The Problem of Combustion

Explanation and Phlogiston

Georg Ernst Stahl

Much early thinking about combustion sought to explain its observable impact. The flickering flames and rising smoke, for example, were interpreted as something escaping from the burning material. Furthermore, combustion of rigid and heavy logs left behind a much lighter and less substantial ash. Many observers claimed that an 'inflammable principle' was escaping during combustion. Thus, when the fire extinguished, this was due to the inflammable principle departing from its original vessel into the air. The objective of many 17th and 18th century chemists was to identify the nature of this 'inflammable principle.'

By the mid-18th century, most chemists referred to the 'inflammable principle' as *phlogiston* — the agent of combustibility. This thinking, originating in the German lands, went against the mechanical worldview that prevailed in science at the time. The work of Isaac Newton and many others during the late 17th and early 18th centuries conceptualized the universe as populated by incredibly small 'corpuscles' ruled by laws of motion and forces.

This framework became established in England and eventually France. The natural philosophers of these countries sought to explain all phenomena (e.g., gravity, chemistry, and even life) in terms of mechanics. However, some chemists rejected the idea that chemistry could be understood in purely mechanistic terms. Many of these chemists were German, and they detested the notion that a "clockwork universe" could explain the various chemical phenomena they observed, much less the phenomena of living things.

These chemists instead proposed non-mechanistic explanations of chemical phenomena. Ideas such as phlogiston were one manifestation of this desire. The theory of phlogiston, and others like it, gave chemists autonomy from the dominance of a mechanical worldview.

> !
>
> **Teaching and learning contemporary well-established science ideas without periodically examining how those ideas were developed and became accepted can create misconceptions regarding the nature of science. As this story regarding the problem of combustion illustrates, science research is an intense puzzle-solving endeavor with no answer-key. Scientists must develop ideas to make sense of nature and assess the viability of those ideas. As you read, keep in mind that the efforts to understand the problem of combustion and uncertainty regarding conservation of mass were occurring at the same time (see the related story "The Development and Acceptance of the Conservation of Mass Law").**

Johann Joachim Becher (1635-1682) thought that all substances contained different amounts of three types of earth: vitreous, fatty (or sulfurous), and metallic (or mercurious). Becher believed that differences in chemical activity were due to a substance's different compositions of these earths. Becher, who was mostly interested in animal and vegetable compounds, believed that the second kind of earth, fatty, was what made these types of materials burn. This fatty earth was the 'inflammable principle' that instigated combustion and left the animal or vegetable body as a result, evidenced by the flames, smoke, and heat lost to the surroundings.

Becher's pupil, Georg Ernst Stahl (1660-1734), took his mentor's ideas further. Stahl put forward the idea of phlogiston that would become the unifying idea in chemistry until the end of the 18th century. He accepted the idea of corpuscles, but unlike prevailing thought among many scientists, also maintained that these entities carried other intrinsic properties besides their motion. Stahl's three earth elements were the same as Becher's, but in 1718 he renamed the fatty earth *phlogiston*. These fundamentally different elements were a clear rejection of a universe populated by identical 'corpuscles' composing all substances. Unlike his mentor, Stahl focused on inorganic compounds (i.e., those that contained a metal). Stahl noted that the rusting of metals was similar to slow combustion. Stahl sought to explain the phenomena of rusting and combustion. He argued that when a metal was heated, it lost phlogiston and converted into a *calx*. Heating the calx and charcoal recovered the original metal. Stahl explained this by claiming that charcoal was rich in phlogiston. The reactions can be represented as follows:

X → Y + phlogiston (general reaction, X can be metal or nonmetal)

metal → calx (metallic ash) + phlogiston (when X = metal)

Y + phlogiston → X (general reaction, X can be metal or nonmetal)

Calx (metallic ash) + phlogiston → metal (when X = metal)

Thus, phlogiston is the central agent in both combustion and restoration. On one hand, phlogiston left a metal to become the calx. On the other, phlogiston rejoined with the calx to restore the metal. Note that Stahl's explanation of combustion is opposite from our current understanding. In modern terms, when a metal is heated, it combines with oxygen to form a metal oxide; the metal transforms from its elemental state to a more complex substance. Stahl thought, however, that a metal loses phlogiston (the 'inflammable principle') during combustion, forming a *less* complex substance, the calx which was thought to be the true elemental substance. Stahl also applied phlogiston to nonmetal combustion. Unlike the reversible nature of metal combustion, however, burnt animal and vegetable substances were irrecoverable.

According to Stahl, air was not involved as a chemical participant in this reaction. Instead, air acted physically as a medium which carried away phlogiston as the object metal burned. This explained why air was important for combustion. While air was not as an element involved in the chemical transformation itself, it contained and transported the liberated phlogiston. When the air became saturated with phlogiston, becoming 'phlogisticated air,' combustion ceased. This explained why fires in enclosed containers would eventually extinguish. Because all combustion would eventually cease, phlogiston had to be removed from the air and Stahl argued that plants absorbed phlogiston. Since animals ate plants, they too contained phlogiston. This explained why plants, like wood, and animals were combustible – they were high in phlogiston. Phlogiston was not just a chemical principle, but one that could be fruitfully applied to explain other phenomena. It was a link between the animal, plant, and mineral kingdoms.

Phlogiston as an explanatory principle was a viable part of 18th century chemical practice. Phlogiston was successful because in many ways it worked. Chemists used the theory in generating new experiments and producing new chemical knowledge. For example, Stahl used phlogiston to explain acidity, chemical reactivity, and composition. As with all theories, some data didn't fit easily. For instance, when an animal or plant substance burned, the remains weighed less than at the start. This made sense given that phlogiston was 'lost' from the starting substance. When a metal burned, however, the resulting calx weighed *more* than the metal. If metal lost phlogiston to become a calx, why would it weigh more? Shouldn't it weigh less as in the organic case? What we may see as an inconsistency hardly worried Stahl and others. Stahl believed that an element such as phlogiston could only be known from its effects in the world. It could not be isolated or bottled. Because he didn't conceive of the principle in a physical way, he was not worried about the weight imbalance. Furthermore, some chemists weren't even sure about the weight change problem itself, given that their instruments and techniques were quite imprecise.

The idea that phlogiston could not be massed or measured may appear silly. But at this time other things in nature, such as light and heat, were also classified as "subtle fluids" that could not be massed. Even today, the primary evidence for the existence of dark matter is based on mathematics and indirect lines of evidence.

Note how phlogiston theory not only explained much about the natural world, but that it also guided thinking and research. Many people wrongly think that theories are merely unsubstantiated guesses. Scientific theories play two essential roles. They explain phenomena and provide a framework for research.

1. Theories often encompass many natural phenomena. Thus, at times some data does not appear to fit what the theory predicts. Why might holding on to a theory in the face of contrary evidence be the prudent choice?

However, as the 18th century wore on and chemists began to think of elements, substances, and reactions as material, the weight gain problem could no longer be ignored. Some tried to explain away the contradiction and save phlogiston by claiming that phlogiston had *negative* weight. A metal would thus 'lose' negative weight as phlogiston burned away, leaving a heavier product. Some attempted to change phlogiston theory itself to account for the difference. Hermann Boerhaave (1668-1738), one of the most famous chemists at the time, argued that air might play a more important role in reactions than Stahl or others thought. He also thought that fire was a substance made up of particles. These particles entered into other substances during combustion, accounting for the weight gain. These *ad hoc* hypotheses revealed the subtle cracks in phlogiston's foundation. Indeed, Boerhaave's new role for air and the materiality of fire would be important parts of the new framework for chemistry. Despite the problems, chemists happily used phlogiston to explain the phenomena they observed in the laboratory. It would take a new emphasis on the importance of materiality – especially mass – and the accompanying precise instruments for phlogiston to finally be discarded.

2. History provides many examples of scientists refusing to give up on a theory despite well-recognized problems. In many cases the difficulty is resolved in favor of the theory and their confidence was justified and turned out to be correct (for example, see the astronomy story “Accounting for Anomaly”). Given that good reasons often exist to hold onto a theory even when some data may not fit, what factors might eventually result in scientists eventually questioning and replacing a theory?

As phlogiston rose to prominence in the 18th century, chemists had begun to investigate air. As a holdover from Aristotle's elements (earth, fire, water, and air), air was rather uninteresting to most chemists at this time. They had no conception of different types of gases that existed in air. Different 'kinds' of air were simply different 'impurities' dissolved in the standard air element. This is how air could be important for chemical reactions — it acted as a mechanism for transfer, something that could move substances in and out of reactions (recall how air was thought to facilitate the transfer of phlogiston during combustion). Many chemists saw air as potentially bothersome, for it could cause dangerous explosions. Some chemists even cut holes in their apparatus in order to prevent this possibility.

In addition, unlike solids and liquids which chemists could work with rather easily, working with air was problematic. Since chemists couldn't isolate components of air, it was hard to determine their properties. Stephen Hales (1677-1761) addressed this problem. Hales was interested in how much air was released when substances were heated. Hales invented a new instrument, the pneumatic trough, to aid him in his studies. The pneumatic trough bubbled air through water, collecting the air over water in an enclosed vessel. Hales thought he was cleaning the 'impurities' out of air by bubbling it through water. The pneumatic trough allowed him to isolate and test particular airs from various sources. The pneumatic trough would eventually become a standard instrument in chemical laboratories.

Hales' work was particularly well received in Scotland, the home of Joseph Black (1728-1799). For an MD thesis Black wanted to cure 'bladder stones.' One cure was to dissolve these stones by drinking an alkali. Most alkalis, though, were very poisonous. Black sought a gentler alkali that would be effective without killing the patient. One candidate alkali was called magnesia alba. During his experiments, Black noticed that heating magnesia alba produced an air which could be collected in a pneumatic trough. This air acted differently than 'ordinary' atmospheric air: bubbling it through limewater made the limewater milky. Black concluded that there were two types of airs: ordinary atmospheric air and this new 'fixed air,' named in 1754. He called this newly isolated air 'fixed air' because it seemed to be 'fixed' in solids, only to be released upon heating. Fixed air inhibited combustion and was detrimental to life. At first, most contemporaries saw this work as a minor addition to work on alkalis. Eventually, however, chemists realized that air, as Boerhaave suggested, could interact with substances chemically. That is, air was no longer thought to be merely a physical medium of transfer.

Now that the 'pneumatic chemists' realized that different 'types' of air existed, they began to isolate and identify others. Henry Cavendish (1731-1810) discovered what he called 'inflammable air.' This air was produced when metals such as zinc, iron, or tin were dissolved in strong acids. Because the acid could be varied and still produce the same air, Cavendish argued that it must come directly from the metals. Given that metals were a combination of calx and phlogiston, and that this new air was highly flammable, Cavendish argued that this 'inflammable' air was actually pure phlogiston.

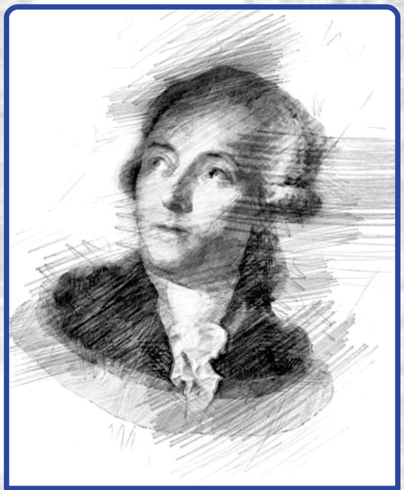
!

Note again how scientific knowledge is both a product and impacts practice. That is, determining that air was more than a mere physical medium impacted future research. Scientific knowledge is a product, but also guides thinking and research.

A prodigious 18th century investigator of gases was Joseph Priestley (1733-1804). Priestley isolated and investigated more gases than any other chemist in this period. Because he used mercury in the pneumatic trough instead of water, he was able to isolate water soluble gases. Neighbor to a brewery and observant of the role of fixed air in fermentation, Priestley began his work on gases in 1770. Like Cavendish and other contemporaries, Priestley strongly accepted the phlogiston theory. He would continue to do so even after many of his colleagues abandoned phlogiston for the new oxygen theory. Priestley's most important work began in 1774 when he heated the “red precipitate” (what we today know is mercuric oxide). Using an instrument that measured air purity, Priestley found that this new gas was very pure and greatly supported combustion and life. Priestley called it “dephlogisticated air.” Though Priestley and other advocates of the phlogiston theory sought to assimilate this new gas into the theory, it would eventually be crucial to a new explanation of combustion and also a new system of chemistry.

3. Some people wrongly think that data tell scientists what to think and that science requires little creativity. How does the work of scientists in this story illustrate that rather than data telling scientists what to think, scientists create ideas to account for or make sense of data?

The architect of this new system and initiator of the so-called “Chemical Revolution” was Antoine Laurent Lavoisier (1743-1794). Trained at the famous Collège Mazarin under the chemist Guillaume-Francois Rouelle (1703-1770), Lavoisier was exposed both to the teachings of Newton as well as Stahl's phlogiston theory. He was also taught to appreciate the importance of quantitative analysis, and as a result Lavoisier was obsessed with precision in his investigations. This would be crucial for future work on combustion. Lavoisier also learned that substances, even air, may be 'fixed' in other substances, and released or captured due to various chemical reactions. One of Lavoisier's early research projects was on gypsum, or plaster of Paris. Lavoisier found that gypsum contained fixed water, making it soft and moldable. This water was released upon heating, explaining why the plaster hardened. Lavoisier's work on gypsum benefited from his concern with the importance of mass changes in substances during reactions, changes which he measured using very precise balances. By 1766, Lavoisier had made his name in the world of French intellectuals. While having the resources to devote his time to scientific pursuits, in 1768 he invested in the Ferme Générale, a private agency of tax collectors, to support his research. He used much of the wealth he gained to purchase very unique and complex instruments. This made repeating his experiments difficult for his contemporaries. For instance, he didn't use a pneumatic trough, but rather a sophisticated gasometer. His textbook, *An Elementary Treatise on Chemistry*, would include a detailed section on chemical apparatus that would be important for future chemical laboratories.



Antoine Laurent Lavoisier

In 1772 Lavoisier read an essay on phlogiston by Louis-Bernard Guyton de Morveau (1737-1816). Morveau showed that metals gained weight when heated. Using the phlogiston theory, Morveau argued that the phlogiston “buoyed” up the metals, and thus made the metal weigh more after it was released. Lavoisier, sensitive to the materiality of substances and to weight changes in reactions, thought this explanation was ridiculous. Lavoisier was not satisfied by the *ad hoc* explanations for the weight discrepancy. Lavoisier thought of a new explanation: air was fixed during combustion, accounting for the increase in weight. Lavoisier set out to test this idea, starting work on combustion and calcinations.

Late in 1772, after completing experiments on the combustion of diamond, Lavoisier began work on the combustion of sulfur and phosphorous. Burning phosphorous produced “acid spirit of phosphorous” (phosphoric acid) and burning sulfur produced “vitriolic acid” (sulfuric acid). Lavoisier realized that the combustion of phosphorous and sulfur was like the combustion of metals, in which a 'calx' was produced. In both cases the end product was produced by the combination, or fixing, of air with the starting material. Lavoisier was very concerned with the priority of his ideas, so he deposited a sealed letter with these results into the archives of the Academy of Sciences in Paris in October 1772.

Moving on to metals like tin and lead, Lavoisier showed through careful and precise quantitative analysis that the mass gain involved in heating metals was not due to loss of negative phlogiston or the penetration of fire particles in the metals, but rather the combination of those metals with air. Lavoisier wasn't sure, yet, which air it combined with: fixed air, ordinary atmospheric air, or some other part. Lavoisier was unfamiliar with much of the work in pneumatic chemistry detailed above, and spent all of 1773 learning about and repeating the experiments of chemists like Black and Priestley. After this work, Lavoisier thought that the air involved in combustion was Black's “fixed air.” His thinking was based on his observation that the charcoal reduction of calx releases a large quantity of fixed air. Because the combustion reaction was reversible, he reasoned that when a metal is burned, fixed air combines with it to form calx.

Lavoisier eventually moved away from fixed air, due in part to two events. First, Pierre Bayen showed that the calx of mercury [HgO] reduced back into the metal without the aid of charcoal. This was devastating to phlogiston theory, argued Bayen, because without the charcoal there was no source for phlogiston to return to the metal. Second, and more importantly, the air produced during this reaction was not fixed air. Lavoisier got this hint when he received a visit from Joseph Priestley in 1774. Priestley told Lavoisier of his work on the 'red precipitate' (again, HgO) and the curious 'pure' gas he isolated from that heating. Repeating Priestley's experiments on red precipitate in 1775, Lavoisier confirmed Priestley's findings, emphasizing that this released gas was not fixed air but a new gas. Lavoisier then made the connection: perhaps it was this gas that was 'fixed' during combustion, and released as fixed air when combined with charcoal in reduction. To explain the role of atmospheric air in combustion reactions, Lavoisier argued that common air was actually a mixture of two types of airs – one, the purer part that supported respiration and combustion and fixed with metals during burning; and an 'impure' part, which he called azote (eventually renamed nitrogen), that extinguished life and burning.

Priestley pointed out to Lavoisier in 1775 that this new 'pure' air was a *component* of atmospheric air, not simply ordinary air 'purified.' Lavoisier in 1776 and 1777 continued investigating this pure air which he called 'eminently respirable air.' He confirmed that it combined with charcoal during reduction of calxes to form Black's fixed air [what we know as carbon dioxide]. He also determined that this respirable air combined with carbon in organisms, releasing fixed air as well as animal heat. In 1778 he wrote: “The principle which unites with metals during calcinations, which increases their weight and which is a constituent part of the calx is: nothing else than the healthiest and purest part of air, which after entering into combination with a metal, [can be] set free again; and emerge in an eminently respirable condition, more suited than atmospheric air to support ignition and combustion.”

Lavoisier then made the connection back to his original sulfur and phosphorous experiments, arguing that since the products of these combustions were acids, this respirable air was a key part of all acids. In November 1779 he renamed this air “oxygen,” which means “to form an acid.” Note that oxygen was not just important for combustion, but represented a 'principle of acidity' for Lavoisier. When a nonmetal such as phosphorous or sulfur burned, the oxygen combined with the nonmetal, producing an acid product. The 'acidifying' oxygen became the new 'universal acid,' replacing the earlier universal acids of the Stahlians and phlogistonists. While oxygen's central place for acidity would eventually be overthrown, it was important to Lavoisier in that it explained how one could synthesize an acid (burn a nonmetal) and explained their varying reactivities. Lavoisier's concern with acids is one way that his work was dependent on continuity with prior traditions of analytical and pharmaceutical chemistry, rather than only complete discontinuity with prior beliefs.

4. Science is often conveyed as a largely solitary undertaking by individuals possessing unassailable intelligence and foresight. List ways that this story illustrates that science is a social endeavor by individuals struggling both together and at times alone to make sense of the natural world.

Despite the oxygen breakthrough, Lavoisier did not yet attack the phlogiston theory directly. His oxygen theory couldn't explain two problems which phlogiston could: first, phlogiston theory could explain why metals released inflammable air when dissolved in acids. Second, Lavoisier couldn't explain why burning inflammable air didn't produce an acid. Only in time would he and others construct an understanding of water that would solve these two problems. Thirteen years earlier in 1766, Cavendish knew that the 'inflammable air' he discovered burned, but he didn't know what the combustion product was. In 1781, however, Priestley noted that dew formed on the inside of a vessel in which inflammable air burned. Cavendish then replicated these experiments, collected this dew, and identified it as water. Cavendish, still a phlogistonist, explained this reaction as a combination of 'pure phlogiston' with 'dephlogisticated air' releasing water as a byproduct.

Lavoisier, hearing of these experiments in 1783, conducted his own. He burned inflammable air and oxygen in an enclosed vessel, obtaining water. He also decomposed steam over red-hot iron back into inflammable air and oxygen. Due to these experiments, Lavoisier reasoned that the reaction was a combination of this inflammable air with oxygen. Eventually, 'inflammable air' was renamed “hydrogen,” meaning “to form water.” While others thought that water was a simple substance, Lavoisier's work indicated that water was a compound substance of hydrogen and oxygen. Lavoisier could then explain why hydrogen was released during the dissolution of metals in acid: the hydrogen came from the water in which the reaction occurred.

Armed with these solutions, Lavoisier attacked phlogiston theory more directly. He wrote a paper in 1783, published in 1786, attacking the weak points of phlogiston theory. He argued that understanding combustion as a combination with oxygen which produced either a calx (for metals) or an acid (for non-metals) helped explain the relevant facts (including the mass gain problem) that phlogiston failed to account for. Lavoisier memorably slammed the shapeshifting nature of phlogiston when he wrote:

> All these reflections confirm what I have advanced, what I set out to prove and what I am going to repeat again. Chemists have made phlogiston a vague principle, which is not strictly defined and which consequently fits all the explanations demanded of it. Sometimes it has weight, sometimes it has not; sometimes it is

> free fire, sometimes it is fire combined with an earth; sometimes it passes through the pores of vessels, sometimes they are impenetrable to it. It explains at once causticity and non-causticity, transparency and opacity, color and the absence of colors. It is a veritable Proteus that changes its form every instant.

The then emerging effort to change how substances were named would result in a new nomenclature that would bring order and, importantly for Lavoisier, an anti-phlogistic rationale to chemical names. Old names for chemicals were confusing, coming from Latin and Greek and having no underlying system or rules for their formation. Names could come from properties of the substance, its origins, or just historical tradition. The names simply had to be memorized. Guyton de Morveau, who quickly turned to Lavoisier's side, wrote a paper in 1782 suggesting a new system of nomenclature. Lavoisier and Morveau, along with two other allies, Claude Louis Berthollet (1748-1822) and A. F. De Fourcroy (1755-1809), formulated this new system. The nomenclature, explained in *Méthode de nomenclature chimique*, 1787, held that names for simple substances should be stable and should describe their properties, and compound substances' names should indicate what simple substances compose them. Much like the Linnaean classification system for organisms, chemical names would be binary, mirroring the genus/species pairing. Finally, the names had to be 'euphonious' with French, ensuring a central place for French chemists in the new chemical world. This system spread quickly, further entrenching Lavoisier's new revolution. Phlogistonists rejected the new system of nomenclature for this reason, as the use of the system required adherence to the oxygen theory and Lavoisier's chemistry. The revolution was not only one of new instruments and techniques but also of new language.

Despite Lavoisier's success and many French chemists' acceptance of the oxygen theory, Priestley and some other chemists still held fast to phlogiston. To further entrench his chemistry, Lavoisier authored a new chemical textbook aimed at reinforcing the principles he had created. The textbook, *An Elementary Treatise on Chemistry*, published in 1789, would be a classic for many decades to come. Included in the book was a table of "simple substances belonging to all the elements of nature, which may be considered the elements of bodies." This was an early, but provisional, list of chemical elements. As further chemical investigations isolated more simple substances, previously "simple" substances were determined to actually be compounds. Thus, the list of elements would change. Lavoisier thus defined the element pragmatically and operationally. Lavoisier included caloric and light on this element table. Lavoisier also formed a new chemical journal, the *Annales de chimie*, in April 1789, with a protégé, Pierre Adet (1763-1834). Other chemical journals at the time, such as the *Journal de physique*, were sympathetic to phlogiston theory. This new journal would be a forum for Lavoisier's new views on oxygen.

!

Priestley isolated what we now know is oxygen gas, but interpreted this as supporting phlogiston theory. Lavoisier, on the other hand, interpreted this newly isolated gas as a convincing refutation of phlogiston theory. Again, the meaning of data is often not clear at the time, and only "appears obvious" in time after the controversy has been settled and the new way of thinking becomes well-established.

Though Lavoisier's chemistry would persevere, his life would end in tragedy as a victim of the Reign of Terror of the French Revolution. Because of his connections to tax collecting and thus the *Ancien Régime*, Lavoisier was guillotined on May 8, 1794. Despite Lavoisier's tragic end, the oxygen theory, his textbook, and the *Annales* would promote further growth in chemistry during the 19th century. Oxygen replaced phlogiston as the unifying chemical concept, one that would be fruitful both as an explanatory resource and as a stimulant of further scientific research.

The Problem of Combustion: Phlogiston and Explanation
written by Melinda Baldwin and Michael P. Clough

Partial support for this work was provided by the National Science Foundation's Course, Curriculum, and Laboratory Improvement (CCLI) program under Award No. 0618446. Project Principal Investigator: Michael P. Clough. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.