1804), Louis-Bernard Guyton de Morveau (1737-1816), Amédée-Barthélemy Berthollet (1748-1822), and Pierre-Joseph Macquer (1718-1784) in France; and Joseph Black (1728-1799), Henry Cavendish (1731-1810), Richard Kirwan (1733-1812), William Henry (1774-1836), and Joseph Priestley (1733-1804) in England. Most of these eventually relented and converted to Antoine Laurent de Lavoisier's (1743-1794) pneumatic chemistry.

Nevertheless, the theory had a basic defect: if phlogiston was a natural material (ponderable), its release by combustion should be accompanied by a *decrease* in weight and not by an increase, as actually observed: The resulting body was always heavier than the original one. This result could not be explained even if phlogiston was assumed to be imponderable or to have a *negative weight* (!). Before the phlogiston theory, Boyle had claimed that the weight of calxes was augmented by fire particles, which stuck to them: "It is no wonder that, being wedged into the pores... the accession of so many little bodies, that want no gravity, should, because of their multitudes, be considerable upon a balance"⁵.

Supporters of the theory were aware of the use of the analytical balance and the fact that metals

increased their weight on calcinations, but they believed that these facts instead of diminishing the value of the theory, actually confirmed it because phlogiston, being lighter than air, tended to suspend the body with which it was combined and made it lose part of its weight. These bodies weighed more after having lost their phlogiston. Guyton de Morveau put forward this hypothesis in his book *Digressions Académiques*⁶.

A somewhat different explanation was proposed by Friedrich Albrecht Carl Gren (1760-1798) in Germany: The weight of a body measured only the part of the mass that was gravitating and there was no proof that gravity acted on all the material parts of the body, the matter of heat had absolute levity and behaved as a negative quantity. Similarly, the matter of light, like all other bodies had extension, porosity, divisibility, impenetrability, and mobility, but in no way it was subject to the laws of gravity. Phlogiston was a compound of the matters of heat and light; when uncombined it was fire or free matter of light and matter or heat. Similarly, electrical matter was like phlogiston or else it was a compound of light and some unknown substance.

Other critical questions were: Why does combustion cease after some time in an enclosed volume of air, and why is the volume of air reduced by it; why things will not burn at all in a vacuum⁷. The first two anomalies were dealt with by adding additional hypotheses: Phlogiston must be carried away from a combustible by air, and a given volume of air can absorb a certain amount of it. Hence, nothing will burn in a vacuum, and combustion ceases in a confined space. As for the reduction in volume of the air, it was enough to assume that air saturated with phlogiston (phlogisticated air) took up less room than ordinary air (just as cotton wool saturated with water takes up less room than ordinary cotton wool)².

It must be remembered that when Stahl put forward his ideas he did not have precise ideas regarding the gas state. After the discovery of nitrogen, oxygen, and hydrogen, elastic fluids that seemed to be related to phlogiston, the supporters of the theory introduced so many modifications hard to grasp that their interpretation varied according to the author. Hofer called this period the decadence period of the phlogiston theory⁸; it saw the appearance of names such as air phlogisticated (nitrogen) or dephlogisticated (oxygen), dephlogisticated marine acid (chlorine), alkali phlogisticated (potassium cyanide), etc.

Chemists had now to admit the existence of two different fluids, phlogiston and fixed air, which had different orders of affinity. Calcination of limestone resulted in the expulsion of fixed air, even in a sealed vessel. During the calcination of a metal, phlogiston was separated from the metallic earth, and, simultaneously, fixed air combined with the air. In other words, the total calcination of a metal could only be realized in the open air; in a sealed vessel the degree of calcinations was limited by the amount of air present in the vessel. The difference between the two elastic fluids could be shown by the action of vitriolic acid on a metal and on limestone, respectively. In the first case phlogiston was liberated, which was inflammable and reduced litharge; in the second case fixed air was released, which was not inflammable and had no action on litharge⁹.

Next, at the beginning of the eighteenth century although the phlogiston theory had clarified and systematized chemistry by the recognition of the analogy between combustion, metal calcinations, and respiration, by neglecting the role of air and scorning the weight relations it had thrown the chemical theory into an inextricable confusion. As explained below, we will see that for Baumé it was a composite substance formed by the direct union of elementary fire and a very simple matter of yet unknown nature (he considered the carbons obtained by calcinations as concentrated phlogiston bound to the earthy matter). For Macquer phlogiston was fixed light, and for Scheele, heat, fire, and light were imponderable combinations between pure air and phlogiston, and the large differences between these three factors depended on the proportion and perhaps, on the form they were combined¹⁰.

Jean-Baptiste André Dumas (1800-1884) was astonished by the fact that the union of two substances having weight could give a weightless substance. For Berthelot this confusion originated from the perpetual and arbitrary mixture between ponderable matter and the matter of fire. Lavoisier condemned strongly this confusion of ideas. According to Vaissais¹¹: “en vérité la notion de phlogiston était pour une bonne part une survivance de ces qualités occultes chère à la vieille scholastique, dont le monopole de l’enseignement détenu par les Églises explique dans une large mesure l’influence encore vivace sur les esprits... Ce n’est pas non plus un hazard si c’est en France, au pays des Encyclopédistes et de la Révolution, et pas ailleurs, que les brouillards

qui obscurcissaient la chimie théorique ont surtout été dissipés“ (the phlogiston notion was in a large manner, one of those occult qualities so much liked by the old scholars, where the monopoly of teaching held by the Churches, explained in a large degree the influence still was still deep-rooted in the souls.... It is not surprising that it was in France the country of the Encyclopedists and of the Revolution and not elsewhere, that the fog that obscured theoretical chemistry was especially dissipated). The serious fight between the phlogiston theory and the theory of pneumatic chemistry dominated the end of the eighteenth century; only part of the scientists had recognized from the very beginning the superiority of Lavoisier's theory.

By 1778 Lavoisier had developed his theory that combustion and calcinations depended on the combination of the combustible or metal with oxygen; he used all the experimental information he had accumulated to attack the concept of phlogiston. He wrote¹²: “Combustion phenomena are explained rather clearly using Stahl's hypothesis, but it is necessary to assume the existence of the matter of fire, fixed phlogiston in metals, in sulphur, and other bodies regarded as combustible; or if it is required from the supporters of the phlogiston theory to prove the existence of the matter of fire in combustible bodies, they fall in a vicious circle and are forced to reply that combustible bodies contain the matter of fire because they burn, and they burn because they contain the matter of fire; we can see then that combustion is explained by combustion... The opposite hypothesis also accounts for the same phenomena observed.” Lavoisier's hypothesis was opposite to that of Stahl because he did not have to assume the existence of fire in combustibles and metals and by interpreting combustion as a process of combination of a combustible with part of the air. The heat and flame came not from a solid combustible; the source of fire was a fluid (*caloric*).

In summary, according to Stahl's theory calcination was an analytical operation because the metal or any other body decomposed into phlogiston and calx, and reduction was a synthetic operation because the calx recovered its phlogiston. In Lavoisier's theory it was exactly the opposite: calcination was a synthesis because the metal absorbed something when it increased in weight; reduction was a decomposition because carbon instead of withdrawing, it added something to the

metal and caused it to reduce its weight, exactly in the same amount it gained during calcinations, and all this according to the law of mass conservation.

These were the principles of the two theories that confronted each other during the last part of the eighteenth century, divided the chemists into two enemy camps, but resulted in a very powerful catalyst for the progress of science.

The position of some scientists

The arguments given by some of the most famous scientists, those supporting the phlogiston theory to the end, or those that changed their mind with Lavoisier's findings has been described below.

(i) Rouelle

Rouelle is considered to be the one who introduced the phlogiston theory in France. He accepted the four-element theory of earth and air, fire and water, but replacing fire by phlogiston (the flammable principle); he accepted that these four elements were more capable of accounting completely for the properties of matter and chemical phenomena than the three ones of Basile Valentine and Paracelsus (1493-1541) (mercury, sulphur, and salt). Rouelle thought that there might be a fifth element, the “mercury” of Becher. Although the existence of mercurial earth was not certain he believed that it was present in marine salt and that it was the cause of the metallic nature of metals. These primordial elements did not combine by themselves to form compounds, but various combinations of them, about ten or twelve in number, which then combined with one another. The transfer of one or more of them from one compound to another in a chemical reaction allowed discovering their properties. The basic tenet was that they were indestructible, immutable, and non decomposable.

Rouelle was still defining the constituent elements of matter the same way as Aristotle had: “We call principles or elements simple, homogeneous, indivisible, immutable and insensible bodies, more or less mobile according to their different configurations, stature and mass, and which are differentiated by their volume and particular shape. It is impossible to detect them in isolation, separated from other elements, unless they come together in a very large numerical quantity. Their particular shape is also unknown and it would be quite ridiculous to pretend to determine it, as several physicists have done. What can be ascertained is that they exist in very small numbers and yet their different combinations suffice to form all

the bodies found in Nature. We acknowledge four principles or elements: phlogiston or fire, earth, water and air"¹³.

According to Rouelle, mercurial earth was the factor that gave metals their peculiar properties and a metallic essence. As mentioned before, Becher's pupils were not sure about the existence of mercurial earth; Rouelle himself suspected that phlogiston and mercurial earth were the same element. He recognized that seemingly different types of earths were formed after certain chemical reactions, but could not decide whether or not these were impure manifestations of a single element. Whatever the solution he concluded, earth was the principle, which gave substances solidity, consistency, and stability¹⁴.

According to Rappaport¹⁴, the sudden popularity enjoyed by the phlogiston theory in the mid-eighteenth century is a product of Rouelle's work both as a teacher and advocate of the theory and as a modifier and adapter of Stahl's ideas.

(ii) Baumé

During his stay with Étienne Louis Geoffroy (1725-1810) Baumé became strongly interested in the phlogiston theory of Becher and Stahl (1660-1734) because they had tried to give one interpretation to phenomena that seemed very different. Although he did not do work to validate it, he remained faithful to it until the very end of his life, even after Lavoisier's discoveries. He wrote: "Fire is a matter essentially fluid, it is the principle of fluidity in bodies and it is always in movement. Phlogiston is the principle of odours, colours, and the opacity of bodies. Phlogiston becomes fixed when it becomes part of the composition of the *terres*, and the contrary, it is very volatile when it is the elementary fire that predominates over the earth principle. Fire is really heavy when it is combined in bodies, it is also very heavy when it is free but in this last case it is impossible to appreciate its weight because it does not touch the bodies that it penetrates, and it has always an excessive movement. Phlogiston is a composed matter, formed by the direct union of fire and a very simple, but yet unknown substance"^{15,16}.

Baumé saw Lavoisier's results "as a brilliant experience that illusions scientists and makes them arrive at the wrong consequences"; he scorned the decomposition of water, one of the first significant achievements of the chemistry of the new school. The recent progress in the manipulation of gases, the

discovery of oxygen, and the evidence on oxidation reactions continued to leave Baumé sceptic. He declared, for example, "I will believe in the recomposition of water when you will perform your experiments without employing water in your equipment"¹⁵. Baumé's refusal to discard the phlogiston theory and accept the new theories of chemistry cost him dearly: The *Institut National des Sciences et Arts* systematically refused his request to be promoted from *associé-non résident* to *titulaire*.

(iii) Guyton

In the beginning of his career Guyton was a staunch supporter of the phlogiston theory and in 1772 he exposed his ideas and conclusions in his memoir *Dissertation sur le Phlogistique Considérée Comme Corps Grave*, the first of three essays published in his *Disgressions Académiques*⁶. This memoir may be considered the most comprehensive exposition of the phlogiston theory available at that time (267 pages).

Guyton first established that when a metal was calcined its weight increased; the decrease in weight reported by earlier workers was due only to mechanical loss or volatilization. He then proceeded to expose his theory that the presence or absence of phlogiston was the only cause of the change in weight. Phlogiston was specifically lighter than air, actually lighter than any substance. Therefore, its combination with any other substance necessarily resulted in an apparent diminution in the weight of the substance, independent of the medium in which the weighing was performed. Phlogiston, or the inflammable principle, was a substance that could not be explained with common arguments; it had never been obtained free from other matter, and its existence and its properties could be deduced only by the fundamental role it played in nature. Common belief had it that phlogiston was material and hence it had weight (*elle est matière donc ell est grave*) as shown by the gain in weight of metals on calcinations. According to Guyton the presence or absence of phlogiston was the real cause of the decrease or increase of the gravity of the bodies that could combine with it. He claimed that phlogiston could not gravitate in air because it was essentially volatile. On being set free by a body it rose immediately in the air and communicated its volatility to the bodies with which it combined. The immediate cause of volatility was the excess of the gravity of the medium over that

of the volatile body. This volatility ceased to be manifested as soon as the quantity of the fixed substance was sufficient to produce a combined density (*densité composée*) exceeding that of the surrounding fluid. All volatile substances owed their volatility to the presence of some phlogiston and lost their volatility when it was removed. The lesser gravity of phlogiston in air was proved by the direction it took when it was free and by the speed with which it moved in that direction^{9,17}.

According to Guyton, the laws of hydrostatics indicated that the gravity of a body in air was wrongly termed its absolute gravity (*pesanteur absolue*); it was really only specific (*pesanteur spécifique*) or relative to that of air, since the force with which a body descended in air was proportional to the excess gravity of its matter over that of air. Since phlogiston was lighter than air then it had to decrease in air the gravity of a body with which its combined, in proportion to the excess of its levity over that of air. Although addition of any amount of matter to a given body resulted in an increase of its absolute gravity, this was not the case when phlogiston was added; the result might well be an increase or a decrease of its specific gravity in air. In simple words, the common method for determining density could not be applied to bodies containing phlogiston, since we did not know their mass or absolute weight exactly, firstly because they contained a matter that did not manifest in air the tendency we call gravity, and secondly, because the force produced by its volatility of this matter is in equilibrium with some of the matter that holds the phlogiston, just as the volatility of cork in water makes equilibrium with a quantity of lead¹⁴.

Guyton's ideas were seriously attacked and criticized; it was argued that if phlogiston was so volatile then it would be unrestrainable as fire and as capable as steam of overcoming great resistances. It would constantly strive upwards and all bodies that contained it would insensibly lose it. Putting in modern terms what an antagonist wrote regarding Guyton's ideas: phlogiston was identical to an *unknown virus* or to *aspirin*. It was a very convenient and versatile idea used by chemists whenever they needed it because of its possibility of explaining the most contradictory facts.

Lavoisier's findings led not only to a turn around of Guyton's position but also to his developing his famous chemical nomenclature. When Guyton was commissioned in 1780 to write the chemical volumes of the *Encyclopédie*, he realized that he had an opportunity to reform the then cumbersome chemical

nomenclature. He set forth his reform in 1782 and applied his principles not only in the first part of the *Encyclopédie*, but also in the translations he had made of the works by Bergman and Scheele.

The application of his nomenclature initially was almost exclusively connected with the naming of acids, basis, and salts; the preparation of these substances was not dependent on any one system of chemistry for interpretation and nomenclature, and, therefore, their names could be used with equal convenience by both phlogistonists and antiphlogistonists. However, in 1786 when Guyton started to prepare his sections on *Air* for the *Encyclopédie*, he was not only confronted with the problem of devising a new nomenclature for the chemical substances involved, particularly gases, but also with the necessity of adopting either the phlogiston or antiphlogiston theory, since his names could only apply to one system, not both. He, therefore, went to Paris to consult with Lavoisier and his disciples about the new chemistry, and it was after a number of months of discussions and convincing experimental demonstrations that he decided to give up the phlogiston theory¹⁸.

The behaviour of heated charcoal presented another riddle. According to Stephen Hales (1677-1761) the unusual behaviour resulted from air being consumed during combustion¹⁹ but Guyton pointed out that if these facts were correct then charcoal would lose weight even when in a sealed vessel, which contained a little air. According to Guyton "combustion could occur in a fluid only when an undulatory motion could be maintained in the vicinity of the combustible; this facilitated the liberation of the combined phlogiston. When the air in an enclosed vessel was heated, it became compressed; this was equivalent to an increase in the density of the air, the undulatory motion was not maintained and the phlogiston could not escape. Combustion was impossible in a vacuum because the medium was too rare to permit the necessary undulatory motion"⁹.

Guyton⁶ believed that the loss of activity of the fire particles was due to the force of attraction or affinity operating between them and the particles of the substances with which they were combined. Phlogiston-containing substances could be looked upon as crystals that formed in a phlogiston solution and retained a certain amount of the solvent in combination, in the same as salts that crystallised in water containing a dose of water of crystallisation

(today, hydrates). Guyton suggested calling this effect *feu de cristallisation* by analogy with *eau de cristallisation*. After his conversion, Guyton became one of the most vigorous advocates of the anti-phlogiston theory. He believed, however, that spite its shortcomings the phlogiston theory had served chemistry well: "Cette hypothèse a été, dans les premiers temps, plus utile que nuisible aux progrès de la chymie; c'est ce que l'on ne peut contester raisonnablement, et j'aurai plus d'une occasion d'en fournir des preuves indubitables; je me bornerai en ce moment à faire quelque liaison entre une multitude de faits épars et d'observations isolées; que ces rapports subsistent, ou plutôt que de nouvelles explications plus directes n'ont servi qu'à leur donner une base plus solide" (In the beginning, this hypothesis was more valuable than damaging for the progress of chemistry; it could not be contested in a reasonable manner, and I had more than occasion to give indubitable proofs for it. I will now limit myself to relate between a multitude of scattered facts and isolated observations, that these relations persist, to which new observations had served to give it a more solid base)^{20,21}.

(iv) *Fourcroy*

In the *Encyclopédie Méthodique*²² Fourcroy wrote that Macquer, occupied during the first years of the chemical revolution in writing the second edition of his *Dictionnaire de Chimie*, discussed the new discoveries about air and elastic fluids. He gave a very exact description of these discoveries in new entries in the Dictionary, but instead of dispensing of the phlogiston theory he believed it to be even more solidly established by the two changes he proposed to the theory: (1) replace fixed fire by light and (2) consider air as the precipitant of light, and reciprocally, light as the precipitant of air. In this manner he explained in 1777 the phenomena of combustion of a flame, calcinations and the increase in weight of metals, the alteration of air by breathing, and the formation of acids. It is evident that in order not to resign from a cherished hypothesis and cause its total loss, Macquer renounced to part of his opinions and consequently gave a deadly blow to the theory of the inflammable principle, where the pretended existence attributed to light, modified in such a manner the nature and the properties that it was no longer Stahl's phlogiston.

In the beginning, Fourcroy supported the phlogiston theory; for him a metal was formed by an unknown earth and phlogiston. During calcinations phlogiston left

the metal and joined the air, part of which became saturated and unable to support further combustion, and part precipitated on the earth of the metal to generate the calx. Sulphur was composed of an unknown principle and phlogiston. On combustion phlogiston combined with part of the air to yield spent air, while the earth of sulphur united with the rest of the air to produce *acide vitriolique* (sulphuric acid). The decomposition of water by red-hot iron was explained by water being formed from an unknown principle and vital air; iron resulted from the union of a martial earth and phlogiston. The final result was iron calx and an inflammable gas.

In the first edition of the notes for his chemistry course²³ Fourcroy presented both the phlogiston and anti-phlogiston theories, although he favoured Macquer's opinion that during combustion and calcinations vital air was absorbed at the same time that phlogiston was released. He explicitly wrote that he did not reject or accept either of the two theories.

Eventually, the overwhelming amount of experimental data accumulated by Lavoisier led Fourcroy to reject the phlogiston theory and adopt the theory of pneumatic chemistry, which would lead to modern chemistry²⁴. As noted by Smeaton⁹ this was an extremely important event because through the large public attending his course and his books Fourcroy became the lever that elevated Lavoisier's ideas to the front of chemistry.

(v) *Kirwan*

In 1787 Richard Kirwan (1733-1812) published his book *Essay on Phlogiston and the Constitution of Acids*²⁵ in which he tried to conciliate Stahl's theory with the new discoveries and assuming that phlogiston was *inflammable air* (hydrogen). Mme Lavoisier translated this book and to it Lavoisier, Guyton de Morveau, Pierre-Simon Laplace (1749-1827), Gaspar Monge (1746-1818), Claude-Louis Berthollet (1748-1822), Jean-Henri Hassenfrantz (1755-1827), and Fourcroy, added their criticism to Kirwan's conceptions. Their arguments were so convincing that in 1791 Kirwan and Joseph Black (1728-1799) accepted the new theory.

(vi) *Macquer*

Macquer did most of his work at the time when the phlogiston theory was the accepted explanation for many chemical and physical phenomena. He was the first Frenchman to give it full recognition and teach it as the central subject in chemistry. He lived to see

Lavoisier develop the alternative oxygen theory of combustion and work hard to reconcile the new experimental evidence to the old theory.

Macquer's dictionary²⁶ shows his strong position regarding the controversy between those advocating the phlogiston theory and those advocating the chemistry developed by Lavoisier. He was a strong supporter of the original phlogiston hypothesis, but the increased experimental evidence provided by Lavoisier led him to modify his position. Macquer explained the increase in weight postulating that the metal first lost phlogiston (as in the classical theory) and then it combined with a quantity of air that exceeded the weight of the phlogiston lost. Macquer continued to affirm that combustion and calcinations released phlogiston and that it was the constitution matter of light. Exchange of phlogiston between two bodies gave place to substantial changes and it was this property that allowed distinguishing it from pure fire and to consider it as the fire element combined with another substance.

Macquer described phlogiston as "le principe inflammable le plus pur & le plus simple (the most pure and simple inflammable principle)...Le phlogistique doit être regardé comme le fue elementaire, combine & devenu un des principes des corps combustibles" (phlogiston must be considered as elementary fire, combined and transformed into one of the principles of combustible bodies)²⁶. The principal property that combustible bodies presented was inflammability, it provoked heat and light and provoked in other bodies all the effects caused by concentrated solar rays or intensive rubbing. Combustion of bodies resulted always in their decomposition, that is, the separation of the principles that composed them. The residue of combustion entered in the category of non combustible bodies and it seemed that this phenomenon left no doubt that elementary fire did enter as a principle in the composition of said bodies: "Ce principe ne pouvoir être separé d'avec les autres principes des corps, & obtenu seul & pur, & que par conséquent it a été impossible de reconnoître toutes celles de ses propriétés qui lui font particulieres, & qui le distinguent de toutes les autres substances" (It cannot be separated from the other principles of bodies, nor can be obtained pure, hence it is impossible to discover all the properties, which are peculiar to it and that distinguish it from all other substances)²⁶. To Macquer, the difficulty of obtaining the inflammable

principle of bodies in a pure form except in the form of fire and its action, was one of the strongest reasons to believe that phlogiston was none other than pure fire, but deprived of its activity by the union it had acquired with a given substance. It was hard to conceive how pure, elementary fire, whose particles seemed always to be agitated by a violent movement having no coherence between them and no disposition to adhere in a fixed manner to other bodies, could be contained within a solid body and be deprived of its fluidity. When phlogiston united with a non inflammable substance, it yielded a completely different body that was nor hot nor luminous, but because of the union it became inflammable, and as such able to generate heat and light in an amount that depended both in the amount of phlogiston it contained and the nature of the primitive material. The union of phlogiston with a naturally solid body did not make it fluid but diminished its hardness and increased its solubility. Substances that were naturally odourless and colorless, always acquired one of these properties, and for this reason chemists tended to believe that phlogiston was the principle of colours and doors. On the one hand, it was true that there were combustible substances that were colourless and odourless, but usually they contained a very small amount of combustible matter. On the other hand, all combustible substances that released large amounts of heat had colour and odour. An interesting observation was that no body was known that formed only by phlogiston, air or water, although phlogiston was able to combine with substances as that contained air or water as their principles (such as oils and salts).

Sulphur was inflammable because it contained phlogiston, but its flame had little luminous and heat power because it contained more sulphuric acid, an incombustible substance, than phlogiston. Combustion of sulphur released its phlogiston, which became free fire and dissipated; the liberated sulphuric acid became free and pure and capable of combining with the phlogiston contained in another body, and return to be sulphur, identical to the original one. Vitriolic acid was sulphur combined with pure phlogiston because the acid did not contain a large amount of water and because combustible bodies treated with this acid formed sulphur. Now, it could be seen that sulphuric acid, a colourless and odourless substance, when it was pure formed with phlogiston a compound having both of these properties, properties which become more accentuated in certain situations.

The volatility of nitrous acid (in those days HNO_3 , not HNO_2), its colour and odour, having strength less than that of vitriolic acid, and added to its inflammability and total decomposition by inflammation, proved that phlogiston entered in its composition. According to Stahl and others, this fact explained why nitrous acid was different from vitriolic acid.

Salt acid (HCl) had odour and colour and was highly volatile, that is, it seemed to possess all the properties characterizing an acid joined to the inflammable principle. Nevertheless, it did not show as vitriolic and nitrous acids did, the same disposition to combine with the principle not in an intimate or superficial manner. It refused to act on many inflammable substances (such as oils) and reacted weakly with metals. No direct combination of salt acid with phlogiston was known (*soufre marin*, marine sulphur). What was the reason for these contradictory properties? According to Becher, it was the mercurial earth, the one that specified and characterized marine acid, this earth prevented the acid to join with phlogiston.

Fixed alkalis showed a strong disposition to combine with phlogiston and their properties showed that phlogiston was part of their composition, however, they seemed to show less affinity for the inflammable principle than vitriolic and nitrous acid and about the same as metallic earths.

Macquer believed that the concepts of *feu principe*, *feu combiné*, *feu fixé*, *principe inflammable*, etc., were actually the same thing, which was the substance of light. Phlogiston was then the substance of light itself fixed in a large number of compounds, and deprived, as long it formed part of them, of its properties (such as mobility) that characterized when it was free. Light was recognized as a material substance possessing movement, elasticity, refrangibility, and reflexibility, which could be directed, diverted, reflected, concentrated, and dispersed, and could also be decomposed and recomposed.

Macquer's strong support of the phlogiston theory may explain why the great prestige with which he was held while he was alive decreased fast after his death. The successors of the chemical revolution judged a contemporary of Lavoisier according to his acceptance of the latter ideas. Scientists that did not convert to the new chemistry were considered pariahs (scientifically incorrect).

Lavoisier's theory

When Lavoisier began his work in chemistry, the phlogiston theory was the generally accepted chemical doctrine on France and was enthusiastically supported by her most famous scientists. The theory provided a satisfactory explanation to completely different phenomena such as combustion, fluidity, and volatility, as well as the physical properties of colour and odour. This situation would change drastically when Lavoisier's experiments led to new insights into the phenomena of chemical reactions in general and combustion in particular, as well as about the composition of air. Lavoisier's results would lead to a new chemistry that would disprove the phlogiston theory and establish the applicability of the principle of mass conservation to chemical reactions. It took Lavoisier almost ten years to convince his contemporaries; when in 1783 he attacked the phlogiston theory no one was at his side. Chemists had good reasons not to abandon a theory that organized all their knowledge for a new theory of limited application²⁷.

In 1766 Cavendish immersed zinc, iron, and tin in vitriolic and hydrogen chloride and collected and studied the gas that was released. He found that it was eleven times lighter than common air and highly inflammable. Cavendish concluded "whereas the metallic substances zinc, iron and tin are dissolved in spirits of salts (HCl) or diluted vitriolic acid then phlogiston flies off without having its nature changed by the acid. But when they are dissolved in nitrous acid (HNO_3) the phlogiston unites with part of the acid used for their solution and flies off with it in fumes, the phlogiston losing its flammable nature by the union"^{28,29}. These new findings led to new problems: (1) Gases rich in phlogiston were supposed to inhibit combustion, the inflammable gas did the opposite, it burned, (2) combustion released phlogiston, now phlogiston was being released from itself, and (3), metals immersed in concentrated vitriolic acid yielded no inflammable air. Cavendish explained these findings by saying that in this situation the inflammable air combined with some of the acid to produce "volatile sulphurous acid", a half stage between vitriolic acid and sulphur²⁹.

During 1770 Lavoisier showed that it was possible to explain quantitatively the weight gain by admitting that they combined with a fraction (about 20%) of ordinary air. According to Lavoisier air was actually a mixture of two fractions, one that had a similar

activity in respiration and in combustion (which he named oxygen) and another (about 80% and named afterwards azote) that did not participate in these phenomena. These two fractions behaved quite differently, while oxygen facilitated combustion and left no residue the second fraction extinguished fire and caused asphyxia.

During September and October of 1772 Lavoisier performed experiments on the burning of sulphur and phosphorus in air confined over water and observed that the volume of the air decreased while sulphur and phosphorus increased in weight. He reported his results in three notes deposited with the secretary of the Académie de Sciences. In the first one, opened on May 5, 1773, Lavoisier wrote: "About eight days ago I discovered that sulphur in burning, far from losing weight, on the contrary, gains it; it is the same with phosphorus; this increase in weight arises from a prodigious quantity of air that is fixed during combustion and combines with the vapours. This discovery, which I have established by experiments, that I regard as decisive, led me to think that what is observed in the combustion of sulphur and phosphorus may well take place in the case all substances that gain weight by combustion and calcinations and I am persuaded that the increase in weight of metallic calxes is due to the same cause." Although the phenomena that accompanied the burning of sulphur and phosphorus were well known, Lavoisier's interpretation was radically different.

In the second note he added the comment that as phosphorus burned it released phlogiston and absorbed air. In his third note he went further, he shed off the concept of phlogiston and insinuated that the fixing of a quantity of air explained both the burning and the weight increase. From this notes we learn that Lavoisier was postulating that combustion was a combination with oxygen, but neither him nor others (supporting or not the phlogiston theory) had been able to isolate and identify the product of the combustion. Lavoisier's conclusion allowed him to give a radically different answer to the mechanism of combustion but he was still unable to explain the difference between the reaction of a metal and an acid that liberated inflammable air, and the reaction between the same acid and the metallic calx, in which no hydrogen was released. According to the phlogiston theory a metal was the result of the combination of its calx with phlogiston, while the reaction of the metal with an acid liberated

inflammable air and phlogiston. During the reaction of a calx with acid there was no liberation of inflammable air the calx was the residue *after* the loss of phlogiston. Lavoisier was unable to explain this difference. The composition of acids was unknown and Lavoisier considered them as oxides. Similarly, the composition of water was also unknown^{27,30}.

Anyhow, after more experimentation Lavoisier went on to improve his elucidation of the mechanism of combustion in order to explain why the phenomenon ceased when the amount (volume) of air available was limited (for example, in an enclosed environment). Now he postulated that ordinary air was composed of two very different substances, a pure part, which supported combustion and another part (mephitic air, azote), which did not. Thus, reduction of a calx to pure metal released a pure air: "The principle which combines with metals during their calcinations, which increases their weight and constitutes them in the state of a calx, is nothing other than the purest part of air and such that, if the air, after having engaged in a metallic combination, becomes free again, it appears in an eminently breathable state"²⁹.

The next giant step forward was the discovery of the composition of water. Several chemists, including Priestley, had noted that the burning of inflammable air deposited dew on the walls of the vessel. All had ignored it as an irrelevant side effect, except for Cavendish who thought that perhaps the dew was what was left behind as phlogiston was released from inflammable air. Further experiments showed him that was pure water and that when inflammable air was burned in dephlogisticated air, the air disappeared in the ratio two to one.

In June 1783 Lavoisier learned that Cavendish had obtained water by burning a mixture of inflammable air and dephlogisticated air. Lavoisier understood immediately the remarkable significance of this result and explained it by saying that water was a compound of both gases.³¹ With this explanation he had the key for the difference between the reaction of a metal or its calx with an acid, by admitting that water participated in the reaction. In the first reaction water decomposed and released its inflammable gas and dephlogisticated air (oxygen). The latter combined with the metal to yield the metallic calx (the name oxide has yet to be defined). The second reaction was simply the combination of the acid with the calx to give the pertinent salt²⁷.

The composition of water was further demonstrated by decomposing it (Lavoisier, Meusner, 1786)³². The

experiments were witnessed and controlled by a commission appointed by the Académie de Sciences, which included, among others, Claude-Louis Berthollet (1748-1822) and Gaspard Monge (1746-1818). Water was placed together with iron filings, which rusted, giving off inflammable air. The weight of the inflammable air plus the weight gain of the rusted filings was shown to be equal to the weight of the water consumed. The commission's report included the following statements: "One of the parts of the modern doctrine the most solidly established is the formation, decomposition, and recomposition of water. And how can we doubt it, when we see that in burning together fifteen grains of inflammable air and eighty-five of vital air, we obtain exactly one hundred grains of water, in which, by decomposition, we find again the same principles and in the same proportions. If we doubt of a truth established by experiments so simple and palpable, there would be nothing certain in natural philosophy".

The demonstration had the desired effect because shortly thereafter Berthollet, Fourcroy, Monge, and Guyton de Morveau announced their conversion to the new theory. There still remained other baffling phenomena that the phlogiston theory did not explain well. Now there were two kinds of inflammable air; Lavoisier distinguished between light inflammable air (hydrogen) and heavy inflammable air (carbon monoxide); its composition was unknown and it yielded fixed air (carbon dioxide) on burning. These results, which could not be explained by Lavoisier's new theory, had an easy interpretation with the phlogiston one. Priestley, for example, had obtained inflammable air by heating finery cinder (iron oxide, Fe_3O_4) with carbon. Since according to Lavoisier inflammable air was a constituent of water, it could only be produced in the presence of water, hence wrote Priestley, this meant that the new theory negated the presence of water in bodies, it saw in finery cinder an oxide composed only of iron and oxygen and did not admit the presence of water in the carbon that formed at higher temperatures. Contrary to this, the phlogiston theory claimed that finery cinder was impregnated with water that replaced the phlogiston, and water was a constituent of all airs, so much that inflammable air resulted of the union of the water contained in finery cinder with the carbon of the phlogiston. This reaction remained totally incomprehensible until 1801 when William Cumberland Cruikshank (1745-1800) showed that the

heavy inflammable air of Lavoisier was not hydrogen but an oxide of carbon, which he named gaseous carbon oxide. This interpretation was accepted gradually but it was, however, powerless to convince Priestley, who remained faithful to the phlogiston theory until his death^{27,33}.

The phlogiston theory was now on its way out to be replaced by Lavoisier's new chemistry.

References

- 1 Stahl G E, *Zufällige Gedanken und Nützliche Bedenken Über den Streit von den Sogenannten Sulphure, un Zwar Sowohl dem Gemeinen Verbrennlichen Oder Flüchtigen, als Unverbrennlichen Oder Fixen*, Halle, 1718.
- 2 White J H, *The History of the Phlogiston Theory* (Edward Arnold Co, London), 1932.
- 3 Stahl G E, *Specimen Becherinum*, Leipzig, 1703.
- 4 Stahl G E, *Experimenta, Observationes, Animadversiones, CCC Numeri, Chemicæ & Physicæ*, 1731.
- 5 Boyle R A, Discovery of the Perviousness of Glass to Ponderable Parts of Flame, in *Essays of Effluvioms*, London, 1673, 66.
- 6 Guyton de Morveau L B, *Disgressions Académiques, ou Essais sur Quelques Sujets de Physique, de Chymie & d'Histoire Naturelle* (L N Frantin, Dijon), 1772.
- 7 Bacon F, *Novum Organum*, Great Books of the Western World, vol. 30, edited by Robert Maynard Hutchins, Encyclopædia Britannica (Inc., Chicago), 1952; Book II, Aphorisms 39 and 50.
- 8 Hoefer F, *Histoire de la Chimie* (Didot, Paris), 1866.
- 9 Smeaton W A, In *Mélanges Alexandre Koyré*, 2 volumes, edited by Cohen-Taton, Paris, 1964, vol I, 552.
- 10 Kersaint G, *Antoine François de Fourcroy, Sa Vie et Son Œuvre* (Éditions du Muséum, Paris), 1966.
- 11 Vassails G, *Revue d'Histoire des Sciences et Leurs Applications*, 3 (1950) 222.
- 12 Lavoisier A, *Opuscules Physiques et Chimiques* (Durand, Paris), 1774.
- 13 Rouelle G-F, *Cours de Chymie*, 27-28, de Grangé, Paris, approximately 1750.
- 14 Rappaport R, *Chymia*, 7 (1961) 73.
- 15 Berton F, *Antoine Baumé, Pharmacien et Chimiste*, Thesis, Faculté des Sciences Pharmaceutiques et Biologiques, Université Paris V: Paris, 1985.
- 16 Baumé A, *Chymie Experimentale et Raisonné* (Didot et Barrois, Paris), 1773.
- 17 Partington J R & McKie D, *Ann Sci*, 2 (1937) 388.
- 18 Duveen D I & Klickstein H S, *Osiris*, 12 (1956) 342.
- 19 Hales S, *Vegetable Staticks* (Innys and Woodward, London), 1727, 230.
- 20 Bouchard G, *Guyton de Morveau - Chimiste et Conventionnel* (Librairie Académique Perrin, Paris), 1938.
- 21 Melhado E M, *Hist Stud Phys Sci*, 13 (1983) 311.
- 22 Fourcroy A F, in *Encyclopédie Méthodique, Chymie, Pharmacie et Métallurgie*, Panckouke, Paris, vols.I to IV, 1786.
- 23 Fourcroy A F, *Leçons Élémentaires d'Histoire Naturelle et de Chimie* (Cuchet, Paris), 1782.

- 24 Fourcroy A F, *Éléments d'Histoire Naturelle et de Chimie*, second edition *des Leçons Élémentaires d'Histoire Naturelle et de Chimie* (Cuchet, Paris), 1786.
- 25 Kirwan R, *Essay on Phlogiston and the Constitution of Acids*, London, 1787.
- 26 Macquer P J, *Dictionnaire de Chymie* (Lacombe, Paris), 1766.
- 27 McKie D, *Endavour* (1959) 144.
- 28 Cavendish H, *Phil Trans*, 56 (1766) 141.
- 29 Musgrave A, In *Method and Appraisal in the Physical Sciences*, edited by Colin Howson (Cambridge University Press, Cambridge), 1976, 181.
- 30 Conant J B *The Overthrow of the Phlogiston Theory* (Harvard University Press, Cambridge), 1950.
- 31 Lavoisier A, *Mém Acad Royale Sci*, (1781) 468 (Published in 1784).
- 32 Lavoisier A & Meusner J P M C, *J Polytype*, 1 (1786) 21.
- 33 McCann H G, *Chemistry Transformed; The Paradigmatic Shift from Phlogiston to Oxygen* (Ablex Publishing Corp., Norwood), 1978.