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RICHARD KIRWAN'S CHEMISTRY:
HEAT, AFFINITY, AND PHLOGISTON IN THE 1780'S

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CHAPTER ONE: LITERATURE REVIEW

Richard Kirwan (1733-1812) was an Irish chemist who developed a new phlogiston theory distinct from that of George Ernst Stahl at the end of the eighteenth century. He was actively engaged in debate with the antiphlogistian camp led by Antoine Lavoisier and maintained extensive correspondence with a trans-European network. In 1782, Kirwan was awarded the Copley Medal, the Royal Society's highest honor, for his work on specific gravities of various saline substances.¹ He was a member of numerous scientific societies including the Royal Society, the Irish Royal Academy, and the Academy of Dijon among others. The refutation of his *Essay on Phlogiston*² was seen by the Arsenal group as the culminating argument in the antiphlogiston campaign and the conclusion of the revolution that replaced the phlogiston theory of combustion with the oxygen theory.

Kirwan's portrayal in histories of chemistry can be broken down into four periods; in his nineteenth century biographies he was seen as a polymath, the lone philosopher of his time in Dublin.³ Here, Kirwan is usually described as a natural philosopher contributing important theories to a broad range of sciences. During the 1930's, J. R. Partington placed him as one of the last adherents to the phlogiston theory that was swept away by Lavoisier's discovery of oxygen.⁴ Kirwan was increasingly

¹ Richard Kirwan, "Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances," *Philosophical Transactions of the Royal Society* 71 (1781).

² Richard Kirwan, *An Essay on Phlogiston, and the Constitution of Acids* (London: Printed by J. Davis, for P. Elmsly, 1787).

³ Michael Donovan, "Biographical Account of the Late Richard Kirwan," *Proceedings of the Royal Irish Academy* 4 (1850).

⁴ Douglas McKie and J. R. Partington, "Historical Studies on the Phlogiston Theory.--I. The Levity of Phlogiston," *Annals of Science* 2, no. 4 (1937).

identified as a chemist on the wrong side during the Chemical Revolution, and thus unimportant in the cumulative progression of science. Kirwan was largely neglected from 1941-1970, but reemerged in the works of E. L. Scott, again portrayed as an influential natural philosopher interested in chemistry, meteorology, and geology.⁵

After the 1988 *Osiris* volume problematizing the Chemical Revolution,⁶ Paul Thagard began evaluating Kirwan's phlogiston theory as it related to Kuhn's paradigms and Lakatos's research programmes.⁷ Kirwan became interesting to those challenging the progressive assumptions of previous historiographies, but was still studied exclusively as an advocate of phlogiston. It has only been in the last ten years that historians have moved beyond Kirwan's adherence to the phlogistic paradigm, to look at his participation in British pneumatic research,⁸ and his role as a leader in the trans-European affinity program.⁹ In the following pages, I will delve more deeply into Kirwan's portrayal in the histories of the Chemical Revolution to this point. In chapter two, I will seek to place Kirwan's phlogiston theory into its wider context in the complex theoretical and cultural milieu of chemistry at the end of the eighteenth century.

The early biographies of Kirwan stress his impact on a broad range of natural philosophy and give some indication as to how he was perceived by his contemporaries.

Michael Donovan, a member of the Royal Irish Academy and friend of Kirwan's,

⁵ Ernest Leonard Scott, "The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time" (Dissertation, University of London, 1979).

⁶ Arthur Donovan, *The Chemical Revolution: Essay in Reinterpretation*, *Osiris* (Chicago: University of Chicago Press, 1988).

⁷ Paul Thagard, "The Conceptual Structure of the Chemical Revolution," *Philosophy of Science* 57, no. 2 (1990).

⁸ Frederic L. Holmes, "The 'Revolution in Chemistry and Physics': Overthrow of a Reigning Paradigm or Competition between Contemporary Research Programs?," *Isis* 91, no. 4 (2000). Also S. Mauskopf, "Richard Kirwan's Phlogiston Theory: Its Success and Fate," *Ambix* 49, no. 3 (2002).

⁹ Mi Gyung Kim, *Affinity, That Elusive Dream: A Genealogy of the Chemical Revolution* (Cambridge, Mass.: MIT Press, 2003). Anthony Travis, "Chemical Affinities," *Minerva* 43 (2005).

produced the first researched account of Kirwan's life for the Academy's 1850 Proceedings.¹⁰ Donovan's narrative appears unreliable, as evidenced by the stories of Kirwan's mastery of languages. Richard Kirwan could apparently conjugate a French verb at the age of four, yet upon arriving at Poitiers he refused to *learn* the language of the land; the clever Jesuit masters used Richard's love of science to force him to learn French by limiting his access to books in the native tongue.¹¹ Donovan also tells the reader of Kirwan's proficiency in Latin:

Richard quitted Poitiers about the beginning of the year 1754, for Paris. He appears about this time to have entered on his novitiate either at St. Omer's or Hesden. He was so excellent a Latin scholar, that the College of Jesuits considered him qualified to act as Professor of Humanity; and during his novitiate he taught in the habit of a Jesuit. Many of the French clergy who survived the revolution have acknowledged him as their best professor. One of his pupils was the Ábbe Lynch, afterwards Vicar-general of Paris.¹²

While probably fluent in Latin, Kirwan expressed great relief in learning that one of his Swedish correspondents, Torbern Bergman, knew French and that they would no longer be forced to use Latin.¹³ Donovan's apparent tendency to exaggerate the capacities and achievements of Kirwan are troublesome in that he is almost universally cited as the source of information on Kirwan's career and personal life.

In 1926, Edgar Smith included Richard Kirwan in a *Journal of Chemical Education* article entitled "Forgotten Chemists."¹⁴ Kirwan's one page entry is substantially the same as his listing in the 1911 *Encyclopedia Britannica*¹⁵ and the other

¹⁰ Donovan, *The Chemical Revolution: Essay in Reinterpretation*.

¹¹ *Ibid.*, lxxxiv.

¹² *Ibid.*

¹³ Torbern Bergman, *Torbern Bergman's Foreign Correspondence*, ed. Göte Carlid and John Nordström (Stockholm: Almqvist & Wiksell, 1965).

¹⁴ Edgar Fahs Smith, "Forgotten Chemists," *Journal of Chemical Education* (1926).

¹⁵ "Richard Kirwan," in *The Encyclopaedia Britannica: A dictionary of arts, sciences, literature and general information* (Cambridge: University Press, 1911).

biographical dictionaries of the nineteenth century. Kirwan's inclusion in an article on forgotten chemists, alongside his contemporary Torbern Bergman, shows how those on the "losing" side of the phlogiston–oxygen debate had fallen out of the collective memory. In the next volume of the journal, C. J. Brockman noted how Kirwan had been "severely neglected by historians."¹⁶ Brockman relates a Kirwan that was widely read and highly esteemed by chemists in both England and Germany. Brockman then turns to Kirwan's writings noting his work on specific gravities and touching lightly on his opposition to the oxygen theory and nomenclature. Brockman concludes by listing Kirwan's non-chemical texts.

After the *Journal of Chemical Education* articles, Kirwan next appeared in the pages of *Isis*.¹⁷ Though they never cite Michael Donovan by name, J. Reilly and N. O'Flynn quote his text extensively. From the story of Kirwan's refusal to learn French, through his altruistic return to Dublin in 1787 to lead the Royal Irish Academy, to his eccentricities, the authors recount Donovan's biography without hesitation. Despite this misplaced credulity, the authors did contribute greatly to the growing history of chemistry through their close analysis of the second edition of Kirwan's *Essay on Phlogiston*. Citing the comments of the various French annotators of the 1788 publication "Essai sur la phlogistique," Reilly and O'Flynn were the first to explicitly identify the differences between Kirwan and the antiphlogistian camp.

"Historical studies on the phlogiston theory," a series of articles by J. R. Partington and Douglas MacKie¹⁸ also attributed significant influence to Kirwan,

¹⁶ C. J. Brockman, "Richard Kirwan - Chemist, 1733-1812," *Journal of Chemical Education* (1927): 1275.

¹⁷ J. Reilly and N. O'Flynn, "Richard Kirwan, an Irish Chemist of the Eighteenth Century," *Isis* 13, no. 2 (1930).

¹⁸ McKie and Partington.

especially in Germany and Sweden. This impressively broad survey teased apart the many threads of phlogiston theory and showed that phlogiston was a widely accepted and thoroughly developed theoretical heuristic during the seventeenth and eighteenth centuries. MacKie and Partington portray Kirwan as a widely read and influential theoretician in the closing years of the eighteenth century.

Reverend P. J. McLaughlin appears to have been the first historian to focus steadily on Kirwan, producing a multi-part article on Kirwan for the Irish journal *Studies*,¹⁹ a biographical sketch for a history of chemistry symposium in Cork in 1940, and an article on the Kirwanian Society. McLaughlin's article in *Studies* gave a more detailed analysis of Kirwan's science than had been offered in either the *Journal of Chemical Education* or *Isis* and has been used in the subsequent research on Kirwan. McLaughlin also appears to have been the first Kirwan historian to visit the Salem Athenaeum to see its collection of Kirwan's library.²⁰ While there, McLaughlin gave a lecture on Kirwan's influence through the Salem Athenaeum on the scholarly community of Salem and Boston.

From 1941 to 1970, Kirwan seems to have lost his appeal for historians, as he was not the focus of a single article. In the vast literature on the Chemical Revolution and the discovery of oxygen, Kirwan was largely forgotten or marginalized as an eccentric amateur, a minor character in the story of Joseph Priestley and Antoine Lavoisier. He was completely omitted from Thomas Kuhn's account of the Chemical Revolution,²¹ and

¹⁹ P. J. McLaughlin, "Richard Kirwan," *Studies* 28 and 29 (1939-1940).

²⁰ Part of Kirwan's library was captured by an American privateer while in transit from Dublin to London in 1780. This collection was eventually incorporated into what would become the Salem Athenaeum.

²¹ Thomas S. Kuhn, *The Structure of Scientific Revolutions* (Chicago: University of Chicago Press, 1962).

the works of the Chemical historian William Smeaton fail to mention the influence of Kirwan on chemical theory.²² Even in Trevor H. Levere's 1971 text on affinity, Kirwan is mentioned only briefly and is portrayed as a confused or even bumbling foil for contrast with Humphrey Davy.²³

F. E. Dixon's article "Richard Kirwan: The Dublin Philosopher" appeared in the *Dublin Historical Record* in 1971²⁴ and again initiated a historiographical reclamation of Kirwan's memory. Dixon's article retells the narrative of Kirwan's life following the guidelines laid down by Michael Donovan and expanding with information on Kirwan's involvement in the United Irishmen, an organization that sought Irish independence in the last two decades of the eighteenth century and led the unsuccessful Rebellion of 1798. Dixon does not draw on the works by Smith, Brockman, or Reilly and O'Flynn. He focuses primarily on Kirwan's life, and his brief section on Kirwan's chemistry misrepresents the chronology of its work. Dixon has Kirwan converting to phlogiston and subsequently meeting William Higgins, a younger Irish chemist. In fact, Kirwan had met Higgins much before his 1791 conversion, and Higgins wrote a treatise comparing the phlogistic and antiphlogistic theories.²⁵ Though his treatment of Kirwan's chemistry is cursory, Dixon does praise Kirwan's meteorological and mineralogical works and goes into greater length in describing them than had previously been pursued.

²² Smeaton published extensively on the Chemical Revolution and Kirwan's correspondent, Gutyon de Morveau.

²³ Trevor Harvey Levere, *Affinity and Matter: Elements of Chemical Philosophy, 1800-1865* (Oxford: Clarendon Press, 1971).

²⁴ F. E. Dixon, "Richard Kirwan: The Dublin Philosopher," *Dublin Historical Record* 24 (1971).

²⁵ J. R. Partington and T. S. Wheeler give an excellent account of William Higgins' life and reproduce his comparison of the two theories in their biography on him. They also detail the relationship between Higgins and Kirwan. See: J. R. Partington and T. S. Wheeler, *The Life and Work of William Higgins Chemist (1763-1825): Including Reprints of 'a Comparative View of the Phlogistic and Antiphlogistic Theories' and 'Observations on the Atomic Theory and Electrical Phenomena' by William Higgins* (Oxford: Pergamon Press, 1960).

In 1978, Diane Heggarty completed a dissertation on Richard Kirwan and his chemical theories.²⁶ Heggarty sought to shift the focus away from phlogiston's role in combustion, spotlighting instead theories of heat. After giving an introduction on theories of heat prior to 1789, Heggarty reports on Kirwan's theory and those of his contemporaries like Lavoisier, Laplace, and Higgins. She then turns to changes in state in order to show the connection between the Irvinist theory of heat and Kirwan's identification of phlogiston with inflammable air. Heggarty explains that the refutation of the British idea of heat was one of the reasons that Lavoisier and the French Academy of Science chose to study and eventually refute Kirwan's *Essay on Phlogiston*.²⁷ Heggarty's analysis of Kirwan and his chemical theories was the most thorough to that date, but she was quickly followed by another burst of scholarship on Kirwan.

In 1979, Ernest Leonard Scott defended his dissertation entitled "The Life and Work of Richard Kirwan."²⁸ This remains the seminal work on Kirwan due to the breadth of Scott's research. Scott presented the first critical reanalysis of Kirwan's biography and was also the first to delve into Kirwan's meteorology. Like Heggarty, Scott revisited archival sources on Kirwan and identified many of the problems in earlier secondary sources. Scott omits many of Michael Donovan's more colorful stories about Kirwan and uses correspondence to recreate a thoroughly researched account of Kirwan's life.

Scott next turns to Kirwan's theories of heat and phlogiston, and finishes his dissertation with extended sections on Kirwan's theories in mineralogy, geology, and

²⁶ Diane E. Heggarty, "Richard Kirwan: The Natural Philosopher and the Chemical Revolution" (Dissertation, University of Washington, 1978).

²⁷ Richard Kirwan, *Essai Sur Le Phlogistique, Et Sur La Constitution Des Acides*, ed. Louis Bernard Guyton de Morveau et al., trans. Marie-Anne-Pierrette Lavoisier (A Paris: Rue et hôtel Serpente, 1788).

²⁸ Scott.

meteorology and includes a discussion of Kirwan's debates with Hutton. Scott also mentions Kirwan's work in applied chemistry and his philosophy, though only briefly. Kirwan's philosophy remains unexplored despite the fact that he published several monographs on his Berkeley inspired immaterialism. Scott published again on Kirwan in 1981²⁹ contributing to the discussion on theories of heat and later contributed Kirwan's entries in the *Dictionary of Scientific Biography*³⁰ and the *Oxford Dictionary of National Biography*.³¹

Duncan Thorburn Burns also wrote in 1979 on Kirwan as part of his survey of "Irish contributors to European Analytical Chemistry."³² Burns sets Kirwan alongside Robert Boyle and J. Emerson Reynolds as the three preeminent chemists in Irish history. Though Burns draws primarily on Michael Donovan's account for this article, he has continued to research and write about Kirwan up through his recent biographical presentation before the Royal Irish Academy in 2003.³³

In 1988, an issue of *Osiris*, edited by Arthur Donovan, was devoted to the Chemical Revolution.³⁴ This collection of articles extended William Smeaton's work in broadening the scope of the Chemical Revolution by looking at chemical studies in the Netherlands, Sweden, and Spain. It also problematized the impact and novelty of Lavoisier's theories, questioned the definitions of chemical paradigms, and examined the

²⁹ Ernest Leonard Scott, "Richard Kirwan, J. H. De Magellan, and the Early History of Specific Heat," *Annals of Science* 38, no. 2 (1981).

³⁰ Ernest Leonard Scott, "Richard Kirwan," in *Dictionary of scientific biography*, ed. Charles Coulston Gillispie and Frederic Lawrence Holmes (New York: Scribner, 1981).

³¹ Ernest Leonard Scott, "Richard Kirwan," in *Oxford Dictionary of National Biography*, ed. H. C. G. Matthew and Brian Harrison (Oxford: Oxford University Press, 2004).

³² Duncan Thorburn Burns, "Some Irish Contributors to European Analytical Chemistry, R. Boyle, R. Kirwan, J. Emerson Reynolds," *Analytical Letters* 12, no. 2 (1979).

³³ Duncan Thorburn Burns, "Richard Kirwan, 1733-1812: 'The Philosopher of Dublin'," in *8th Annual lecture to the National Committee for the History and Philosophy of Science of the Royal Irish Academy* (Dublin: Royal Irish Academy, 2003).

³⁴ Donovan, *The Chemical Revolution: Essay in Reinterpretation*.

methodological influences of several of the participants. This volume represents a great stride in developing a nuanced history of the chemical revolution and led to extensive research and publishing in the next decade.

In 1994, Emmanuel Grison, Michelle Sadoun-Goupil and Bret Patrice published newly uncovered correspondence between Richard Kirwan and Guyton de Morveau.³⁵ Drawing from the work of William Smeaton, the authors found a cache of letters between the two chemists in a departmental library in Dijon, France. The book includes an introduction with biographical information on the two men along with text on the development of their chemical theories. The section on Kirwan's life is succinct and well written but draws largely from Scott. The correspondence, though, has proven an immensely useful resource with its first hand account of the evolution of the theories of Kirwan and Guyton de Morveau. Thirty-eight letters ranging from 1782-1802 track the rise of Lavoisier's antiphlogistian camp, the conversion of Morveau to the oxygen theory, comments on common acquaintances, and numerous other insights into their lives and theories. This text, in conjunction with the letters that had earlier been tracked down by E. L. Scott, has been drawn on heavily since its publication.

Sequels to Kuhn's account of the history of science in terms of paradigms³⁶ continued to use the chemical revolution as an exemplar for case study throughout the 1990's. In 1978, H. Gilman McCann used statistical analysis of the Chemical Revolution as evidence for Kuhn's theory of paradigm shifts.³⁷ I. B. Cohen also couches the

³⁵ Louis Bernard Guyton de Morveau and Richard Kirwan, *A Scientific Correspondence During the Chemical Revolution: Louis-Bernard Guyton De Morveau and Richard Kirwan, 1782-1802*, ed. Emmanuel Grison, Michelle Sadoun-Goupil, and Bret Patrice, Berkeley Papers in History of Science (Berkeley, CA: Office for History of Science and Technology, University of California at Berkeley, 1994).

³⁶ Kuhn.

³⁷ H. Gilman McCann, *Chemistry Transformed: The Paradigmatic Shift from Phlogiston to Oxygen*, Modern Sociology (Norwood, N.J.: Ablex Publication Corporation, 1978).

Chemical Revolution in Kuhnian terms in his 1985 book, *Revolution in Science*.³⁸ Paul Thagard looked closely at Kirwan's theories in both his 1990 *Philosophy of Science* article, "The Conceptual Structure of the Chemical Revolution."³⁹

Though published in 1990, Thagard's article in *Philosophy of Science* was written and revised in 1988, and he therefore does not draw from the 1988 volume of *Osiris*. Thagard represents the Chemical Revolution as the shift from phlogiston theory to oxygen theory and uses it as an exemplar of Kuhnian paradigm shift analyzing the conceptual changes in Lavoisier's theories. Thagard thus bypasses Heggarty's concern with heat and Irvinism along with suggestions by J. B. Gough that Lavoisier was completing a methodological paradigm shift started by George Ernst Stahl, subordinating chemistry to physics.⁴⁰ While he does not address this more nuanced understanding of the Chemical Revolution, Thagard's conceptual analysis remains insightful in tracing the thoughts of Lavoisier. In applying methodologies from the study of artificial intelligence, Thagard utilizes a representational graphing method to diagram changes in Lavoisier's theory over time. He graphs and analyzes Lavoisier's theories from four snapshots in time: 1772, 1774, 1777, and 1789 noting changes along the way. Thagard develops this method further in his follow up 1992 monograph, *Conceptual Revolutions*.⁴¹ Hanne Andersen, Peter Barker, and Xiang Chen have developed a similar methodology in their book, *The Cognitive Structure of Scientific Revolutions*,⁴² which I will apply in chapter two.

³⁸ I. Bernard Cohen, *Revolution in Science* (Cambridge: Belknap Press of Harvard University Press, 1985).

³⁹ Thagard.

⁴⁰ J. B. Gough, "Lavoisier and the Fulfillment of the Stahlian Revolution," *Osiris* 4 (1988).

⁴¹ Paul Thagard, *Conceptual Revolutions* (Princeton: Princeton University Press, 1992).

⁴² Hanne Andersen, Peter Barker, and Xiang Chen, *The Cognitive Structure of Scientific Revolutions* (Cambridge: Cambridge University Press, 2006).

In recent work Frederick Holmes challenges the identification of Joseph Priestley as a participant in the phlogiston-oxygen paradigm shift by claiming that the British phlogiston theory had departed from earlier Stahlian theories, and should be considered a new paradigm.⁴³ Holmes claims that the pneumatic chemistry of Cavendish and Priestley was significantly different from earlier Stahlian theories of phlogiston, which centered around studies of earths. While not mentioned by Holmes, Kirwan fits well into his depiction of British pneumatic chemistry and the identification of inflammable air as pure gaseous phlogiston is emblematic of this focus. As with Priestley's pneumatic phlogiston theories, Kirwan's understanding of phlogiston can be differentiated from those of both the early phlogiston advocates like Stahl and those of the French phlogistians like Macquer, who focused their attention on transferring phlogiston from one substance to another in the study of salts.⁴⁴

Michael Akeroyd's short article from 2003 applies Larry Laudan's delineation between conceptual and empirical problems to the Lavoisier-Kirwan debate.⁴⁵ Akeroyd attempts to show that Lavoisier's oxygen system was superior to Kirwan's at overcoming empirical problems and that the conceptual differences were ignored for the sake of scientific expediency. Akeroyd's argument serves as another interpretation of conceptual change in the chemical revolution but his articulation of the methodology is unconvincing.

⁴³ Holmes.

⁴⁴ Pierre Joseph Macquer's early work on arsenic salts was published in the *Mémoires de l'Académie Royale des Sciences* in 1746. His textbooks, *Éléments de chymie théorique* (1749) and *Éléments de chymie pratique* (1751), were highly influential in both France and England as was his later *Dictionnaire de chymie* (1766). For more information see William Smeaton, "Pierre Joseph Macquer," In *Dictionary of scientific biography*, edited by Charles Coulston Gillispie and Frederic Lawrence Holmes. New York: Scribner, 1981.

⁴⁵ F. Michael Akeroyd, "The Lavoisier-Kirwan Debate and Approaches to the Evaluation of Theories," *Annals of the New York Academy of Science* 988 (2003).

In 2002, another collection of manuscripts related to Kirwan was published.⁴⁶ Trevor Levere and G. L'E. Turner published the minutes of the Coffee House Philosophical Society, a scientific social group led by Richard Kirwan that met in London from 1780 through 1787. Levere introduces the book with a social contextualization of coffee houses and their shift in reputation from fertile grounds for industrial innovation at the beginning of the decade to dens of radicalism at the outbreak of the French Revolution. He notes that several of the members of the Coffee House Philosophical Society, most notably Joseph Priestley and Richard Price, were republican sympathizers. However, Levere points to the minutes of the society as evidence for the purely philosophical nature of the society. Turner's analysis of the membership of the club and their attendance confirms that many of the more radical members, like Priestley and Price, were honorary members who did not actually attend the meetings.

Jan Golinski's analysis of the phlogiston debates within the society is particularly useful for this study.⁴⁷ Golinski contrasts an established British rhetorical style of science with the more didactic arguments of Lavoisier. Rather than insisting on the verity of the phlogiston theory or later its obviation, Kirwan and Cavendish presented their facts with minimal interpretation, leaving decisions up to the autonomy of the reader. Golinski contrasts this rhetorical style with that of Lavoisier who felt he could mathematically prove his oxygen theory and thus negate the usefulness of phlogiston as a concept.⁴⁸ The minutes of the Coffee House Society thus prove an interesting view into the British

⁴⁶ Trevor Harvey Levere and others, *Discussing Chemistry and Steam: The Minutes of a Coffee House Philosophical Society, 1780-1787* (Oxford University Press, 2002).

⁴⁷ Jan Golinski, "Conversations on Chemistry." In *Discussing Chemistry and Steam*.

⁴⁸ Golinski, 202.

debate over the phlogiston theory and the initial aversion to the dogmatism of Lavoisier's new theories.

In the most influential recent treatment of eighteenth century chemistry, Mi Gyung Kim suggested that we turn our focus away from the oxygen-phlogiston debate and focus on the affinity theory as the key heuristic of the time.⁴⁹ While affinity had been discussed by Partington, Levere,⁵⁰ and later McCann, Kim was the first to focus on it as a trans-national paradigm unto itself. This theory based on elemental attractions was promulgated by Guyton de Morveau in France, Torbern Bergman in Sweden, and Richard Kirwan in Britain. Kim has shown that the affinity theory was important throughout eighteenth century chemistry and remained important after the discovery of oxygen.

Seymour Mauskopf continued the discussion on the Kirwan-Lavoisier debate with an article in *Ambix* in 2002.⁵¹ Mauskopf draws on the correspondence between Kirwan and Guyton de Morveau as well as the work of Holmes on British pneumatic chemistry and that Mi Gyung Kim on affinity theory. Mauskopf synthesizes the information well and creates a well-developed account of Kirwan's phlogiston theory. However, Mauskopf's conclusion that there were no Kuhnian incommensurabilities between the French and British chemical camps reveals a misunderstanding of Kuhn and an under appreciation for the development of the new chemical nomenclature of the Arsenal group. I will address both of these issues in the following chapter.

⁴⁹ Kim.

⁵⁰ Trevor Harvey Levere mentions Kirwan briefly in his analysis of affinity, saying of Kirwan, "His supposed measurements of affinity were in fact measurements of equivalents, and although celebrated in their time, had almost no effect on subsequent developments." Levere and others, *Discussing Chemistry and Steam: The Minutes of a Coffee House Philosophical Society, 1780-1787*, 22.

⁵¹ Mauskopf. Mauskopf worked with Mi Gyung Kim in the development of his article and apparently had access to her book on affinity, though it was not published until 2003.

In the next section, I will use Kim's affinity analysis in conjunction with the earlier texts on Kirwan's phlogiston theories to create a composite understanding of his chemical theories. Drawing on Diane Heggarty's thesis, I will show that Kirwan's understanding of heat, distinct from phlogiston, was controversial and drew the attention of Antoine Lavoisier and Pierre-Simon Laplace. Kirwan's work on meteorology, often perceived as unrelated to chemistry, drew from a tradition dating back to Robert Boyle, and Edmond Halley, and Kirwan's mineralogy was, likewise, tied to his chemical nomenclature. Lavoisier's experiments on calcification and water synthesis and analysis have been termed his crucial experiments in the fight against phlogiston, chemists converted to the new nomenclature slowly. Phase shifts, affinity theory, mineralogy, and other fields of chemistry still had use for phlogiston in explaining experimental phenomena. The international network of chemists working on these issues also sought to maintain the older nomenclature for its pedagogical uses and to maintain trans-national communications. I do not mean to undermine the notion of the Chemical Revolution, which was recognized even by the participants, but rather to develop a more nuanced understanding of how this conceptual shift came about, using Kirwan's chemical theories as a case study.

CHAPTER TWO: KIRWAN'S CHEMISTRY

Despite the work of Diane Heggarty and Ernest Leonard Scott, Richard Kirwan has largely remained associated with a failed phlogiston paradigm and has been passed over in the majority of chemical historiography. In the following chapter, I will attempt to synthesize Kirwan's chemical theories in order to place phlogiston within the broader context of his work. Kirwan's understanding of heat and his association with Adair Crawford were in themselves very controversial and set him apart not only from Antoine Lavoisier and the French school, but also from other phlogiston theorists like Carl Wilhelm Scheele. Kirwan's research on affinities displays parallel experimental methods to his work on heat, but brought him into closer theoretical alignment with the theories of the Dijon based Guyton de Morveau and Swedish Torbern Bergman than with fellow countrymen like Henry Cavendish. Though Kirwan participated in an international correspondence network, he was also involved in nationalistic and institutional developments between the British and French chemical schools that clearly influenced his theories. This chapter will explore each of these areas in order to develop a full synthesis of his chemical theories and to place him within the context of the chemical community at the end of the eighteenth century.

Heat

During the eighteenth century, heat was a central area of concern in physics and chemistry. Francis Bacon, Isaac Newton, and Robert Boyle advocated a vibratory theory of heat predicated on the idea that the vibrations of small particles create heat. Diane Heggarty draws a parallel with the rise of fluid theories of electricity and magnetism, and

the development of a fluid theory of heat in the second half of the century.⁵² Students of Joseph Black and William Cullen were taught the fluid theory in their courses at Glasgow and Edinburgh. Heggarty points out the utility of the fluid theory of heat for explaining evaporation, fluidity, expansion, heat capacity, and radiation while the vibration theory was better at explaining ignition.⁵³ Adair Crawford and William Irvine were especially influenced by Black's fluid theory, and their influence can in turn be seen in the works of Richard Kirwan.

While Irvine did not publish during his lifetime, two of his students, Adair Crawford and William Cleghorn published works on heat in 1779.⁵⁴ Both Crawford and Cleghorn were charter members of the Chapter Coffee House Society with Richard Kirwan,⁵⁵ and Kirwan quotes both in his works. Crawford was also a guest of Kirwan at the Royal Society on several occasions before ultimately being sponsored by Kirwan and elected in 1786. Crawford's first text was his 1779 doctoral thesis, which developed Irvine's theory of heat capacity.⁵⁶ Crawford's theory was that every chemical substance had a unique heat capacity expressible as a ratio compared to a standard. If common air was given as the standard with heat capacity 1, dephlogisticated air had a heat capacity of 4.6. Thus dephlogisticated air would require 4.6 times more fluid heat to change its temperature one degree than would common air. In general the less phlogiston

⁵² Heggarty, 10.

⁵³ Ibid., 11.

⁵⁴ William Cleghorn, *Disputatio Physica Inauguralis, Theoriam Ignis Complectens* (Edinburgh: Balfour et Smellie, 1779), Pierre Joseph Macquer, *Dictionnaire De Chymie*, 2 vols. (Paris: Chez Lacombe, 1766).

⁵⁵ Levere and others, *Discussing Chemistry and Steam: The Minutes of a Coffee House Philosophical Society, 1780-1787*, 45.

⁵⁶ One of Kirwan's first works in print came in Jean Magellan's French exposition of Crawford's views. Magellan included a table of specific heats, which Kirwan and Crawford had developed. Jean Magellan was Portuguese and generally published as João Jacinto de Magalhães. I will refer to him as Magellan, which is how Kirwan and the Royal Society knew him. João Jacinto de Magalhães, *Essai Sur La Nouvelle Théorie Du Feu Élémentaire, Et De La Chaleur Des Corps Avec La Description Des Nouveaux Thermometres, Destinés Particulièrement Aux Observations Surce Sujet* (Londres: De l'Impr. de W. Richardson, 1780).

something contains, 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*.⁵⁷ Kirwan and Crawford's table was widely used and translated, while numbers from this and subsequent experiments during the 1780's were used by Lavoisier and Laplace, John Dalton, Thomas Thompson and others.⁵⁸

In 1780, the English translation of Karl Wilhelm Scheele's *Chemical Experiments and Observations on Air and Fire* was printed with notes from Kirwan.⁵⁹ Kirwan had been asked by Joseph Priestley and John-Reinhold Forster, the translators of the book, to add notes to Scheele's work.⁶⁰ Both Kirwan and Scheele maintained the fluid theory of heat. However, for Scheele, this heat was a combination of the inflammable principle with fire-air (*Feuerluft* - what Priestley would call dephlogisticated air).⁶¹ If more phlogiston is added to regular heat, radiant heat is produced, and the addition of even more phlogiston will yield light. Scheele 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 phlogiston.

Kirwan, in his notes, rejected this 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"⁶² and that fire, heat, and

⁵⁷ Scott, "The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time", 180.

⁵⁸ Heggarty, 112.

⁵⁹ Carl Wilhelm Scheele, *Chemical Observations and Experiments on Air and Fire with a Prefatory Introduction by Torbern Bergman*, trans. J. R. Forster, To which are added notes, by Richard Kirwan with a letter to him from Joseph Priestley ed. (printed for J. Johnson, 1780).

⁶⁰ Scott, "The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time", 152.

⁶¹ Scheele independently isolated fire-air (dephlogisticated air) about two years before Joseph Priestley. See *Ibid.*, 154.

⁶² Heggarty, 82.

light were all repulsive to phlogiston. If a body is exposed to an amount of fire, heat, or light, a proportional amount of phlogiston will be expelled from that body and the heat capacity of the body will be increased. Alternatively, adding phlogiston to dephlogisticated air produces common air. Because dephlogisticated air has a higher heat capacity than common air, the conversion from the former to the later will cause the release of heat as a byproduct. While Scheele saw heat as the product of phlogiston and dephlogisticated air, Kirwan saw it only as a byproduct of the synthesis.⁶³ Kirwan said that light and heat are different expressions of the same fundamental substance, though he did note that they interacted differently in chemical combinations. For example light will turn silver nitrate black while heat will not.⁶⁴

Kirwan and Crawford also used the idea of heat capacity to explain combustion. Combustion was the rapid expulsion of heat from dephlogisticated air through the addition of phlogiston. The more phlogiston that was released from the combustible, the faster that phlogiston 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 in exchange for heat. The animal then exhaled fixed air.

Questions on change of state proved one of the most useful grounds for employing Irvinist 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. Also, there is a larger amount of heat needed to convert liquid to vapor than there

⁶³ Scheele, 43.

⁶⁴ Heggarty, 90-100.

was to convert solid to liquid. Heggarty clarifies, “It was an elementary step to equate the dissolution of a salt in water and the subsequent cooling, with the heat absorbed when a solid such as ice melted into a liquid.”⁶⁵ The difference in heat capacity of the states of matter explains the absorption or release of heat during a change of state or a chemical change. If a liquid were vaporized during a chemical reaction, little heat would be given off, because that heat was used in the vaporization.

One of the problems for those that adhered to the fluid theory of heat was the heat created by friction or percussion. Heggarty points to Kirwan’s as the best solution to these questions. Though not recorded in Kirwan’s texts, William Nicholson, a member of the Chapter Coffee House Society, cites Kirwan in his *Introduction to Natural Philosophy*⁶⁶ for the theory that friction and percussion diminished the heat capacity of a body expelling some of its heat and raising the surrounding temperature.

Cavendish (and later Lavoisier) claimed that the decomposition and synthesis of water presented a challenge to Kirwan’s identification of fixed air as the product of inflammable air and dephlogisticated. Kirwan used Irvinist heat theories to explain the formation of water from dephlogisticated air and inflammable air. Though the two airs usually combined to form fixed air, an electric spark or extreme heat could cause this fixed air to phase shift into water, the two being different phases of the same substance. In their rarified states, dephlogisticated and inflammable air have greater affinity for each other forming a closer bond. They also have less specific heat; thus the fixed air normally formed would phase shift to water, which is denser and has a lower heat

⁶⁵ Ibid., 187.

⁶⁶ William Nicholson, *An Introduction to Natural Philosophy*, 2nd ed., 2 vols. (London: J. Johnson, 1787), 121-122. Nicholson was a friend of Kirwan’s and served as the translator for the second edition of Kirwan’s *Essay on Phlogiston*. See Heggarty, 97 for more information on their relationship

capacity. While normally considered one of the crucial experiments in disproving the phlogiston theory, Kirwan maintained that his Irvinist understanding of chemical processes explained the synthesis of water.

Kirwan and Crawford's Irvinist theories were by no means universally accepted, but they were widely read. In Germany, Lorenz Crell published both letters and translated articles from Kirwan and Alessandro Volta in Italy and Du Carla in Spain also cited their works.⁶⁷ Efforts by Lavoisier and Laplace to disprove much of the Irvinist doctrine had substantive value,⁶⁸ but Kirwan commented in a letter to Bergman that their work was unoriginal and Josiah Wedgwood found their experimental method to be unreliable.⁶⁹ The Irvinist theory of heat capacity also had greater meteorological and electrical explanatory power than the solution theory of Lavoisier (and the French school at large), which relied on chemical unions.⁷⁰

Affinity

In 2003, Mi Gyung Kim published an exemplary analysis of affinity theory, with which she sought to shift the focus of chemistry in the last quarter of the eighteenth century from Lavoisier to Guyton de Morveau. Kim tracks the development of chemistry from Paracelsus through Dalton focusing largely on the writings and influence of George Ernst Stahl. At the beginning of the eighteenth century, Claude-Joseph Geoffroy's analysis of salts introduced Stahl into French chemistry, while the lectures of Rouelle and

⁶⁷ Heggarty, 147-149.

⁶⁸ Angela Bandinelli, "The Isolated System of Quantifiable Experiences in the 1783 "Mémoire Sur La Chaleur" of Lavoisier and Laplace.," *Ambix : the journal of the Society for the Study of Alchemy and Early Chemistry* 54, no. 3 (2007). This very recent article is illustrative of the continuing production of the Lavoisier industry and the need for further historiographic study conceptions of heat.

⁶⁹ Heggarty, 145-146.

⁷⁰ The vapor solution theory was popularized in Horace Bénédict de Saussure, *Essais Sur L'hygrométrie* (Neuchatel: Samuel Fauche pere et fils, 1783).

the textbook and dictionary of Macquer further promoted Stahlian theories. Kim shows how Stahl's theories were tied to Newtonian physico-chemistry, and how they benefited from the backlash against both alchemical traditions and Cartesian mechanical corpuscular theory. Kim also shows how French pharmaceutical and medical chemical traditions were influenced by German and Scandinavian metallurgical interests, along with the English empiricism of Boyle, through international channels of correspondence and the rise of scientific societies. Kim ultimately points to affinity theory as a unifying research program for Western Europe. In the last quarter of the eighteenth century, this theory was led in France by Guyton de Morveau, in Sweden by Scheele and Bergman, and in Great Britain by Richard Kirwan.⁷¹

Kirwan received an early introduction to Stahlian theory while attending the lectures of Guillaume-François Rouelle from 1754 through 1755.⁷² Rouelle lectured on chemistry at the Jardin du Roy beginning in 1743 and taught a generation of chemists including Pierre Bayen, Jean-Baptiste-Marie Buquet, Antoine Lavoisier, Pierre-Joseph Macquer, and Guillaume-François Venel.⁷³ While Rouelle never published a textbook, his student, Pierre-Joseph Macquer, produced both a textbook and a dictionary of chemistry.⁷⁴ Rouelle and Macquer dominated French chemistry for the middle third of the eighteenth century. During that time they firmly cemented the legacy of Stahl and focused the attention of French chemistry on analysis of salts and affinities.

⁷¹ Kim.

⁷² Kirwan's notes on Rouelle's lectures are held by the Royal Irish Academy. See Kim and Heggarty for more. Kirwan also owned copies of Stahl's papers from the *Memoirs of the Berlin Academy*, a society notable for its collection of medical chemists. The *Memoirs of the Berlin Academy* were amongst Kirwan's books captured while crossing the Irish channel in 1780 by an American privateer. See chapter 3

⁷³ For more information on Rouelle see Rhoda Rappaport, "G.F.Rouelle : His 'Cours De Chymie' and Their Significance for Eighteenth Century Chemistry" (Thesis (M A), Cornell University, 1958).

⁷⁴ Pierre Joseph Macquer, *Elemens De Chymie Theorique* (Paris: J.-T. Herissant, 1749), Macquer, *Dictionnaire De Chymie*.

From 1781 through 1783, Richard Kirwan presented a series of three papers on salts and affinity theory, for which he was awarded the Royal Society's highest honor, the Copley Medal. The over arching goal of the three papers was to quantify the affinity between acids and bases. In 1720, Geoffroy had developed a chemical affinity table to visually represent the affinity of acids and alkalis in the production of salts. Intense study on affinity tables throughout the second half of the eighteenth century had culminated in 1775 with Torbern Bergman's monumental table with fifty rows and columns representing not only the alkalis and acids but also the salts they produced in order to examine double affinities. However, the size and complexity of Bergman's table showed that visual representation was becoming overly complicated. For every new acid or salt, a set of experiments, growing geometrically with each discovery, was needed to place it in the table. Kirwan's goal was to measure affinities numerically, rather than comparatively. Mirroring his work on the specific weight and heat of various airs, Kirwan now analyzed the affinities of substances for a common substance, marine air. This would also allow for easier study of double affinities by simply adding together and comparing affinity measurements through algebra.⁷⁵

Kirwan's first paper, "Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances,"⁷⁶ laid out this experimental method for finding specific gravities and the results of experiments on several key chemical substances like spirit of salt and spirit of nitre. Kirwan, at times, draws from the chemical literature for his data rather than conducting new experiments. He quotes the work of Homberg, Lavoisier, and others. Kim notes several changes between Kirwan's

⁷⁵ Kim, 258-277.

⁷⁶ Kirwan, "Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances."

papers and previous affinity research. For each acid and alkali, Kirwan experimentally found how much marine acid air was needed to form a neutral salt. In finding the “point of saturation” for acids and alkalis, Kirwan was drawing on the work of Homberg, whom he quoted. Unlike Homberg though, Kirwan studied the point of saturation in gases rather than aqueous solutions, giving him greater ability to isolate the substances involved.⁷⁷ Kirwan suggested that there was a range of affinities dependent upon the respective quantities of the substances involved. When there were very different quantities of the substances, affinity would be high and the compound density would be low. When the substances were perfectly balanced, affinity would be low and the compound density would be at its maximum.

Kirwan, in his second paper, ⁷⁸ corrects some of the experimental and mathematical mistakes of his first paper. One of the subjects Kirwan looks at here is variation in specific gravity at different temperatures. Kirwan finds a proportional relationship between the temperature using Fahrenheit’s system, and the specific gravity of spirit of nitre and nitrous acid. For every degree increase in temperature, the specific gravity of each substance increased. Kirwan continued this research in 1785 with another paper entitled “Remarks on Specific Gravities taken at different degrees of heat.”⁷⁹ Kim notes the novelty of Kirwan’s attention to detail in temperature variation and points to it as an example of Kirwan’s experimental precision.⁸⁰ The bulk of Kirwan’s second paper discusses phlogiston and its relation to inflammable gas. Kirwan states the identity of

⁷⁷ Kim, 270-272.

⁷⁸ Richard Kirwan, "Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances," *Philosophical Transactions of the Royal Society* 72 (1782).

⁷⁹ Richard Kirwan, "Remarks on Specific Gravities Taken at Different Degrees of Heat, and an Easy Method of Reducing Them to a Common Standard," *Philosophical Transactions of the Royal Society* 75 (1785).

⁸⁰ Kim, 270.

phlogiston and inflammable gas and then goes through several proofs. After briefly refuting alternate theories, including those of Lavoisier, Kirwan proceeds to measure the amount of phlogiston in various gases. I will return to Kirwan's phlogiston theories later.

The third paper focused on combinations of marine acid with metals.⁸¹ In this third paper, Kirwan continued to develop the idea that the saturation capacity for each basis is a distinct chemical property that can be used to predict complex decompositions.

Kirwan says,

In all decompositions we must consider, first, the powers which resist any decomposition, and tend to keep the bodies in their present state; and, secondly, the powers which tend to effect a decomposition and a new union. The first I shall call *quiescent* affinities, and the second sort *divellent*.

A decomposition will always take place when the sum of the divellent affinities is greater than that of the quiescent; and, on the contrary, no decomposition will happen when the sum of the quiescent affinities is superior to, or equal to, that of the divellent.⁸²

Kirwan then gives an example of the algebraic evaluation of a possible decomposition:

Quiescent affinities.		Divellent affinities.	
Vitriolic acid to fixed veget. alkali	215	Vitriolic acid to calcareous earth	110
Nitrous acid to calcareous earth	96	Nitrous Acid to vegetable alkali	215
Sum of the quiescent affinities	311	Sum of the divellent	325

Hence a double decomposition must necessarily happen.

Table and text from Kirwan, Conclusion, 40.

When tartar vitriolate (vitriolic acid and fixed vegetable alkali) is mixed with nitrous selenite (nitrous acid and calcerous earth), the two substances will decompose. The vitriolic acid will join with the calcerous earth to form a true selenite, while the nitrous

⁸¹ Richard Kirwan, "Conclusion of the Experiments and Observations Concerning the Attractive Powers of the Mineral Acids," *Philosophical Transactions of the Royal Society* 73 (1783).

⁸² Ibid.: 40.

acid will join the vegetable alkali to form nitre. Kirwan goes on to explain how the results would vary if the vitriolate was replaced with other compounds. The key though, is that decompositions can now be determined without recourse to complex visual tables through basic math.

Kirwan's papers on specific gravity and affinity used decomposition and synthesis experiments to empirically find the weights of water, acids, alkalis, and salts. Using these values, Kirwan could speak on the gravimetric composition of commonly used chemical substances. In his third paper, Kirwan used these gravimetric measurements to establish an algebraic affinity theory that could replace the growingly onerous affinity tables originated by Geoffroy and culminating with Torbern Bergman. Kirwan's use of marine acid gas as a standard for analysis allowed for more controlled measurement and his attention to temperature represented a step forward in experimental precision. His extensive use of gravimetric measurement and accounting clearly invalidates the naïve historiographic notion that Lavoisier was the first to use the balance.

Phlogiston

During the 1780's, Antoine Lavoisier was not refuting the early eighteenth century phlogiston theory of George Ernst Stahl or mid-eighteenth century phlogiston theory of his teacher, Rouelle, but rather the phlogiston theory of Richard Kirwan. As has already been shown, Lavoisier's collaboration with Pierre-Simon Laplace in 1783 on heat was targeted at refuting Kirwan and Crawford's theory of heat. After the publication of Kirwan's *Essay on Phlogiston* in 1787, Lavoisier again sought to refute the Irish chemist's theories. Working from the French translation produced by his wife, Marie-Anne-Pierrette Paulz Lavoisier, Antoine collaborated with Claude-Louis Berthollet,

Pierre-Simon Laplace, Guyton de Morveau, Antoine Fourcroy, and Gaspard Monge to produce a section-by-section refutation of the Kirwan's phlogiston theory.⁸³ By looking at Kirwan's work over the 1780's, we find a phlogiston theory very different from the earlier works of Stahl, Macquer, and Rouelle, and featuring significant differences even from contemporaries like Carl Wilhelm Scheele. This conception could account for the decomposition of water into dephlogisticated and phlogisticated air, weight gains during calcinations, and combustion. It was predicated on an Irvinist understanding of heat and the pneumatic studies of Joseph Priestley.

Kirwan's notes in the English translation of Carl Wilhelm Scheele's⁸⁴ *Chemical Obsesrvations and Experiments on Air and Fire*⁸⁵ offer a view on his understanding of phlogiston in 1780 and how it differed from that of Scheele. While Kirwan praised Scheele's genius, he notes that the author's lack of familiarity with the work of Joseph Black and Adair Crawford have limited his understanding of phlogiston and the role of heat in chemical reactions. Scheele said that heat was the product of air and phlogiston. Kirwan, in agreement with Adair Crawford, maintained that heat was only a byproduct from the lowering of air's heat capacity due to its absorption of phlogiston. This difference in the understanding of heat has implications for understanding combustion.

Scheele's early experiments on fire air (his term for dephlogisticated air) were based on the decomposition of heat by combining with acid of nitre. "This heat it is, which during the distillation of concentrated acid of nitre is decomposed, and resolved

⁸³ Kirwan, *Essai Sur Le Phlogistique, Et Sur La Constitution Des Acides*.

⁸⁴ Carl Wilhelm Scheele (1742-1786) was a Swedish pharmacist best known for his isolation of dephlogisticated air. Scheele corresponded with Torbern Bergman and Lavoisier, and his death was mourned by Kirwan and de Morveau as evidenced in a letter from their correspondence.

⁸⁵ Scheele.

into its integrant parts.”⁸⁶ Phlogiston has a greater affinity for nitrous acid than dephlogisticated air, so nitrous acid will strip heat of its phlogiston, leaving only dephlogisticated or fire air. This fire air, when introduced to an open flame, produced a brighter fire than that of common air. In note twenty-eight to Scheele’s work, Kirwan shows that nitrous acid is itself partially composed of dephlogisticated air along with an alkaline base. The dephlogisticated air that Scheele had found was from the nitrous acid itself, not decomposed heat. The two differed fundamentally in their understandings of heat, phlogiston, and the relationship between the two. Even within a community actively engaged in affinity research and pneumatic analysis, multiple conceptions of heat and phlogiston existed.

In 1782, Kirwan presented a paper to the Royal Society entitled “Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances.”⁸⁷ Here Kirwan identifies phlogiston with inflammable air. Though originally proposed in 1766 by Henry Cavendish,⁸⁸ the equivalence of phlogiston and inflammable air had not been fully developed. Drawing on the analogy of elastic fixed air, which in its unelastic state can be fixed with “calcareous earth, alkalies, or magnesia,” Kirwan says that elastic inflammable air is, when in a fixed state, phlogiston.

This identification of inflammable air with phlogiston had huge implications for Kirwan’s explanations of chemical processes. Seymour Mauskopf has called this identification “an ambition *synthesis* of the traditional functions of phlogiston with the more recent British pneumatic chemistry, and the experimental discoveries of Lavoisier

⁸⁶ Ibid., 33.

⁸⁷ Kirwan, "Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances."

⁸⁸ Scott, “The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time”, 217.

concerning combustion and calcinations.”⁸⁹ For Kirwan, fixed air was produced from the chemical combination of inflammable air and dephlogisticated air. When heated, the phlogiston would be released from inflammable air and combine with dephlogisticated air eventually reaching equilibrium as fixed air.

Kirwan saw combustion as the rapid combination of dephlogisticated air with phlogiston. The fixed air produced had a lower heat capacity than dephlogisticated air, so sensible heat was produced in the form of fire. The formation of fixed air also occurs in calcinations. As dephlogisticated air rushes into the metal (as Lavoisier maintained), it is joined with the metal’s phlogiston. While some phlogiston is released into the air, the formation of fixed air results in a net gain in weight. When a calx was restored, this fixed air was released. Kirwan admits that “mercurial calx, and also the calces of lead, and many others, yield dephlogisticated air; but then the mercury is always revived, so that it is evident, it retakes the phlogiston from the fixed air, of which nothing remains then remains but the dephlogisticated part.”⁹⁰ This was a much more satisfactory explanation for weight gain than the idea that phlogiston has negative weight, which many proposed but few actually held.

One of the primary objections to Kirwan’s explanation of fixed air came from Henry Cavendish. Cavendish pointed out that inflammable air and dephlogisticated air often formed water when combined, rather than fixed air. Kirwan, using his Irvinist understanding of heat, responded that the formation of water was predictable when the two airs were combined at high temperatures. Because of the rarified state of the airs and their lack of specific heat (evident from the high sensible heat), the resulting combination

⁸⁹ Mauskopf: 191.

⁹⁰ Kirwan, "Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances," 228.

would be of the highest affinity and a denser physical state than usual. Rather than producing fixed air, the particles would be more closely combined in liquid water. Kirwan's chemical theory thus had consistent explanations for combustion, calcinations, and the composition of water. This was not a theory in a state of crisis but rather a stable paradigm parallel to the French system led by Lavoisier. Joseph Priestley, James Watt, and much of what Frederick Holmes identified as the British pneumatic community adopted Kirwan's concept of phlogiston.⁹¹

Kirwan published his *Essay on Phlogiston* in 1787.⁹² This was by far his longest and most thorough treatment of phlogiston. Kirwan used the work to refute several of Lavoisier's claims. In 1784, Lavoisier had conducted his gun barrel experiment; here he had heated a gun barrel to red-heat and passed water through it. Lavoisier, claimed that the water had been decomposed, the oxygen joining the iron to form a calx, while the left-over inflammable air was collected separately. Kirwan acknowledged the experiment but said that the water joined with the iron to form a calx, and the displaced phlogiston was collected as inflammable air. The two theories were thus shown to predict the same, experimentally verified result.⁹³ Kirwan also took this opportunity to attack Lavoisier's affinity table and used it to show that iron was more likely to have bonded with water in the gun barrel experiment than to have decomposed it.

Kirwan also elaborated a few new ideas on phlogiston. Kirwan had used the terms fixed air and aerial acid interchangeably since at least 1782 in his "Continuing Experiments." Kirwan believed that fixed air was the basis of acidity rather than either

⁹¹ Holmes.

⁹² Kirwan, *An Essay on Phlogiston, and the Constitution of Acids*.

⁹³ *Ibid.*, 101-102.

phlogiston or dephlogisticated air.⁹⁴ Kirwan admitted that Lavoisier's belief that oxygen was basis of acidity was more simple, but pointed to vegetable acids as a counter-example. Kirwan shows that the distillation of the acid of sugar results in water, inflammable air and fixed air. Neither charcoal nor dephlogisticated air is present. The production of fixed air rather than dephlogisticated air from this acid, suggests that fixed air is the principle of acidity.

The French Academy received Kirwan's Essay and quickly commissioned its translation to French. Marie-Anne-Pierrette Paulz Lavoisier translated the work anonymously.⁹⁵ 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?⁹⁶

⁹⁴ This is confirmed in a letter from Kirwan to Torbern Bergman from January 1793. See Scott, 256 for the text of the letter.

⁹⁵ Keiko Kawashima, "Madame Lavoisier Et La Traduction Française De L'essay on Phlogiston De Kirwan," *Revue d'Histoire des Sciences* 53 (2000).

⁹⁶ Richard Kirwan, *An Essay on Phlogiston, and the Constitution of Acids. A New Edition by R. Kirwan. To Which Are Added, Notes, Exhibiting and Defending the Anti-Phlogistic Theory; and Annexed to the French of This Work by Messrs. De Morveau, Lavoisier, De La Place, Monge, Berthollet, and De Fourcroy: Tr. Into English. With Additional Remarks and Replies, by the Author.* (London: J. Johnson, 1789), xiv-xv.

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.⁹⁷ 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.

This French translation was annotated by a battery of six French chemists: Claude-Louis Berthollet, Antoine Lavoisier, Pierre-Simon Laplace, Guyton de Morveau, Antoine Fourcroy, and Gaspard Monge. The authors draw out experimental differences in the two theories showing that they are not experimentally equivalent. Lavoisier notes that while hydrogen and oxygen always combine to form water, Kirwan would have inflammable air and dephlogisticated air forming fixed air, water, phlogisticated air, nitrous gas, and/or nitrous acid.⁹⁸

In 1789, Kirwan published a second edition of his *Essay* and included the notes of the French Academicians and his own replies. However, by 1791 Kirwan had admitted the defeat of phlogiston. In a letter to Berthollet from January 26, 1791, Kirwan lays down his arms, abandoning the system of phlogiston. Without a clear experiment to confirm the presence of inflammable air in fixed air, it is impossible to maintain the

⁹⁷ Académie des Sciences, *Registre*, 106 (1787), 255-257. See Heggarty, 194-195 for more on the position of the French Academy.

⁹⁸ Kirwan, *An Essay on Phlogiston, and the Constitution of Acids. A New Edition by R. Kirwan. To Which Are Added, Notes, Exhibiting and Defending the Anti-Phlogistic Theory; and Annexed to the French of This Work by Messrs. De Morveau, Lavoisier, De La Place, Monge, Berthollet, and De Fourcroy: Tr. Into English. With Additional Remarks and Replies, by the Author.*, 57.

presence of phlogiston in metals, sulfur, etc.⁹⁹ A letter to Crell, likely written at about the same time, also admits the abandonment of the phlogiston theory on the basis that fixed air cannot be shown to consist of vital air and phlogiston.¹⁰⁰

Though he may have relented to the aesthetically simpler French doctrine, he did not fully adopt the new nomenclature. Seymour Mauskopf points to the extensive dialog between the French and British chemical camps to refute the idea of Kuhnian communication gaps and incommensurabilities.¹⁰¹ However, Mauskopf appears to miss the point. The French campaign for a new nomenclature was in larger part an effort at escaping the accrued incommensurabilities of multiple phlogiston theories. Kirwan's reluctance to move to this new nomenclature was also because of his attention to the works of everyone from Becher and Stahl through Rouelle and Macquer up to Scheele, Bergman, and Priestley. In changing nomenclatures, his and the earlier works would either have to be translated or discarded. He recognized the pedagogical cost of this change in that these theories would become unintelligible to students of chemistry. Kirwan makes this point explicitly in several of his letters to Guyton de Morveau.¹⁰² In fact, Kirwan never fully adopted the French nomenclature. He still used the terms pure air, inflammable air, and charcoal as equivalent to the new counterparts. His works on

⁹⁹ "Enfin je mets bas les armes, et j'abandonne le phlogistique. Je vois clairement qu'il n'y a aucune expérience averée qui atteste la production de l'air fixe par l'air inflammable pur; et cela étant, il est impossible de soutenir le système de la présence phlogistique dans les métaux, le soufre, etc. Sans des expériences décisives, nous ne pouvons soutenir un système contre des faits avérés. Je donnerai moi même une réfutation de mon Essai sur le phlogistique." Letter from Kirwan to Berthollet, January 26, 1791, in Scott, 260

¹⁰⁰ Scott, "The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time", 260. Kirwan's letter to Crell admits the failure of the Stahl's theory. It is unclear though, whether he is differentiating here between Stahl's conception of phlogiston and his own. In chapter three, I will discuss how further research might elucidate how Kirwan's views on phlogiston changed in 1791.

¹⁰¹ Mauskopf: 205.

¹⁰² Guyton de Morveau and Kirwan.

mineralogy and meteorology from the 1790's show little trace of his conversion. In *On chymical and mineralogical nomenclature*,¹⁰³ Kirwan lampoons the new system:

This maxim, unhappily too easily adopted by the French School, tends to the subversion of the received language of all sciences, and even of common life. By this rule we are to banish the name water, and instead of it substitute its component ingredients hydrogenated oxygen or oxygenated hydrogen; and instead of ice we are to say decaloricated hydrogenated oxygen, and for steam, caloricated hydrogenated oxygen. Instead of common soap we are to say oleaginated soda.¹⁰⁴

While somewhat exaggerated, Kirwan's point is that the standard usages have an element of familiarity and a cultural acceptance lost in the acceptance of new nomenclature.

Applied Chemistry

In 1794, Kirwan responded to a contest sponsored by the Royal Irish Academy asking, "What are the manures most advantageously applicable to the various sorts of soils, and the cause of their beneficial effects in each particular instance?"¹⁰⁵ Kirwan's entry won the prize and was published in at least eight British editions and one American edition by 1822 and was also translated into German. Kirwan systematically lays out the properties of the various kinds of soils and manures before moving onto the "Food of Plants and the Composition of Fertile Soils."¹⁰⁶ Drawing on the chemical works of Hales, Priestley, Lavoisier, and others, Kirwan describes the chemical composition of the nutrients of plants, the plant's physical composition, and that of their byproducts. It is interesting that Kirwan uses the terms coal and fixed air, rather than carbon and carbon

¹⁰³ Richard Kirwan, "On Chymical and Mineralogical Nomenclature," *Transactions of the Royal Irish Academy* 8 (1802).

¹⁰⁴ Ibid.: 59. Reprinted in Scott, "The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time", 275.

¹⁰⁵ Richard Kirwan, *What Are the Manures Most Advantageously Applicable to Various Sorts of Soils, and What Are the Causes of Their Beneficial Effect in Each Particular Instance* Uniform Title: *Manures Most Advantageously Applicable to the Various Sorts of Soils* (Dublin: George Bonham, 1794). This text had gone through eight editions by 1822.

¹⁰⁶ Ibid., ch. 3.

oxide. Though he had renounced his belief in phlogiston in 1791, he never fully converted to the French nomenclature of Lavoisier and de Morveau.

In 1825, Joseph Hayward laid out the principles of agriculture drawing on the chemical theories of Kirwan, Humphrey Davy, Joseph Priestley, and others.¹⁰⁷ Hayward explicitly states the chemical equivalences between what he describes as Kirwan's gases, pure air, inflammable air, charcoal etc., with the French nomenclature. Having defined his chemical principles, Hayward studies the nutrition of plants and animals in a conscious effort to develop a systematic understanding of agriculture. Hayward's book shows that Kirwan's essay on manure and his relation of agriculture to chemistry had remained influential. The fact that Kirwan is clearly identified with the older nomenclature reiterates that Kirwan never fully accepted the terms oxygen, hydrogen, and carbon.

"Perhaps Kirwan's most important accomplishments were in the practical aspects of meteorology," suggests Diane Heggarty. She continues, "His knowledge of pneumatic chemistry was put to practical use in the study of the atmosphere."¹⁰⁸ Kirwan wrote extensively on the atmosphere and meteorology beginning with "An Estimate of the Temperature of Different Latitudes"¹⁰⁹ in 1787. Kirwan published meteorological observations in Ireland for 1793¹¹⁰ and, in the same year, a comparison of observations

¹⁰⁷ Joseph Hayward, *On the Science of Agriculture Comprising a Commentary on and Comparative Investigation of the Agricultural Chemistry of Mr. Kirwan and Sir Humphry Davy: The Code of Agriculture of Sir John Sinclair, Sir Joseph Banks, and Other Authors on the Subject* (London: Longman, Hurst, Rees, Orme, Brown, and Green, (A. & R. Spottiswoode), 1825).

¹⁰⁸ Heggarty, 270.

¹⁰⁹ Richard Kirwan, *An Estimate of the Temperature of Different Latitudes*. (London: printed by J. Davis, for P. Elmsly, 1787).

¹¹⁰ Richard Kirwan, *Meteorological Observations in Ireland in the Year 1793* (Dublin, 1794).

for the years 1788 through 1793.¹¹¹ Kirwan published a series of articles in the Transactions of the Royal Irish Academy, entitled “Synoptical view of the state of the weather at Dublin” for the years 1795 through 1808. In 1801, he published *On the variations in the atmosphere*¹¹² and in the 1810 volume of the *Transactions*, he presented a paper on a new design for the anemometer.¹¹³

Scott suggests that Kirwan’s interest in meteorology grew from his participation in the Chapter Coffee House meetings, although the meteorological uses of Irvinist studies of vapor, as exemplified by the Spanish meteorologist Du Carla, may have also inspired him.¹¹⁴ Meteorological papers by James Keir, Francois-Pierre Aimé Argand, Adair Crawford, and Kirwan himself show that the society was clearly interested in meteorology as a science. Upon returning to Ireland in 1788, Kirwan gave meteorological papers to the Royal Irish Academy and set up an observatory at his house collecting data from 1791 to 1808.¹¹⁵ Kirwan’s meteorological works largely studied how the atmospheric distribution of heat and vapor influenced barometric pressure and wind patterns. Kirwan repeatedly lamented the lack of consistent and precise data noting variations in thermometric scales and vague qualitative data which prevented him from studying broad international weather patterns. Nonetheless, Kirwan was successful

¹¹¹ Richard Kirwan, "A Comparative View of Meteorological Observations Made in Ireland since the Year 1788: With Some Hints Towards Forming Prognostics of the Weather," *Transactions of the Royal Irish Academy* (1794).

¹¹² Richard Kirwan, "Of the Variations of the Atmosphere," *Transactions of the Royal Irish Academy* 8 (1801).

¹¹³ Richard Kirwan, "A Description of a New Anemometer," *Transactions of the Royal Irish Academy* (1810).

¹¹⁴ Scott, "The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time", 390.

¹¹⁵ *Ibid.*, 400.

enough to be considered a good weather prognosticator by his contemporaries and served as a model for Dalton's fifth essay in his *Meteorological Observations and Essays*.¹¹⁶

In 1789, Kirwan wrote on bleaching calling it "a particular application of the general principles of chymistry."¹¹⁷ Kirwan notes that bleachers have become proficient in applying saline substances to their art, but says that they are less adept at understanding the powers of each substance or producing them. Kirwan then discusses barilha, a commonly used bleach, describing its production, physical appearance, chemical composition by specific weight, and bleaching efficacy.¹¹⁸ Kirwan begins to repeat his experiments and analysis on Dantzic Pearl Ash, but stops saying, "Disgusted by the tediousness of these experiments, and recollecting that the alkaline part of these salts was that alone with which bleachers had any concern, I bethought myself of an early practical method of discovering the presence of this principle."¹¹⁹ Kirwan then describes this experimental method for measuring the alkali content of a substance and presents a table of experimental results. Kirwan's analysis of alkali bleaching shows his belief in the usefulness of chemistry in everyday life and industrial production and his self-positioning as a popularizer of chemistry in Ireland.

While Kirwan's interest in bleaching was limited to his one abbreviated article, his work on mineralogy was much more extensive. In fact, entries on Richard Kirwan in biographical dictionaries often contrast the ultimate failure of his chemical theories with the success of his *Elements of Mineralogy*.¹²⁰ The eleventh and subsequent editions of

¹¹⁶ John Dalton, *Meteorological Observations and Essays* (London: W. Richardson, J. Phillips and W. Pennington, 1793).

¹¹⁷ Richard Kirwan, "Experiments on the Alkaline Substances Used in Bleaching, and on the Colouring Matter of Linen-Yarn," *Transactions of the Royal Irish Academy* 3 (1789): 3.

¹¹⁸ *Ibid.*: 5-13.

¹¹⁹ *Ibid.*: 14.

¹²⁰ Richard Kirwan, *Elements of Mineralogy* (London: Printed for P. Elmsly, 1784).

the Encyclopaedia Britannica refer to the book as the “first systematic work on the subject in the English language.”¹²¹ In the 1961 edition of the Encyclopaedia Britannica, Kirwan is identified not as a chemist, but as an “Irish scientist and author of a long-standard work on mineralogy.”¹²² However, contrasting Kirwan’s mineralogical and chemical legacies is ironic in that Kirwan considered mineralogy a sub-discipline of chemistry. In the *Elements of Mineralogy*, Kirwan says, “Mineralogy must, ... on the whole, be considered as a branch of Chymistry.”¹²³ Kirwan was involved in translating A. F. Cronstedt’s *Försök til Mineralogie*,¹²⁴ and he was also influenced by Torbern Bergman’s mineralogical work, both of which sought to classify minerals based on their chemical properties. Kirwan’s *Elements of Mineralogy* is a continuation of this effort to systematically classify minerals based on their chemical compositions.

Kirwan also wrote *An Essay on the Analysis of Mineral Waters*¹²⁵ in 1799.

Chemical analysis of mineral waters had been a focal study in France at the beginning of the eighteenth century. Claude Francois Geoffroy applied his Stahlian theories on salts and affinity to the study of sal ammoniac, a valuable medicinal salt manufactured in the Levant. Gilles-François Boulduc applied Geoffroy’s theories to other mineral waters,

¹²¹ “Richard Kirwan,” *Encyclopaedia Britannica*, 11th edition, (Cambridge: University Press, 1910). The same phrase is used in *A Biographical Dictionary of Scientists* edited by Trevor I. Williams, the *Biographical Encyclopedia of Scientists* (1984), the 14th edition and the 1961 edition of the *Encyclopaedia Britannica*, and elsewhere.

¹²² “Richard Kirwan,” *Encyclopaedia Britannica*, ed. Harry S. Ashmore, John V. Dodge, and Howard E. Kasch, (Chicago: Encyclopaedia Britannica Inc., 1961).

¹²³ Kirwan, *Elements of Mineralogy*, xii.

¹²⁴ Axel Fredrik Cronstedt, Gustav von Engeström, and João Jacinto de Magalhães, *An Essay Towards a System of Mineralogy*, The 2d ed. (London,: C. Dilly, 1788). For information on Kirwan’s involvement in the translation see Scott.

¹²⁵ Richard Kirwan, *An Essay on the Analysis of Mineral Waters* (London: Printed by J.W. Myers, for D. Bremner, 1799).

studying their compositions in order to artificially synthesize the valuable minerals through industrial processes.¹²⁶

Jan Golinski has suggested that medical practitioners in England seeking to show their education through knowledge of philosophical chemistry appropriated this tradition of chemical analysis. In *Science as Public Culture*, Golinski identifies the competitive self-marketing of medical practitioners saying, “By publishing analyses of the waters, practitioners could display their scientific skills and hope to enhance their reputation with prospective patients.”¹²⁷ Kirwan’s publication of *An Essay on the Analysis of Mineral Waters* thus fit into a popular chemical genre that included texts not only by Torbern Bergman, Antoine Fourcroy, and Joseph Black but also many, many others.¹²⁸

Kirwan also applied his interest in mineralogy to the study of mines and was appointed to the honorary position of Inspector of His Majesty’s Mines in Ireland, a designation that he used on the title page of his *Geological Essays*.¹²⁹ This was a compilation of short treatises like, “Of the Composition and Proportion of Carbon in Bitumens and Mineral Coal”¹³⁰ and “An Essay on the Declivities of Mountains.”¹³¹ Again, Kirwan was following in the footsteps of Bergman and Cronstedt.

Conclusion

Kirwan has been almost exclusively associated with his failed identification of phlogiston with inflammable air. Though an important part of his theories, phlogiston

¹²⁶ See Kim, 154-157 for more information

¹²⁷ Jan Golinski, *Science as Public Culture: Chemistry and Enlightenment in Britain, 1760-1820* (Cambridge; New York: Cambridge University Press, 1992), 62.

¹²⁸ According to Golinski, more than a hundred books were published on mineral waters during the eighteenth century. See Golinski, 62 for more information.

¹²⁹ Richard Kirwan, *Geological Essays* (London: Printed by T. Bensley for D. Bremner, 1799).

¹³⁰ Richard Kirwan, *Of the Composition and Proportion of Carbon in Bitumens and Mineral Coal* (Dublin: George Bonham, 1796).

¹³¹ Richard Kirwan, *An Essay on the Declivities of Mountains* (Dublin: George Bonham, 1800).

was only one area of research in Richard Kirwan's interlocking matrix of chemical work. Kirwan's participation in research on salts and affinity fit into a continental tradition of chemistry, that drew on the works of Stahl and Geoffroy and was an active area of research for Europe's leading chemists. Kirwan's application of mathematical analysis of affinities, similar to his work on specific gravities and heats, won him the Copley medal and international recognition.

Kirwan's studies on air also placed him in a distinctly British paradigm,¹³² which posed questions on heat and phase shift that had not been as important in the earlier studies of salts. Kirwan's Irvinist heat theory derived from the work of Joseph Black, William Irvine, and Adair Crawford was crucially important to his understanding of chemical reactions and properties and placed him in opposition to the French school and to Scheele.

Kirwan's participation in the Royal Society may have also had an effect on his epistemological beliefs. Many in Britain felt that Lavoisier and the French school had eschewed the gentlemanly collection of fact in favor of Cartesian systematic theories. The unified theoretical focus of the Académie des Sciences was antithetical to the empiricist tradition of science advocated by the Royal Society. The epistemological divide between the French understanding of science and that of the English was further exacerbated by nationalism and concern over the French Revolution. Through a historical style, citing a broad range of chemists, Kirwan developed a rhetoric of communal involvement that was sharply juxtaposed with Lavoisier's notoriously under-cited papers.

¹³² Holmes.

Although Lavoisier's experiments on calcification and water synthesis and analysis have been termed crucial experiments in the fight against phlogiston, chemists converted to the new nomenclature slowly. Kirwan's Irvinist theories of continued to be used to explain phase shifts into the nineteenth century. Lavoisier, himself, though admitting the deficiencies of affinity tables, continued to work on affinity theory, and it remained an important research topic for de Morveau and Berthollet. Even after Kirwan admitted the defeat of phlogiston in chemical experimentation, mineralogy, meteorology, and other fields of applied chemistry still used the old nomenclature in explaining experimental phenomena. Many within the correspondence network of chemists continued to apply the older nomenclature for its pedagogical uses and to maintain cogent trans-national communications. I hope that by exploring Richard Kirwan's novel interpretation of the phlogiston theory I have helped to develop a more nuanced understanding of phlogiston at the end of the eighteenth century and problematized historiographical understandings of Lavoisier's "crucial" experiments.

Chapter Three: Research Past, Present, and Future

In 1777, Richard Kirwan moved from Ireland to London to be closer to the intellectual elite and attend the meetings of the Royal Society. Upon his election to the Royal Society in 1780, Kirwan arranged for part of his scientific library to be shipped from his ancestral home, Cregg Castle in County Galway, to his new house in London. The collection was placed aboard the sailing ship, *Duke of Gloucester*, which departed on September 5, 1780 from Galway for Bristol. However, on the first day of the passage, the ship came under the lee of the American privateer *Pilgrim*, one of the most successful privateers of the American War for Independence. The Cabot brothers, perhaps the most successful financiers of American privateering, had fitted out the *Pilgrim* under the captaincy of Joseph Robinson for a cruise from March of 1780 to April 1781. Captain Robinson captured nine prizes, including the *Duke of Gloucester*. The primary cargo of kelp and the ship itself appear to have been burned but the books were apparently considered valuable enough to be preserved. In April, 1781, the books appeared at the auction of the rest of the *Pilgrim*'s prizes in Salem, Massachusetts.¹³³

Joseph Willard, Reverend at the First Church in Beverly, Massachusetts and founding member of the American Academy of Arts and Sciences, learned of the auction of the scientific collection in early April and quickly put together a group to buy the books. The Reverend Willard was joined by reverends John Prince and Thomas Barnard of Salem, and Manasseh Cutler of Ipswich Hamlet. In addition to the four reverends, the

¹³³ This account taken from the work of Harold Burstyn. Burstyn convincingly refutes earlier reports, which had claimed that different ships and different captains had been involved. For more information see Harold Burstyn, "The Salem Philosophical Library: Its History and Importance for American Science," *Essex Institute Historical Collections* 96, no. 3 (1960).

assembly had three doctors, Edward Augustus Holyoke, Joshua Fisher, and Joseph Orne. This group purchased Kirwan's books for 858 pounds, 10 shillings in paper money, or roughly thirty-eight dollars in hard currency.¹³⁴ (This group later offered remuneration to Kirwan, but he declined, noting that he was pleased his books were being put to good use and even made a donation to the library.)

The purchasers were educated, influential men with strong ties to the growing American scientific culture. A study of the Salem Athenaeum completed in 1960 by Harold Burstyn¹³⁵ notes that six of the founders were graduates of Harvard College and the seventh, of Yale. Willard, Holyoke, and Orne were among the founding members of the American Academy of Arts and Sciences in 1780, while Cutler, Fisher, Prince and Barnard joined soon afterwards.¹³⁶ Willard was chosen as the corresponding secretary for the American Academy of Arts and Sciences and was considered one of the best astronomers in America. In 1781, he was chosen to be President of Harvard College.¹³⁷ Reverend Manasseh Cutler published on botany, astronomy, and meteorology, while Reverend John Prince was a noted instrument maker; Thomas Barnard was the teacher of Benjamin Thompson (later Count Rumford), and Edward August Holyoke was a well-respected physician and the third president of the American Academy of Science.¹³⁸

Though some of these men were already members of the Salem Social Library – another subscription library based in Salem - they wanted to form a community library

¹³⁴ Cynthia B. Wiggin, "The Kirwan Collection at the Salem Athenaeum : With a Biographical Sketch of Richard Kirwan and History of Acquisition of the Collection," *Essex Institute Historical Collections* 102 (1966): 28.

¹³⁵ Burstyn.

¹³⁶ *Ibid.*: 175.

¹³⁷ *Ibid.*: 176-177.

¹³⁸ *Ibid.*: 180-184.

concentrated on science.¹³⁹ They named their new institute the Philosophical Library – the Philosophical Library was combined with the Social Library in 1810 and renamed the Salem Athenaeum. The list of early donations to the Philosophical Library confirms its scientific focus. Works by Buffon, Bernoulli, Wolff, Newton, Priestley, and Franklin were quickly acquired, as were the *Memoirs of the American Academy of Science* and the *Transactions* of the American Philosophical Society and the Royal Society of Edinburgh. After the merger of the two libraries, many of the patrons continued this scientific tradition. Nathaniel Bowditch, President of the American Academy of Arts and Sciences and a Fellow of the Royal Society of London, said of the Athenaeum,

I found near me a better collection of philosophical and scientific works than could be found in any other part of the United States nearer than Philadelphia. And by the kindness of its proprietors, I was permitted freely to take books from that library, and to consult and study them at pleasure. This inestimable advantage has made me deeply a debtor to the Salem Athenaeum.¹⁴⁰

Records of Bowditch's use of the library are still available from the first librarian's register. John Pickering, also President of the A.A.S. and Charles Grafton Page, one of the first to work on the electric motor, were also scientific patrons of the Athenaeum. Nathaniel Hawthorne and Supreme Court Justice Joseph Story are two of the more notable non-scientific users of the Athenaeum.

I came across the Salem Athenaeum's Kirwan archive while composing a reading list for this thesis. The acting director at the time, Gus Souza, was nice enough provide an article on Kirwan's collections written in 1966 by then librarian, Cynthia Wiggins. After several pages of explanation as to how Kirwan's library came to be in

¹³⁹ Ibid.: 174.

¹⁴⁰ Charles W. Upham, "Memoir of Francis Peabody," *Essex Institute Historical Collections* 9, no. 1 (1868): 24.

Massachusetts, Wiggin lists thirty-nine different titles from the collection, many of which were multi-volume works. Included were works by Robert Boyle and Isaac Newton as well as Kirwan's contemporaries like Joseph Priestley, Erasmus Darwin, and Benjamin Franklin. There were also up to date runs of the *Philosophical Transactions* of the Royal Society and the *Memoirs* of the French Academy of Science. Kirwan's books represented an extremely current working scientific library that spanned a wide breadth of subjects. Wiggin's list noted that eight of these monographs and many of the journals contained Kirwan's signature.

Between reading Wiggin's account of the collection and my trip to Salem Athenaeum in January of this year, I came across a footnote about the library in E. L. Scott's 1979 dissertation on Kirwan.¹⁴¹ Upon visiting the Athenaeum, Scott found that many of the books listed by Wiggin could not have been in Kirwan's original collection, because they were published after they would have been captured in September of 1780. One assumes that he is referring to the later issues of the various society's journals, but Scott does not clarify the point. He concludes that the only books that can be definitively traced to Kirwan are those with his signature.

When I visited the Athenaeum, I particularly wanted to see Richard Kirwan's signature and look for possible marginalia in his books. I hoped that I might be able to find a sample of his bookplate, or a shelf mark, which I could use to definitively clear up the confusion between Scott's account and that of Cynthia Wiggin. I first looked at

¹⁴¹ Scott, "The Life and Work of Richard Kirwan (1733-1812): With Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time".

George Costard's *The History of Astronomy*,¹⁴² one of the books on Wiggin's list that was supposed to have Kirwan's signature. I opened the book expecting to see an owner's signature on the front page, the inside of the front cover or even on the title page. When I failed to find a signature in any of these places, I turned to the back cover and the back pages. After these pages proved blank, I resorted to flipping page by page through the text; however, the book did not have any markings other than the Athenaeum bookplate. I next turned to Priestley's *The History and Present State of Discoveries Relating to Vision, Light, and Colours*.¹⁴³ Kirwan and Priestley corresponded extensively and much of Kirwan's chemical theory was based on Priestley's experiments. I had thus hoped that I would find notes, marginalia, or simple underlining from Kirwan. However, this book was also blank other than the library's bookplate. After this, I asked for the rest of the quarto's on Wiggin's list that were supposed to have contained Kirwan's signature. One by one, I flipped through these, but failed to find any signatures, until I got to entry thirty-six out of thirty-nine on Wiggin's list. Many of the volumes of the *Histoire de L'Academie Royale Des Sciences* did in fact contain a clear signature, usually "R. Kirwan." The volumes of the *Philosophical Transactions* also often contained Kirwan's name.

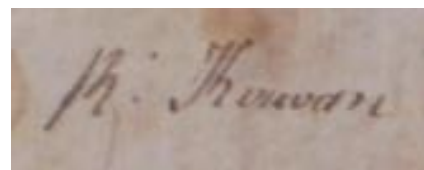


Figure 2 – Courtesy of the Salem Athenaeum from the *Philosophical Transactions* vol. 9

Whether these were in fact examples of Kirwan's signature can be evaluated by comparison with texts from the Royal Irish Academy (RIA). Kirwan was president of the RIA from 1799 until his death in 1812. In his will, Kirwan bequeathed many of his

¹⁴² George Costard, *The History of Astronomy, with Its Application to Geography, History, and Chronology; Occasionally Exemplified by the Globes* (London: Printed by J. Lister, and sold by J. Newberry, 1767).

¹⁴³ Joseph Priestley, *The History and Present State of Discoveries Relating to Vision, Light, and Colours* (London: Printed for J. Johnson, 1772).

books to the Academy, a list of which is still held by in the Academy's library.¹⁴⁴

Kirwan's copy of Joseph Priestley's *Experiments and Observations on Different Kinds of Air* has his signature and an inscription on the title page (see figure A).

Kirwan's inscription reads, "Vos Exemplaria [Graeca] Nocturna versate manu, Versate diurna Vos."¹⁴⁵ This is a quote from Horace's *Ars Poetica* instructing the young to "study the pages of your Greek exemplars by day and night." In studying the handwriting between Kirwan's signature and inscription, and Kirwan's name in several of the Athenaeum's texts (see appendix), we see an initial resemblance. The "R: d" with which he signs his first name appears similar both in style and in pen strokes. However, the "K" in Kirwan has an exaggerated flourish in the RIA signature that is lacking in any of the Athenaeum's characters. The "a's" in Kirwan's

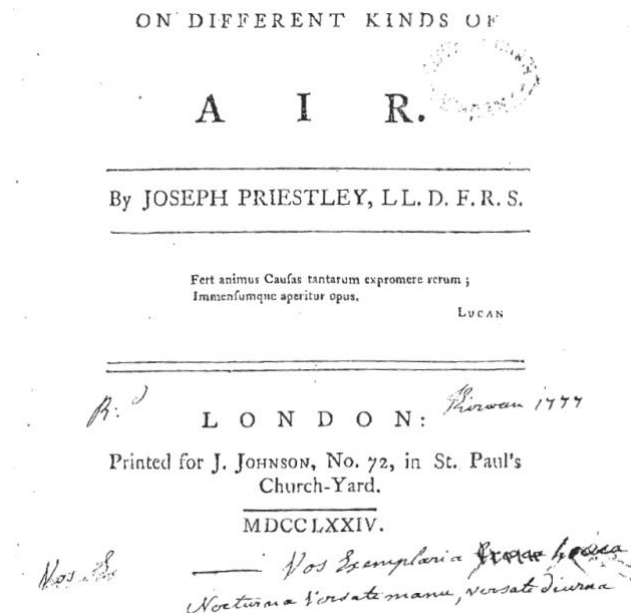


Figure 3 - Courtesy of the Royal Irish Academy

RIA signature and inscription usually do not have ligatures and are round. The "a's" in the Athenaeum signatures do have ligatures and are more square. The "n's" also lack ligatures in the RIA signature and inscription while they are connected to the "a" in Kirwan's Athenaeum signatures.

¹⁴⁴ William Brooke, *A Catalogue of Books Bequeathed by the Late Richard Kirwan Esq. To the Royal Irish Academy* (Dublin: Royal Irish Academy, 1813).

¹⁴⁵ "Graeca" is crossed out in Kirwan's inscription. This suggests that Kirwan saw Priestley's book as a modern exemplar to be thoroughly studied.

I think it is possible that the books at the Salem Athenaeum featuring Kirwan's name, may have been inscribed by Reverend John Prince when he bought the books or by one of the other librarians simply marking the origin of the books. However, Kirwan did put his name in many of his books, as evidenced by this volume of Priestley and many others in the RIA, and the signatures are close enough that I cannot make any definitive judgments on their validity.

Whether or not the handwriting in these books is from Kirwan, many of the books that Wiggin claims are signed, contain no writing at all. I asked the current librarian of the Salem Athenaeum, Jean Marie Prociou, about the discrepancy between Wiggin's account of Kirwan's collection and the physical copies of the books, and she pointed me to the original list of Kirwan's books in the library charter titled, "The Records of the Philosophical Library." Currently stored at the Peabody Phillips Library, also in Salem, for preservation, this charter appears to have eluded the attention of Scott on his visit to Salem.

The charter contains two treatises, the first by librarian Joseph Willard and the second by the clerk, Reverend John Prince; both men include narratives of the founding of the library; Willard also has a list of the books in the library, and Prince includes minutes from the yearly meetings. It is Prince's account that shows the constitution of the collection as originally purchased.

Prince bought the collection in April 1781, and his account was written just three months later, in June. He says, "On the 12th of April, 1781, the said books, consisting of the greater part of the Philosophical Transactions of the French Academy, the Royal Society of London, and the Society of Berlin in Quarto and the works of Sir Robert Boyle

complete in Folio, making in all one hundred and sixteen volumes sold to him for £858.10 in paper money..."¹⁴⁶ This narrative seems straight forward and unambiguous in its account of the books in the Kirwan library: one hundred sixteen volumes were divided between the journals of these societies and the folio works of Robert Boyle. From where then did Wiggin's extensive list of monographs by Newton, Priestley, Franklin and others, come? The confusion about the contents of the collection appears to arise from the librarian's list of books in the original charter.

Willard lists eleven volumes of the *Philosophical Transactions* abridged, seventeen volumes of the *Philosophical Transactions at Large*,¹⁴⁷ eleven of the *Memoires de l'Academie Royale des Sciences*, sixty-three of the *Histoire de l'Academie Royale des Sciences* and seven of the *Miscellanea Berolinensia*. These journals comprise the bulk of the collection and match well with Prince's account. It is the next page where the two accounts differ. Willard lists Ame's *Art of Printing*, fifteen volumes of Buffon's *Histoire Naturelle*, five of Boyle in folio, and two of Harris' *Lexicon Technicum* also in folio. It appears from this librarian's list that these books were added to the collection at the same time. However, Prince says that only Boyle's works were in the original purchase. There is no explicit delineation between the original, Kirwan library, and the philosophical library as a whole. Willard's list is likely a better representation of the state of the Philosophical Library in 1810 when it was merged with the Social Library.

Resolution between Willard's and Prince's accounts can be found in the minutes of the meetings of the library group. The notes show that Ame's *Art of Printing* was a gift from Prince at the first meeting and that the *Lexicon Technicum* was a gift from

¹⁴⁶ Joseph Willard and John Prince, "Records of the Philosophical Library, 1780," Salem.

¹⁴⁷ While the entry for the *Philosophical Transactions at Large* lists volumes forty-seven through ninety-seven, a line clearly indicates that volume sixty-four was the last in the original purchase.

Reverend Barnard. The minutes reflect continuing purchases of new volumes of the journals, further donations, and subscription purchases. Further confirmation of Prince's account can be found in the books themselves. All five of Boyle's folio books have Kirwan's name in them. Many of the *Philosophical Transactions* volumes and the majority of the *Memoires* and *Histoires* of the Academie des Sciences are also marked with his name.

Wiggin was not the first to mistake Willard's list of the books in the Philosophical library, for Kirwan's collection, which had formed its foundation. The Philosophical Library and the Salem Athenaeum have been the focus of several articles in the journal, *Essex Institute Historical Collections*. Henry Wheatland was the first to write about the library in 1862.¹⁴⁸ Wheatland notes the scientific focus of the library and recounts the story of Kirwan's library from Bowditch's will. Wheatland also reproduces passages from the then recently rediscovered charter of the library, "The Records of the Philosophical Library." Wheatland reprints the rules and regulations of the library, as well as interesting excerpts from the minutes. Wheatland's article was followed six years later in a eulogy of Francis Peabody by Charles W. Upham.¹⁴⁹ This long, rambling account contains a basic narrative of the founding of the library along with biographical information about the founders and numerous other patrons and people from the Salem area. The next text was published in 1927 by Harriet S. Tapley. Though again published by the Essex Institute, Tapley's work was a monograph on the history of books, printing,

¹⁴⁸ Henry Wheatland, "Historical Sketch of the Philosophical Library at Salem, with Notes," *Essex Institute Historical Collections* 4, no. 1 (1862).

¹⁴⁹ Upham.

and sales in Salem.¹⁵⁰ Tapley revisited “The Records of the Philosophical Library,” quoting several passages from this original manuscript that were not in Wheatland’s 1862 article. While Tapley agrees with Wheatland that there were 116 volumes in the original purchase, she reproduces the librarian’s list of books in the Philosophical Library, blurring the line between it and the original Kirwan Collection.¹⁵¹

Tapley’s conflation of the library holdings was repeated by J. R. Partington and T. S. Wheeler.¹⁵² While looking at Kirwan’s influence on the Irish chemist William Higgins, Partington and Wheeler came across Kirwan’s collection at the Salem Athenaeum. In 1956, Wheeler visited the library, and noted the discrepancy between the notes on the original number of books (116) and the much larger collection as shelved. Wheeler and Partington concluded that there was no way to reestablish which books had been in the original purchase and reproduced the list from Tapley.

In 1960, another article was published in the *Essex Institute Historical Collections*, this time by Harold Burstyn.¹⁵³ Burstyn examined the original collection and retold the entire narrative of the library correcting several long-standing mistakes. Michael Donovan, Kirwan’s first biographer, had claimed that the privateer was captured by a cousin of Richard Kirwan who allowed “the domestics of his illustrious relative to proceed on their voyage to London” while keeping the books as prize.¹⁵⁴ Henry Wheatland had also misidentified the captain while Harriet Tapley had misidentified the

¹⁵⁰ Harriet Silvester Tapley, *Salem Imprints, 1768-1825: A History of the First Fifty Years of Printing in Salem, Massachusetts, with Some Account of the Bookshops, Booksellers, Bookbinders and the Private Libraries* (Salem: Essex Institute, 1927).

¹⁵¹ Ibid., 250-251.

¹⁵² Partington and Wheeler.

¹⁵³ Burstyn.

¹⁵⁴ Donovan, "Biographical Account of the Late Richard Kirwan," xcii.

ship captured.¹⁵⁵ Burstyn established that the *Duke of Gloucester*, was captured on September 5, 1780 by Captain Joseph Robinson. He also agrees with Wheatland's account of Kirwan's library and appears to have returned again to the original manuscript for verification.¹⁵⁶

Burstyn's definitive article could have signaled the end to publication on the history of the Philosophical Library, but it was followed by a publication in 1966 by then Salem Athenaeum curator Cynthia Wiggin. Though she cites Burstyn's article, she makes the same mistakes as Tapley on the boats involved in the capture of Kirwan's library. What is far more troubling though is Wiggin's account of the books in the Kirwan Collection. Wiggin cites Burstyn and paraphrases him. She says, "Included in the sale were the greater part of the Philosophical Transactions of the French Academy, The Royal Society of London, and The Society of Berlin in quarto, and the Works of Sir Robert Boyle in Folio,"¹⁵⁷ which is correct. However, she goes on to reproduce Tapley's list of thirty-nine different titles, now resorted into alphabetical order.

While Wiggin was not the first to make the mistake of confusing the Kirwan collection with the rest of the Philosophical Library, her claims about Kirwan's signature were novel. At first, one might give her the benefit of the doubt, assuming that the ink had faded in some volumes since her report or that library bookplates covered the signatures. However, Burstyn had written his article only six years earlier and had not found any of these signatures. John Prince's records in the library charter further confirm

¹⁵⁵ Tapley had concluded, based on the initial auction announcement in the April 3, 1781 *Salem Gazette* that Kirwan's collection had been aboard the *Mars*, one of the other ships captured by the *Pilgrim*. Burstyn shows that this was not the case. Burstyn: 171.

¹⁵⁶ Ibid.: 172.

¹⁵⁷ Wiggin: 28.

that these books were not in the original collection. Why Wiggin claimed that Kirwan's signature was in these volumes remains a mystery.

Though the number of books captured from Kirwan's library is much smaller than I had originally expected, several things stand out when reviewing the list. The collection of journals and Kirwan's extensive citations in his works shows that he was interested in the most up to date writings on science in a broad range of topics. While Nathaniel Bowditch attributed much of his success to Kirwan's collection, the only volumes that were unique to it in the Boston area were the *Memoirs of the Berlin Academy*. However this is interesting in that the *Memoirs* contained the early works of George Ernst Stahl, one of the founders of the phlogistic theory. It is also noteworthy that Kirwan ultimately replaced all of the books lost, as is evidenced by the library that he bequeathed to the Royal Irish Academy at his death.

Future Research

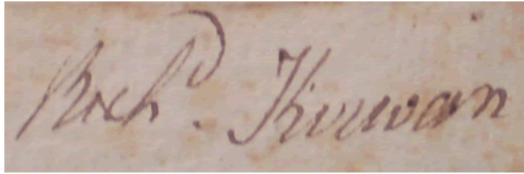
While I have shown that phlogiston was only one part of a Kirwan's novel and extensive chemical theory, further research is need to understand how Kirwan's theory changed in 1791 when he admitted the defeat of phlogiston. Douglas Allchin has shown that phlogiston theories did not disappear even after the broad acceptance of oxygen.¹⁵⁸ The volume of Kirwan's writings on theoretical chemistry declined after 1791, but he continued to write on meteorology, mineralogy, and other fields that he felt would benefit from the application of chemical principles. Through closer study of Kirwan's works over the last two decades of his life, I think we can better understand how chemical theories were changing from 1790-1810. Research on the field practices of agriculture

¹⁵⁸ Douglas Allchin, "Phlogiston after Oxygen," *Ambix* 39, no. 3 (1992).

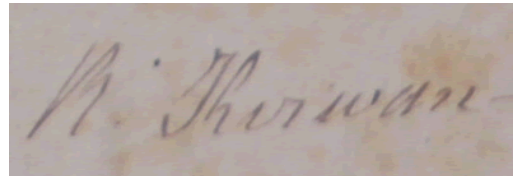
and meteorology in Ireland and the rest of Europe may also show how chemistry was being applied by a broader segment of the population.

A key resource that has been overlooked, at least in Kirwan's case, is his correspondence. While the collected correspondence of Torbern Bergman, Antoine Lavoisier, and Joseph Priestley have been separately published, Kirwan's has not. Nonetheless, Kirwan was at the center of an international correspondence network that included well-known experimenters, publishers, society heads, industrialists, and amateurs. Archival research at the Royal Irish Academy and the Chemical Heritage Foundation along with the caches of several other libraries in France will illuminate Kirwan's participation in the development of chemistry at this time, along with the ever changing and largely unpublished thoughts of a broad swath of his contemporaries. I believe that this analysis will further show that Kirwan was at the center of both British and European science, and that Lavoisier was more concerned with refuting Kirwan's theories than the long outdated principles of Stahl. Furthermore, a study of the larger network surrounding Kirwan during this time will hopefully shed new light on how chemical science was conducted by means of correspondence networks.

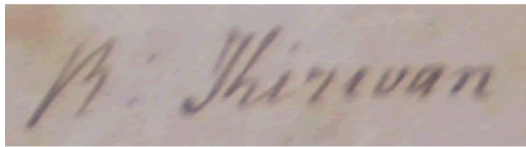
APPENDIX



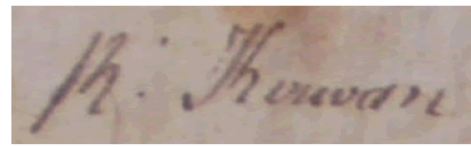
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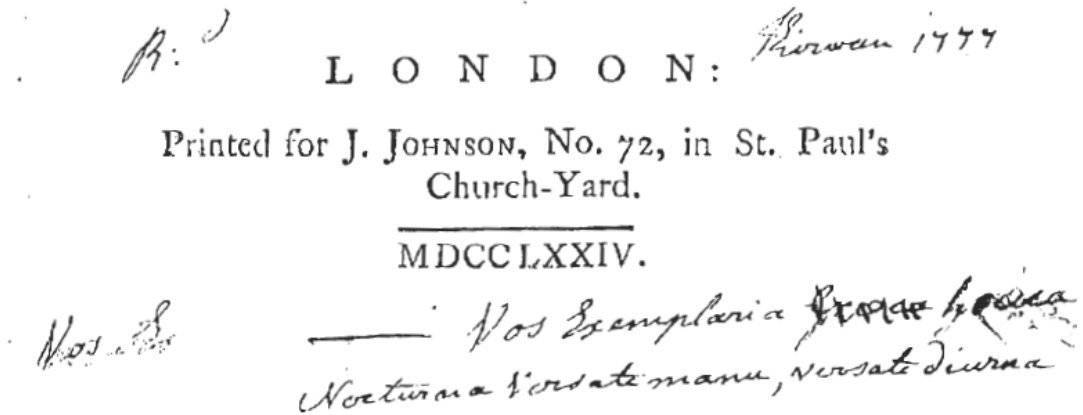


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Philosophical Transaction vol 9

Courtesy of the Salem Athenaeum.



Courtesy of the Royal Irish Academy.

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