The Reality of Phlogiston in Great Britain

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Abstract: Mi Gyung Kim (2008) has challenged the historiographical assumption that phlogiston was the paradigmatic concept in eighteenth century chemistry. Her analysis of the operational, theoretical, and philosophical identities of phlogiston demonstrates how Stahlian phlogiston was appropriated into the burgeoning field of affinity theory. However, this new French conception of phlogiston was destabilized by the introduction of Boerhaave’s thermometrics. By extending this story through 1790, I will show that British pneumatic chemists integrated new understandings of heat with an affinity based operational definition of phlogiston and thereby stabilized the concept. What resulted was a new and very different phlogiston.

Keywords: Eighteenth-century chemistry, Chemical Revolution, historical ontology, Richard Kirwan, phlogiston, fire.

1. Introduction
Phlogiston has long been regarded as the paradigmatic concept in eighteenth-century chemistry. In his classic work, A Short History of Chemistry (1939), J. R. Partington attributed the development of phlogiston to the German metallurgical chemists Johann Joachim Becher (1635-1682) and Georg Ernst Stahl (1660-1734). This phlogiston was analogous to Aristotle’s elemental fire in its roles in creating heat, light, and fire. Though conceptions of phlogiston changed over the course of the century, it could generally be defined operationally as that which “escapes from burning bodies in a rapid whirling motion, and is contained in all combustible bodies and also in metals” (Kuhn 1962, p. 87). The roasting or calcination of metals was explained as the separation of phlogiston from the metallic calx. By 1720, French chemist Étienne-François Geoffroy (1672-1731) had appropriated phlogiston, identifying it with Homberg’s sulfurous principle (Kim 2008, pp. 38-9) and this French conception of phlogiston was promoted in the 1740s by the influential professors of the Jardin du Roi, Guillaume-François Rouelle (1703-1770) and Pierre Joseph Macquer (1718-1784), who subsequently taught two genera-
tions of French apothecaries, doctors, and chemists. Thomas Kuhn (1962) identified Stahl's phlogiston as the central, paradigmatic concept of chemistry until 1775, due to its role in explaining so many chemical processes. However, he also identified anomalies in the phlogiston paradigm, which eventually caused the Chemical Revolution in the 1770s and 1780s. Antoine Lavoisier's (1743-1794) crucial contribution in this story was to notice that metal actually gains weight during calcination. With his supposedly novel emphasis on gravimetrics, he recognized the absurdity of calcined metals gaining weight while emitting phlogiston. While Guyton de Morveau (1737-1816) suggested that phlogiston somehow had negative weight, Lavoisier argued that something must be absorbed during calcination to explain weight gain. He thus replaced phlogiston with oxygen as the element of calcination and developed parallel explanations for combustion and respiration. This narrative for the Chemical Revolution was popularized by Kuhn but had been adopted from earlier works including Partington's *Historical Studies of the Phlogiston Theory* (1937-1939) and J. B. Conant's *The Overthrow of the Phlogiston Theory* (1950). It has become the standard narrative for general surveys of the history of science and for more detailed studies on the history of chemistry and on the process of scientific change. However, in recent years, historians have begun to question this narrative and the paradigmatic role of phlogiston in the eighteenth century.

In her 2008 *Hyle* article, 'The ‘Instrumental’ Reality of Phlogiston', Mi Gyung Kim argues that phlogiston “did not provide a comprehensive theoretical framework for pre-Lavoisian chemistry. It was a relatively ordinary substance involved in a multitude of chemical actions” (Kim 2008, p. 30; see also Kim 2011). In place of a phlogiston-centered theory or research program she says, “French chemists worked within a well-defined research field of salts (akin to Kuhn’s notion of normal science) equipped with a clear, methodical representation of their operational knowledge” (Kim 2008, p. 30). Phlogiston was a particularly useful chemical substance in that it was used in a variety of chemical processes, but it was ultimately only one substance amongst many in the new chemical taxonomies of Étienne-François Geoffroy and his successors. While denying its central role in guiding eighteenth-century chemistry, Kim does maintain that phlogiston “was as ‘real’ as any other chemical substance, even if chemists could not exactly put it in a bottle and label it” (*ibid.*, p. 31). Phlogiston was not just a hypothetical place holder in chemical equations. Having argued that phlogiston was neither a paradigmatic concept nor an imaginary substance, she studies how phlogiston was used by eighteenth-century French chemists.

Kim identifies three primary roles for phlogiston in eighteenth-century chemistry. She first acknowledges phlogiston’s philosophical or ontological identification with the sulphur principle. Wilhelm Homberg (1652-1715),
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one of the leading chemists at the Parisian Academie Royale des Sciences, drew from the work of fellow Academician Samuel Cottereau Du Clos (1598-1685) and Robert Boyle (1627-1691), in identifying the sulphur principle as "the active principle in all bodies" and tried to use a Tschirnhaus burning glass to isolate and harness this pure fire, which he regarded as a corpuscular matter of heat and light (ibid., p. 32). Geoffroy fused Homberg's work on sulphur with Stahl's similar active sulphur conception of phlogiston. Geoffroy also used the burning glass to show that "sulphur could restore metallicity to imperfect metals such as iron, copper, tin and lead" (ibid., p. 34) after they had been reduced to a calx and that this process was reversible. Phlogiston's second identity, according to Kim, was derived from this operational role in analysis and synthesis of metals. For Geoffroy, phlogiston was a "concrete oily substance separated out in chemical analysis" (ibid., p. 34). Louis Lemery (1677-1743) developed a third theoretical identity of phlogiston as the "first and most powerful solvent", which at times "failed to dissolve solid bodies and became imprisoned in them" as fixed fire (ibid., p. 35). According to Kim, Lemery tied together the theoretical, ontological, and operational identities of phlogiston into a coherent and stable system that became the standard interpretation of phlogiston in French chemistry for the next fifty years.

Kim says that this conceptual system of elemental fire was upset by the thermometric experiments of Herman Boerhaave (1668-1738). For Boerhaave, fire was the instrument of expansion and analysis and was not a corpuscular element. Phlogiston thus had no ontological reference in Boerhaave's system of chemistry. While pedagogues like Rouelle and Macquer tried to blend Boerhaave's thermometrics with the French-Stahlian phlogiston theory, the results were, according to Kim, "a long list of inchoate meanings that destabilized [phlogiston's] identity" (ibid., p. 44). She concludes, "By the 1760s, phlogiston had become primarily a textual entity in France, while the British chemists tried to reinvent its operational identity through pneumatic chemistry. Its discursive identity consisted of an ensemble of its past identities without close association with the ongoing investigation" (ibid., p. 46).

In a follow up article in Foundations of Chemistry entitled, "From Phlogiston to Caloric: Chemical Ontologies," (2011) Kim juxtaposes the conceptual matrix of phlogiston with Lavoisier’s new chemical ontology of caloric:

The interlocking identities of phlogiston depended on the distillation method, the affinity table, and a metaphysical commitment to the reigning philosophical system; those of oxygen and caloric required metric measurements, algebraic representation and an alliance with the emergent philosophical project of epistemology. [Kim 2011, p. 204]

Kim explains, “Instead of identifying fire with phlogiston as his teachers did, [Lavoisier] sought to present a rational discourse of fire based on thermo-
metric and pyrometric measurements, following Hermann Boerhaave’s cue with more refined instruments” (ibid., p. 209). Abandoning Aristotelian metaphysical fire, Lavoisier argued for a chemical ontology of empirically defined substances resultant from reduction by decomposition. Using his measurements on the weight, volume, and heat of substances, Lavoisier developed an algebraic language for chemistry. This algebra served as a new analytical tool, replacing the affinity tables, which had grown increasingly complex in their attempts to represent the variables of heat and volume that complicated affinity relations. Kim thus argues for an operational, theoretical, and ontological dichotomy between the “laboratory reality” ofphlogiston and that of caloric.

By contrast, this paper will argue that from the 1750s through the 1780s, British chemists conceptualized a new phlogiston, empirically produced through decomposition reactions and submitted to metric measurement and algebraically controlled chemical reactions. Frederic Holmes has argued that Joseph Priestley’s (1733-1804) conception of phlogiston broke from that of Stahl and the French Stahlians and thus represented a “revolutionary movement in physics and chemistry”. Holmes claims, “The confrontation between Priestley and Lavoisier was less a challenge launched by a theoretical innovator against a defender of the ‘reigning’ theory than a competition between two new research programs” (Holmes 2000, p. 737). Seymour Mauskopf extended this line of analysis through the end of the 1780s with a study of Richard Kirwan’s (1733-1812) phlogiston (Mauskopf 2002). British phlogiston was stripped of its ontological associations with both the sulfur principle and corpuscular heat and identified instead as inflammable air. Using the chemical and thermal theories of the Scottish professors William Cullen (1710-1790) and Joseph Black (1728-1799), Kirwan developed this new ontological identity of phlogiston as inflammable air, which accommodated Boerhaave’s thermometric theories and a new algebraic understanding of affinity reactions. During the 1780s, phlogiston occupied the same laboratory reality and often the same lab bench as oxygen. The demise of this new British phlogiston resulted from a shift in understanding of the ontology of pneumatic chemistry from transmutation to chemical combination.

2. Inflammable Air
Parallel to the development of affinity-based salt analysis in France was the emergence of pneumatic chemistry in Britain. This focus on pneumatics began when Stephen Hales (1727) and Joseph Black (1756) discovered fixed air, so called because it was often found fixed inside of calcareous earths. Each of these earths (limestone, marle, chalk, etc.) emitted the same type of air when
exposed to an acid. The early work of Hales and Black sparked further investigation into the properties of air and the discovery of other species such as vitriolic acid air, vegetable acid air, nitrous air, and eventually dephlogisticated air, with each of these being differentiated from common air. Like fixed air, most of these species were produced during the reaction between acids and an earth or metal. Joseph Priestley and others conducted systematic studies of the species of air to determine their specific gravities, their ability to support life, their interactions with water and heat and their sensible properties such as taste, color, and smell (Priestley 1786, vol. 3). Each air’s purity was also measured based on the air’s ability to support respiration and the burning of a flame. An aerial-phlogiston spectrum was developed ranging from dephlogisticated air, through common air and fixed air, and up to phlogisticated air, and nitrous air (Priestley 1775, p. 392). During the 1780s, inflammable air was identified as pure phlogiston in its aerial form. Species of air could be transmuted by adding phlogiston as Priestley demonstrated in converting alkaline air into inflammable air through the addition of heat (Priestley 1786, pp. 197-202). The ontological identification of inflammable air as aeriform phlogiston provided novel explanations for combustion, weight gain during calcinations, and the decomposition of water.

Though he published relatively little in comparison to some of his peers, William Cullen was one of the most influential figures in eighteenth-century British chemistry and an early contributor to phlogiston theory and pneumatic studies. As a professor of chemistry at the University of Glasgow from 1747-1755 and then professor of medicine at the University of Edinburgh until 1790, Cullen taught a generation of British students his chemical theories, which centered on elective attraction. Cullen’s theories were further developed and disseminated by several of his students including Joseph Black and George Fordyce (1736-1802) who themselves became professors.

Georgette Taylor has recently analyzed a set of lecture notes written by Will Falconer (1732-1769) in 1765 (Taylor 2006, pp. 496-8). In these lectures, Cullen proposed a novel, gas-based identity for phlogiston. He said that phlogiston was not a simple, indivisible element but rather a chemical compound composed of an acid and mephitic air. Cullen based this theory on the empirical observation that any object when inflamed releases a noxious/mephitic form of air that does not support animal life and that the remaining ash or calx is acidic. Noting that phlogiston had never been isolated, Cullen concluded that phlogiston’s constituent mephitic air and acid did not have a high enough affinity to combine with each other unaided, but rather joined only when a third substance such as a metal or earth was introduced. While phlogiston remained the principle responsible for combustion, it was now a compound. Cullen said, “To me indeed Inflammation seems to depend on the decomposition of this Compound by the Common Air, which attracts
the Mephitic Air" (ibid., p. 498). We might represent Cullen’s ideas schematically as follows:

:\[
\text{Inflammable body} = \text{metal/earth} + (\text{acid} + \text{mephitic air}) \\
\text{Inflammable body} + \text{common air} \rightarrow (\text{metal/earth} + \text{acid}) + (\text{common air} + \text{mephitic air})
\]

For Cullen then, combustion was a dissociative reaction in which common air drew away the mephitic air from the inflammable body by virtue of having a higher affinity. Despite the wide ranging impact of Cullen’s chemical theories, neither his definition of phlogiston nor this particular theory of combustion seem to have been widely adopted. However, it does mark an early example of a British operational definition of phlogiston, which was stripped of the French-Stahlians’ ontological identification of phlogiston as sulfur.

An alternative ontological identity of phlogiston was presented by Henry Cavendish (1731-1810) in a paper presented to the Royal Society in 1766. Cavendish suggested that inflammable air was the aerial form of phlogiston (Cavendish 1766). He noted that certain metals, including zinc, tin, and iron, release an inflammable air when exposed to vitriolic acid. He concluded that as the metals dissolved in the acid, the calx combined with the acid and released the phlogiston as a gas (ibid., p. 144-6). Here, Cavendish drew on the analogy of Joseph Black’s fixed air. Just as acids released fixed air from calcareous earths, so inflammable air could be released from metals. Cavendish’s papers on ‘Factitious Airs’ presented to the Royal Society were so well received that he was awarded the Copley medal, the society’s highest honor. However, Cavendish backed off this identification of inflammable air with phlogiston. By 1784, he had modified his claim to say that inflammable air was actually “water united to phlogiston” (Cavendish, 1784a, p. 137). As we will see, Cavendish would later explicitly deny his original claim that phlogiston was inflammable air.

In 1780, an English translation of a book by Carl Wilhelm Scheele (1742-1786) was printed as Chemical Experiments and Observations on Air and Fire with notes by Richard Kirwan. In these notes, Kirwan restated Cavendish’s 1766 ontological claim that the purest form of phlogiston is “that of inflammable air from metals” (Scheele 1780, pp. 232-3).\(^1\) In 1782, he repeated this identification in a paper presented to the Royal Society entitled ‘Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances’ (Kirwan 1782).\(^3\) Here, he said that phlogiston “can never be produced in a concrete state, single and uncombined with other substances; for the instant that it is disengaged from them, it appears in a fluid and elastic form, and is then commonly called inflammable air” (ibid., pp. 195-6). Arguing that like effects prove like causes, Kirwan asserted that the fixation of inflammable air in metals as phlogiston
was an analogous chemical process to the trapping of fixed air in calcareous earth. This argument by analogy provided an answer to critics’ calls for samples of solid phlogiston. Although fixed phlogiston had never been isolated, neither had the solid state of fixed air. Kirwan further extended this conception of phlogiston with the operational and theoretical claim that all substances that contain phlogiston will produce inflammable air when subjected to the proper chemical analysis. Inflammable air could also be used as a source of phlogiston to restore malleability and shininess to metallic calxes and would combine with vitriolic acid to form sulphur (ibid., p. 199). He thus combined Cavendish’s rhetorical strategy of argument by analogy, with the operational arguments from analysis and synthesis to prove the ontological identification between phlogiston and inflammable air (Mauskopf 2002).

In pneumatic chemistry, phlogiston made the transition from metaphysical principle to empirically defined, chemically irreducible element. By 1783, inflammable air was a chemical substance with a stable, broadly accepted operational identity. Kirwan, Cavendish, and Lavoisier would all agree that it was the product of a reaction between acids and metals, identifiable by its low specific gravity and its explosiveness. However, those three men held three different ontological identities for inflammable air. Kirwan thought it was a chemical simple, the aerial form of phlogiston. Cavendish thought it was a compound of water and phlogiston, and Lavoisier thought it was a compound of hydrogen and caloric. The three men had even more divergent understandings of inflammable air’s role in chemical theory. Kirwan’s theoretical identification that inflammable air was involved in the production of fixed air would ultimately create severe strain on his conception of phlogiston. Cavendish pointed to Kirwan’s inability to produce inflammable air through the analysis of fixed air as a refutation of Kirwan’s entire theory of phlogiston (Cavendish 1784b). The two men would debate the issue for several years, while the argument would eventually be adopted by Lavoisier as the key point of weakness in Kirwan’s chemistry.

3. Heat

During the eighteenth century, there were two primary explanations for heat. Francis Bacon (1561-1626), Robert Boyle (1627-1691), and Isaac Newton (1748-1826) had advocated a mechanical theory of heat predicated on the idea that the vibrations of small particles create heat. Stahl along with the French pedagogues at the Jardin du Roi taught that heat was caused by the imponderable fluid phlogiston. Adding phlogiston to a substance increased that substance’s total heat. The fluid theory of heat was particularly useful for
explaining evaporation, fluidity, expansion, heat capacity, and radiation while the vibration theory was thought to be better at explaining ignition.

Cullen's theory combined the mechanical and fluid explanations of heat. He rejected Boerhaave's definition of fire as the instrument of expansion and focused instead on the role of fire in creating heat and light. "Fire consists in certain Oscillatory motions excited in a Subtle Elastic Fluid, present everywhere in Bodies interposed betwixt the particles of them and filling their Pores" (Taylor 2006, p. 489). That is, the mechanical vibration of a Newtonian aether creates heat. This vibrating aether existed in different quantities in different bodies and the quantity of aether determined the amount of heat in that body. Aether could be transmitted between different substances in chemical reactions or new vibrations could be generated through condensation, exhalation, or combustion. Phlogiston entered this theory as the substance which allows for condensation, exhalation, or combustion. Thus, only those substances that contained phlogiston – again for Cullen this was a compound of an acid and mephitic air – could undergo the chemical processes which generated mechanical heat. Cullen thus recognized a mechanical means of creating heat and a chemical means of transmitting it between bodies (ibid., pp. 489-91).

Cullen's student, Joseph Black examined ice to show that a greater volume of heat was required to change the sensible temperature of ice by a degree than was required to change the temperature of the same volume of water by a degree. A student of both Cullen and Black, William Irvine (1743-1787), developed this idea of heat capacity further. He proposed that every chemical substance has a heat capacity which reflects what volume of fluid heat is required to change its sensible temperature. Like Cullen and Black, Irvine was a professor at Glasgow, and he did not publish during his lifetime, but his student, Adair Crawford (1748-1795), published his dissertation on heat in 1779. Drawing heavily on Irvine's theory, Crawford explained that every chemical substance had a unique heat capacity expressible as a ratio compared to a standard. This ratio represented the volume of fluid heat required to change the sensible temperature of a body. Common air was given as the standard with heat capacity 1, while dephlogisticated air had a heat capacity of 4.6. Thus dephlogisticated air would require 4.6 times more fluid heat to change its sensible temperature one degree than would common air. In general the less phlogiston something contained, the higher its heat capacity. Crawford and Kirwan confirmed this correlation in a table of specific heats compiled for Jean Magellan's *Essai sur la Nouvelle Theorie du Feu Elementaire* (Magalhães 1780, p. 177). Their table was widely used and translated, and numbers from this and subsequent experiments during the 1780s were used by Lavoisier and Laplace, John Dalton, Thomas Thompson, and others.
Kim says, “The most innovative aspect of Lavoisier’s algebra for chemical actions consisted in recognizing that all bodies could assume solid, liquid or aeriform states depending on the ratio of the quantities of heat” (Kim 2011, p. 215). However, questions on change of state proved one of the most discussed and useful grounds for employing Irvine’s theories. Irvine, Crawford, and Kirwan held that vapors and gases have higher heat capacities than liquids, which, in turn, have higher heat capacities than solids. The difference in heat capacity of the states of matter also explained the absorption or release of heat during a change of state or a chemical change. Crawford wrote,

Thus cold is produced by the evaporation of water, and heat by the condensation of vapour. Like effects have been observed by the ingenious Dr. Black, in a very great variety of natural phenomena. And as no instance can be shown to the contrary, we may safely conclude, in general, that when a body produces cold in consequence of a change of form, it will produce heat when it returns to its former state. [Crawford 1779, p. 47]

Also, there was a larger amount of heat needed to convert liquid to vapor than there was to convert solid to liquid. If a liquid were vaporized during a chemical reaction, little heat would be given off, because that heat was used in the vaporization. For example, Crawford argued,

In the burning of oil, the phlogiston is separated from its former basis, and combined with the air. The air is converted into fixed and phlogisticated air – the oil into vapour. By this process the capacity of the air for containing heat is diminished, and that of the oil increased. And, therefore, from the first and third Corollaries, it follows, that if, in the inflammation of oil, equal quantities of air and oil were changed in a given time, and if the difference of the capacities of oil and the vapour of oil, were equal to the difference of the capacities of fixed and atmospheric air, the whole heat separated from the air, would be absorbed by the vapour. [Ibid., pp. 104-5]

The British operational identity for phlogiston allowed for the measurements of heat and the algebraic representations of phase change within chemical reactions. Lavoisier’s work on heat in phase changes was only innovative in comparison to the French phlogiston of Macquer and Rouelle.

One of the problems for those that adhered to fluid theories of heat was the heat created by friction or percussion, both mechanical events. Though not recorded in Kirwan’s texts, William Nicholson (1753-1815), a member of the Chapter Coffee House Society with Kirwan, cites Kirwan in his *Introduction to Natural Philosophy* (Nicholson 1787, vol. 1, pp. 121-2) for the theory that friction and percussion diminished the heat capacity of a body thus expelling some of its heat and raising the surrounding temperature.

Kirwan’s comments in Scheele’s *Chemical Observations and Experiments on Air and Fire* reveal another shift in the ontological identity of his phlogiston. According to Scheele, “Heat is composed of that kind of air which
makes up the third part of ordinary air and of an inflammable principle” (Scheele 1780, p. 30). Heat was thus a chemical compound of fire-air and phlogiston. As analytical proof of this identification, Scheele proposed, “This heat it is, which during the distillation of concentrated acid of nitre is decomposed, and resolved into its integrant parts” (ibid., p. 33). Because phlogiston had a greater affinity for nitrous acid than dephlogisticated air, nitrous acid would strip heat of its phlogiston, leaving only dephlogisticated or fire air. Scheele also believed phlogiston was the limiting reagent in the creation of sensible heat. For a fixed amount of feuerluft, the greater the amount of phlogiston added, the greater the yield of radiant or sensible heat that would be produced. If enough phlogiston was added, the product would cease to be heat and would instead be light. Scheele even correlated the visible spectrum with a phlogiston spectrum by asserting that violet light contained the least amount of phlogiston, while red light contained the most. Thus for Scheele, as for Stahl, phlogiston was the inflammable principle and was an ingredient in both heat and light.

Kirwan, in his notes, rejected the idea that heat was a compound of phlogiston and dephlogisticated air or that light was a compound of phlogiston and heat. Kirwan maintained that light was the “rapid impulse of elementary fire” (Heggarty 1978, p. 82) and that fire, heat, and light were all repulsive to phlogiston. When a body was exposed to an amount of fire, heat, or light, a proportional amount of phlogiston would be expelled from that body and the heat capacity of the body increased. Alternatively, adding phlogiston to dephlogisticated air produced fixed air. Because dephlogisticated air had a higher heat capacity than fixed air, the conversion caused the release of heat as a byproduct. Unlike Stahl and the French Stahlians – Rouelle, Macquer, and their students – Kirwan did not identify phlogiston as ontologically equivalent with elemental heat, fire or light.

Kirwan and Crawford also used the concept of heat capacity to explain combustion. Combustion was the rapid expulsion of heat from dephlogisticated air through the addition of phlogiston. The more phlogiston was released from the combustible, the faster it would fuse with dephlogisticated air and the more heat would be released. Similar theories were used to explain heat change in chemical mixtures, changes of state, and respiration. In respiration, dephlogisticated air was inhaled, and, as it circulated through the body with blood, the blood absorbed phlogiston from the body in exchange for heat. The animal then exhaled fixed air.

Kirwan and Crawford’s Irvinist theories were not universally accepted, but they were widely read. In Germany, Lorenz Crel (1744-1816) published both letters and translated articles from Kirwan, while Alessandro Volta (1745-1827) in Italy and Marcellin du Carla-Boniface (1738-1816) in Spain also cited their works (ibid., p. 147-9). Efforts by Lavoisier and Pierre-Simon
Laplace (1749-1827) to disprove much of the Irvinist doctrine were widely read (Bandinelli 2007), but Kirwan commented in a letter to Torbern Bergman (1735-1784) that their work was unoriginal and Josiah Wedgwood (1730-1795) found their instrumental techniques with a calorimeter to be unreliable (Heggarty 1978, pp. 145-6). The Irvinist theory of heat capacity also had greater explanatory power than the solution theory of Lavoisier for electrical and meteorological theory.¹⁵

4. The new phlogiston

Kirwan published his Essay on Phlogiston in 1787. This was by far his longest and most thorough treatment of phlogiston. In an introductory history of chemistry, Kirwan acknowledged the demise of Stahlian phlogiston and then claimed an operational success for his new phlogiston, having transformed “a mere hypothetical substance,” to one that “could be exhibited in an aerial form in as great a degree of purity as any other air” (Kirwan 1787, as quoted in Mauskopf 2002, p. 196). Phlogiston appeared in reactions as a red vapor and had a distinctive smell. Kirwan also addressed the main operational challenge to his phlogiston, the gun barrel experiment. In 1784, Lavoisier had heated a gun barrel to red-heat and passed water through it. He claimed that the water had been decomposed, the oxygen joining the iron to form a calx, while the leftover inflammable air was collected separately. Rather than phlogiston being released during calcification, Lavoisier argued that oxygen was absorbed by the metal. This explained the weight gain during calcification and showed that water could be decomposed into oxygen and hydrogen. Kirwan countered that the water joined with the iron to form a calx, displacing phlogiston which was collected as inflammable air. The two theories predicted operationally identical results (Kirwan 1787, pp. 101-2). He argued,

According to Mr. Lavoisier’s table, water should be decomposed by charcoal at least in a boiling heat, which is full sufficient to communicate as much specific heat to the inflammable part of water as is necessary to its aerial form: yet water has not been decomposed in that manner; whereas water and iron will produce inflammable air in the temperature of the atmosphere, though iron has in his system less affinity to the oxigenous principle than charcoal has to that principle, an evident sign that it is not from the water, but from the iron, that the inflammable air proceeds. [Ibid., p. 27]

Using Lavoisier’s affinity table, Kirwan argued that iron was more likely to have bonded with water than to have decomposed it. For this experiment, the two systems were operationally equivalent and epistemically underdeter-
mined. In appealing to the authority of affinity theory, he claimed chemical theory as a tiebreaker between the two systems.

Kirwan expanded the theoretical role of phlogiston in pneumatic chemistry with his theory that fixed air was the principle of acidity. Like Priestley, he thought that airs exist on a spectrum of phlogiston saturation. Dephlogisticated air could be transmuted into fixed air or even phlogisticated air through the addition of inflammable air or any other source of phlogiston. He used the terms fixed air and aerial acid interchangeably. Because phlogiston was required in the formation of acids and any combustible substance, its presence or absence in the analysis of key chemical substances could serve as a test between the phlogistic system and the “antiphlogistic hypothesis”. He wrote,

The controversy is therefore at present confined to a few points, namely, whether the inflammable principle be found in what are called phlogisticated acids, vegetable acids, fixed air, sulphur, phosphorus, sugar, charcoal, and metals. [Ibid., pp. 6-7]

Kirwan acknowledged that this was a short list of substances to be arguing over, but he reminded the reader of the importance of these substances,

The bodies above-mentioned are the subject of many, and the instruments of almost all chymical operations: without a knowledge of their composition, and a clear perception of their mode of action, it will be impossible to form even an approximation to a solid theory of this science; the daily accumulation of facts will only increase perplexity and confusion, and if any useful discovery be made, it will be the mere result of chance. [Ibid., p. 7]

He thus set for himself the test of proving the presence of phlogiston in all acids, metals, and other combustible substances.

Kirwan used the detonation of niter as one test for the presence of phlogiston in combustibles. Having shown that the phlogiston rich sal ammoniac and volatile ammoniac will both detonate niter while phlogiston deficient substances like metallic calxes will not, he argued by analogy “that other substances which make nitre detonate, contain phlogiston”. Thus, “sulphur, charcoal, and most of the imperfect metals” contain phlogiston (Kirwan 1789, p. 282). He offered several proofs of the phlogiston content of metals: “Metallic calces are reduced to metals, by merely heating them in inflammable air, which they visibly absorb”. He continued, “Inflammable air has been expelled from them in vacuo, by mere heat, at least with the assistance of moisture.” And “Imperfect metallic substances are never restored to their perfect metallic state, but by the substances that contain the inflammable principle” (ibid., p. 169). Drawing on the common knowledge of a century of chemical research, he could provide ample evidence for the presence of phlogiston in combustible substances.
To support his claim on acid formation, Kirwan wrote a section each on the analysis of vitriolic, nitrous, muriatic, saccharine, and phosphoric acids as well as aqua regia. In studying phosphorus and phosphoric acid, he reasoned,

The celebrated Mr. Sage has shown that phosphorus precipitates copper, silver, and other metals from their diluted solutions in their metallic form, and that at the same time it is converted into an acid. This is a full proof that phosphorus contains phlogiston, if metals contain any, when in their metallic form. [Kirwan 1787, pp. 86-7]

Here, Kirwan argued that phosphorus is itself a compound of a radical and phlogiston. In a double affinity reaction, phlogiston will be stripped from phosphorus by various metals to which it has a higher affinity, leaving the phosphorus radical to combine with fixed air displaced from the metallic calxes to form phosphoric acid. Kirwan described similar reactions, which convert phosphoric acid back into phosphorus, “If the phosphoric acid be distilled with zinc it will be converted into phosphorus […] So it will if distilled with tin, which contradicts Mr. Lavoisier’s table of affinities” (ibid., p. 87). Kirwan used such metallic precipitations as evidence of phlogiston content for phosphorus, sulphur, and many of the other acid bases. Kirwan appealed to the widely accepted authority of affinity relations to support phlogiston’s theoretical identity as a constituent of fixed air and thus an acid maker. Having satisfied himself of phlogiston’s presence in all combustibles and acids, Kirwan concluded his Essay reaffirming “that inflammable air and phlogiston are the same substance, just as ice and the vapour of water are called the same substance” (Kirwan 1789, p. 283).

The French Academy received Kirwan’s Essay and quickly commissioned its translation to French. Marie-Anne-Pierrette Paulze Lavoisier (1758-1836) translated the work anonymously. In the translator’s preface, she says of the phlogiston theory and its chief advocate, Kirwan:

Whatever difficulties this theory might present, it could not be expected that the disciples of these justly celebrated men [Stahl, Bergman, and Scheele] would abandon it without resistance. They accordingly employed, at first, every exertion of their abilities in palliating the contradictions; afterwards they insisted on all the experiments which might seem to favor it; and lastly, some among them, while they retained the word Phlogiston, concluded by giving it another signification. This is particularly the case with Mr. Kirwan. Among the philosophers who have not yet adopted the new doctrine, he is certainly one of those who is the most capable of producing uncertainty in the minds of such persons as decide by authority. His acquaintance with every part of natural philosophy; the discoveries which he has enriched the sciences, and even the ingenious modifications he has introduced into the theory of phlogiston; all contribute to give weight to his opinions. If the French chemists, whom he has opposed, should destroy his objections, will they not perhaps have a right
to conclude that there are not any other solid objections to be made? [Ibid., pp. xiv-v]

From this introduction, we see several things. First, Kirwan’s use of the term phlogiston was seen as signifying something different from that of his predecessors. This is confirmed by the Registre of the Académie des Sciences, which noted that the British conception of phlogiston was not that of Stahl and Becher (Académie des Sciences 1787, pp. 255-7). Kirwan’s phlogiston was the elastic aerial phlogiston, and his Irvinist theory of heat made the substance of heat distinct from and repulsive to the physical substance phlogiston. Kirwan was also seen as a leading member of the extended phlogiston camp and depicted as the last barrier to the widespread acceptance of the French chemical doctrine.

The notes in this French translation teased out experimental differences between Kirwan’s phlogiston theory and Lavoisier’s oxygen-caloric theory showing that they were not operationally equivalent. In his section on vitriolic acid, Kirwan claimed sulfur was a compound composed of an unidentified radical, saturated with phlogiston. When this radical was instead saturated with fixed air, the product was fixed vitriolic acid. When the radical was combined with both phlogiston and fixed air, the product was volatile vitriolic acid (Kirwan 1787, p. 28). In his notes on vitriolic acid, Lavoisier finds two flaws in this ontological structure:

The first, that sulphur contains inflammable or hydrogenous gas, which he has not yet proved; and the second, that the union of hydrogen and oxigene forms fixed air, or carbonic acid. [Kirwan 1789, p. 71]

This second objection was the more damming. Fixed air or carbonic acid was one of the first gases isolated from common air and had been studied since Stephen Hales published his Vegetable Staticks in 1727. Lavoisier argued, “It is rigorously proved, on the contrary, that the carbonic acid is nothing else but the result of the dissolution of charcoal in vital air or oxigenous gas. The assertion of Mr. Kirwan therefore included a gratuitous supposition, and an error” (ibid., p. 71).

Kirwan’s conceptualization of phlogiston ultimately failed because of its theoretical identity within pneumatic chemistry. According to his phlogiston theory, by adding phlogiston in the form of inflammable air to dephlogisticated air, the two gases would be transmuted into fixed air. However, under the new French nomenclature this was absurd. As Lavoisier noted, Kirwan could not expect to combine hydrogen with oxygen and get carbon oxide. Kirwan’s inability to experimentally synthesize fixed air from dephlogisticated and inflammable airs or produce inflammable air through the analysis of fixed air undermined his entire theory. While he defended his claims in the
Kirwan’s ontological, operational, and theoretical identities of phlogiston were all founded in pneumatic chemistry. Without a decisive experiment to show the presence of inflammable air in fixed air, Kirwan’s theoretical identity of phlogiston crumbled. Irvinist heat theory was so intertwined with a pneumatic conception of phlogiston, that it too lost coherency and utility. Irvinist combustion, which had been defined as the rapid expulsion of heat from dephlogisticated air through the addition of inflammable air/phlogiston, was no longer tenable (Berthollet 1789). Nor was respiration as the production of fixed air from inflammable and dephlogisticated air (Priestley 1797, p. 77). The algebraic understanding of heat exchange in chemical reactions and even the system of heat capacity, which had been based on volume of phlogiston, lost their meaning. Empirically defined inflammable air/hydrogen was separated from its phlogistic theoretical identities and its operationally measurable relationship with heat. Unable to experimentally support the presence of inflammable air in fixed air, Kirwan abandoned his belief in the phlogistic system.

5. Conclusion

In her article, Mi Gyung Kim identifies a “complex ‘substance identity’” for phlogiston in mid-eighteenth-century France made up of ontological, operational, and theoretical components. Ontologically, phlogiston was the substance of fire and light. Operationally, it was an “oily matter distilled from various substances” (Kim 2008, p. 44). Theoretically, it was a component of salts. “Embedded in the affinity table, phlogiston acquired a secure place in the evolving chemistry of salts, which provided a comprehensive framework of investigation for eighteenth-century French chemistry” (ibid.).

However, this substance identity was destabilized in the 1750s and 1760s by Herman Boerhaave’s thermometrics.

His effort to craft a singular ontology of material fire by fusing the chemical (burning glass) weighing fire and the thermometric weightless fire destabilized
the ontological status of phlogiston as a natural substance. This discursive development, which served to distance phlogiston from its operational roots, created much confusion for the younger generation of chemists who learned chemistry as a public discourse rather than as the apothecary’s material practice. [ibid., p. 46]

In this article, I have shown how British pneumatic chemists developed a novel conceptual matrix of phlogiston in the second half of the century. Kirwan inverted the former ontological identification with light and fire, proposing instead that phlogiston was repulsive to light, fire, and heat. Through decomposition reactions, phlogiston could be obtained in its chemically pure, elemental form as inflammable air. Operationally, Kirwan deemphasized the idea of phlogiston as an oily substance produced in solution analysis focusing instead on its utility in pneumatic chemistry. It could be measured by the same metrics (weight, volume, heat content) as any other chemical substance and subjected to the same algebraically controlled affinity reactions. While he retained Lemery’s idea that phlogiston was essential to the production of salts, Kirwan also extended phlogiston’s role in chemical theory by making it a component of fixed air and thus all acids. His phlogiston offered interesting explanations of calcinations, the composition of water, and the transmutability of the various species of air that were accepted during the 1780s by Guyton Morveau, Antoine Fourcroy, Alessandro Volta, and others throughout Europe.

As Holmes (2000) and Mauskopf (2002) have argued, Lavoisier was not competing during the 1770s and 1780s with a Stahlian phlogiston or even the phlogiston ‘substance identity’ of Lemery, Rouelle, and Macquer. Instead he was competing with a new pneumatic paradigm and a new, British conceptualization of phlogiston. Both in his work with Laplace from 1782 through 1784 and in the more direct Essai sur la phlogistique et sur la constitution des acids, he engaged in a discourse with Kirwan over phlogiston. Kim argues we “need to go beyond his rhetoric that phlogiston was an ‘imaginary’ substance” to see that phlogiston provided a “unique resistance” to Lavoisier’s “vision of rational chemistry […] based on metric measurements and expressed in algebraic terms” (Kim 2008, p. 46). However, Kirwan’s phlogiston could be numerically measured in every conceivable way. Its weight or volume could be measured when in aerial form, or it could be quantified using a calorimeter via its inverse proportionality to heat. Kirwan had even quantified the affinity between phlogiston and the many elements of the latest affinity tables. Phlogiston in 1787 was not an imaginary substance, an imponderable fluid, or even an air that was particularly difficult to measure. The portrayal of phlogiston as the last domino to fall in Lavoisier’s rationalization of chemistry no longer seems sufficient. Phlogiston was not disproved by the weight gain of mercury during calcination as the traditional historiography of
Partington and Kuhn argued. Nor did phlogiston hinder the development of quantifiable, algebraic chemistry as Conant, Margolis, and Kim have argued. The new conceptualization of airs as non-transmutable, elemental species separated the ontologically defined hydrogen gas from its theoretical roles in pneumatic transmutation and heat theory. Phlogiston was a chemical artifact that was replaced in the affinity tables by a set of new elements, namely hydrogen, oxygen, carbon, and caloric.

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Notes
1 For a defense of the Chemical Revolution as a Kuhnian paradigm shift, see Hoyningen-Huene 2008.
2 For a recent rendition of this Chemical Revolution narrative, see Bowler & Morus 2005, ch. 3.
3 See for example Bowler & Morus 2005.
6 Kim addressed phlogiston’s role as a chemical substance within the broader research program of chemical affinity in Kim 2003 and 2011.
7 Lawrence Principe has recently shown the alchemical roots of Homberg’s sulfur principle and tied him into a chrysopoeia tradition that included seventeenth century chymists Etienne de Clave, Robert Boyle, and George Starkey. Stahl also maintained the reality of metallic transmutation in his earlier writings, although he appears to have abandoned this position as he aged. Nonetheless, phlogiston’s identification as the active sulphur principle would appear to link it to the alchemical traditions of the late seventeenth century in ways that have yet to be fully examined. For more on Homberg’s chrysopoeia see Principe 2001.
8 Kirwan did not credit Cavendish as the originator of the identification of inflammable air as phlogiston. It is evident that he knew of Cavendish’s claim, because he cited Cavendish’s 1766 paper ‘On Factitious Airs’ in his 1782 paper ‘Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances’. It is unclear why Kirwan did not give Cavendish credit for this identification, although it may have been because Cavendish had developed a different ontological theory of gases by the 1780s.
As with Cavendish's first papers in 1766, Kirwan's three papers analyzing the properties of salts won him the Royal Society's Copley medal in 1782.

For further analysis of heat theories see Mendelsohn 1964. For more on heat and chemistry in Britain see Heggarty 1978.


Nicholson was a friend of Kirwan and served as the translator for the second edition of Kirwan's Essay on Phlogiston. See Heggarty 1978, p. 97 for more information on their relationship.

Scheele independently isolated fire-air (dephlogisticated air) about two years before Joseph Priestley.

Kirwan did maintain that light and heat are different expressions of the same fundamental substance, though he thought that they interacted differently in chemical combinations. For example light will turn silver nitrate black while heat will not.

The vapor solution theory was popularized in Saussure 1783.

On the sensory characteristics of phlogiston in experiments, see Boantza & Gal 2011.

For more on Paulx Lavoisier's work in chemistry and chemical translation see Kawashima 2000.

See Heggarty 1978, pp. 194-5, for more on the position of the French Academy.

References


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