An Arc Across Fields of Study:
Electricity in Physics and Chemistry (1751-1807)

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Abstract

Electricity does not obey disciplinary boundaries, yet its history is dominated by stories of heroic physicists and engineers. These histories do not reflect its dynamic nature. My dissertation analyzes how the concept ‘electricity’ evolved from a material fluid to a force as scientists’ chemical concepts changed. By analyzing the history of electricity from a chemical perspective, my dissertation demonstrates that the study of electrical phenomena played an important role in the emerging field of chemistry. It focuses on the period between 1751, when Benjamin Franklin published *Experiments and Observations on Electricity*, and 1807, when Humphry Davy published *On Some Chemical Agencies of Electricity*.

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A Note on Terminology

For clarity, I have included in parentheses the modern chemical terms for substances to help the reader more easily follow technical aspects of the discussion. I hope this does not diminish the conceptual difficulties facing chemists in the late eighteenth and early nineteenth centuries. This was a transformative period in which materials, chemical behaviors, and properties were being redefined. It is, therefore, important to recognize not only chemists' efforts to systematize their terminology, but also the theoretical implications of that language.[1]

Antoine Lavoisier argued for a new nomenclature in the joint work, *Methods of Chemical Nomenclature* (1787),[2] and in *Elements of Chemistry* (1789).[3] Drawing on developments in systematics, he noted that "the name of the class or genus is that which expresses a quality common to a great number of individuals: the name of the species, on the contrary, expresses a quality peculiar to certain individuals only." He then applied this philosophy to the naming of chemical compounds.[4]

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[1] See for example, Bernadette Bensaude-Vincent and Ferdinando Abbri, eds., *Lavoisier in European Context: Negotiating a New Language for Chemistry*, *European Studies in Science, History and the Arts* (Canton: Science History Publications, 1995); Marco Beretta, *The Enlightenment of Matter: The Definition of Chemistry from Agricola to Lavoisier* (Canton, MA: Watson Publishing International, 1993); Maurice Crosland, *Historical Studies in the Language of Chemistry* (Cambridge, MA: Harvard University Press, 1962); Jan Golinski, "The Chemical Revolution and the Politics of Language," *The Eighteenth Century* 33 (1992): 238-251; Frederick L. Holmes, *Eighteenth Century Chemistry as an Investigative Enterprise* (Berkeley: University of California-Berkeley, 1989), 16; Ursula Klein and Wolfgang Levfèvre, *Materials in Eighteenth Century Science: A Historical Ontology* (Cambridge, MA: The MIT Press, 2007).

[2] Guyton de Morveau et al., *Method of Chymical Nomenclature... To Which Is Added a New System of Chemical Characters*, trans. James St. John (London: G. Kearsley, 1788).

[3] Antoine Lavoisier, *Elements of Chemistry [1789]*, trans. Robert Kerr (New York: Dover Publications, 1965).

[4] Ibid, xxvi.

For instance, when an element was experimentally found to be a common constituent in many acids (a group of sour-tasting, corrosive substances), Lavoisier named it oxygen, meaning “acidifying principle”. He also suggested that “every combination of oxygen with a combustible substance” be denoted “by the term… oxygenation.”[5] He then argued that the substance “peculiar to each acid”, that which “distinguishes it from the rest”, should determine “the name of the species.”[6] For example, nitrous acid, synthesized by Henry Cavendish in 1788,[7] indicated an acid composed of azote (nitrogen) and oxygen. It is interesting to note that although Lavoisier advocated calling the element azote, meaning “noxious” because in its gaseous form it did not support respiration, he adopted nitrogen as the root word for its compounds.[8] Others supported using the term nitrogen for the element, meaning “generator of saltpeter” because it was a key ingredient in gunpowder.[9]

To differentiate between acids made of the same kind of materials, but in different proportions, Lavoisier suggested the following:

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[5] Ibid, 61-62.

[6] Ibid, xxvii-xxviii.

[7] Henry Cavendish, "On the Conversion of a Mixture of Dephlogisticated and Phlogisticated Air into Nitrous Acid, by the Electric Spark," *Phil. Trans.* 78 (1788): 261-276; Lavoisier, *Elements of Chemistry [1789]*, 197.

[8] Lavoisier, *Elements of Chemistry [1789]*, 53.

[9] Ibid, 214 and Jean-Antoine Claude Chaptal, *Elements of Chemistry*, trans. William Nicholson (Philadelphia: Lang & Ustick, 1796).

Lavoisier's Name	**Old Name**[10]	**Degree of Oxygenation**[11]	**Compound Properties**	**Chemical Formula**
Nitrous oxyd	Base of Nitrous gas	First	Weak base of nitrogen and oxygen	NO
Nitrous acid	Smoaking nitrous acid	Second	Weak acid of nitrogen and oxygen	HNO_2
Nitric acid	Pale nitrous acid	Third	Stronger acid of nitrogen and oxygen	HNO_3
Oxygenated nitric acid	Unknown	Fourth	Acid of nitrogen and oxygen	NO_3

Table I: Nomenclature for Combinations of Azote [Nitrogen] and Oxygen

The endings referred to the degree of oxygenation of the substance. For instance, the ending -yd (or -ide) referred to the first degree of oxygenation. Nitrous oxide was a known base in which small amounts of oxygen were present. The ending –ous in nitrous acid indicated a compound of azote (nitrogen) and oxygen of the second degree. It contained more oxygen than nitrous oxide and so correspondingly took on the qualities of a weak acid, its oxygen-like properties overshadowing the qualities of azote. The ending –ic referred to a substance of the third degree. Nitric acid was, therefore, more acidic than nitrous acid, and so on.

Often in the late eighteenth century, the name given to a material reflected its perceived role in chemistry. For instance, each of these terms, azote, nitrogen, and oxygen, privileged a specific property of the substance. This, however, led to confusion. Difficulties arose, for example, when it was discovered that a number of acids, such as muriatic (hydrochloric) and fluoric (hydrofluoric) acid, did not contain oxygen.

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[10] Lavoisier, *Elements of Chemistry [1789]*, 194. Columns one and two are from "Table of the Binary Combinations of Azote [nitrogen] with the Simple Substances".

[11] Ibid, 184. Column three comes from "Table of the Binary Combinations of Oxygen with Simple Substances".

Derivatives of certain acids, like oxygenated muriatic (chlorine) gas,[12] were also revealed not to be compounds.[13] Furthermore, many strong bases, such as lime (calcium oxide) and soda (sodium bicarbonate), were shown to contain oxygen.[14] Thus, further experiments demonstrated that oxygen's role in chemical combinations was much more complex than its name *acid generator* indicated.[15]

Nomenclature reflected both chemists' experimental observations and their theoretical commitments.[16] Although modern chemistry continues to use many of the terms developed between the seventeenth and nineteenth centuries, such as acid and oxygen, the meaning of these words have changed to reflect our current understanding of chemical processes. Understanding the etymology of these terms reveals important information about the conceptual development of science. For the interested reader, I have included a glossary of terms (Appendix I), which incorporates the definition used in the late eighteenth and early nineteenth century and its modern meaning where possible.

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[12] Humphry Davy, "Researches on the Oxymuriatic Acid, Its Nature and Combinations; and on the Elements of the Muriatic Acid. With Some Experiments on Sulphur and Phosphorus, Made in the Laboratory of the Royal Institution," *Phil. Trans.* 100 (1810): 231-257.

[13] Humphry Davy, "Some Experiments and Observations on the Substances Produced in Different Chemical Processes on Fluor Spar," *Phil. Trans.* 103 (1813): 263-279; Humphry Davy, "Some Experiments and Observations on a New Substance which becomes a Violet Coloured Gas by Heat," *Phil. Trans.* 104 (1814): 74-93.

[14] Humphry Davy, "The Bakerian Lecture: On Some Chemical Agencies of Electricity," *Phil. Trans.* 97 (1807): 1-56.

[15] Homer E. Le Grand, "Ideas on the Composition of Muriatic Acid and Their Relevance to the Oxygen Theory of Acidity," *Annals of Science* 31 (1974): 213-226, 224.

[16] William Nicholson, *A Dictionary of Chemistry*, 2 vols. (London: printed for G.G. and J. Robinson, 1795), preface.

List of Abbreviations

Joseph Priestley, *Experiments and Observations on Different Kinds of Air* – Air
Joseph Priestley, *History and Present State of Electricity* - HPSE
Journal of Natural Philosophy, Chemistry, and the Arts – Nicholson's Journal
Nuova Voltiana: Studies on Volta and His Times – Nuova Voltiana
Philosophical Transactions of the Royal Society – Phil. Trans.

Preface

This dissertation is about three things: the study of electricity, experimentation, and disciplinary identity or the lack thereof in the eighteenth and early nineteenth centuries. In the process of becoming acquainted with the historical literature, I was struck by historians' tendency to pigeonhole scientists' practice. For example, a recent debate on the chemical revolution examines whether Joseph Priestley is best described as a chemist or a natural philosopher.[17] I do not think these two categories need to be mutually exclusive. Priestley did not question whether it was appropriate to be interested in both the development of electrometers, instruments designed to detect and measure electricity, and chemical experiments. He comfortably conducted research in both areas.[18] Similarly, historians often draw lines between instrument makers and scientific practitioners, theoreticians and experimentalists.[19] This dissertation demonstrates that such divisions perpetuate false premises about the character of eighteenth-century science. Joseph Priestley, Henry Cavendish, Antoine Lavoisier, William Nicholson, Tiberius Cavallo, Alessandro Volta, and many others were actively involved in the practice of natural philosophy, chemical experimentation, and the development of

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[17] See, for example, Frederick L. Holmes, "The Revolution in Chemistry and Physics: Overthrow of a Reigning Paradigm or Competition between Contemporary Research Programs," *Isis* 91 (2000): 735-753; John McEvoy, "Electricity, Knowledge, and the Nature of Progress in Priestley's Thought," *British Journal for the History of Science* 12 (1979): 1-30.

[18] See, for example, Joseph Priestley, *Experiments and Observations on Different Kinds of Air* (London: J. Johnson, 1775a) and Joseph Priestley, *History and Present State of Electricity, with Original Experiments* (London: J. Dodsley, 1767).

[19] See, for example, Christine Blondel, "Electrical Instruments in 19th Century France, between Makers and Users," *History and Technology* 13 (1997): 157-182; Deborah Warner, "Review: What is a Scientific Instrument, When did It become One, and Why?," *British Journal for the History of Science* 23 (1990): 83-93.

instruments. They also advocated experiment-based theory. They were harbingers of quantitative experimental science.

There can obviously be good intellectual reasons for examining one facet of a scientist's life and practice, but something is lost when analyzing a broader change in scientific methods and discourse. Historians argue that experimental physics became a quantitative science over the course of the eighteenth and nineteenth centuries. Traditionally, one way to analyze this development is through the study of electricity. Eighteenth-century electrical research demonstrated that careful experimentation could lead to the development of laws, mathematical expressions of the physical relationships between dependent variables, as evidenced by Charles-Augustin Coulomb's study of electrical forces with a torsion balance.[20] Although this is a key aspect of experimental physics, there were other features of conceptual importance to the development of quantitative science emerging in this period, such as measurement, e.g. precision, accuracy, experimental error, knowing how an instrument works, and what it measures, and new emphasis on procedure, e.g. knowing how the order of operations affects experimental results, their reliability, and the conclusions that can be drawn from observation and/or measurement. Moreover, by advocating that the study of electricity belongs to the history of physics, historians have neglected the variety of experimental methods and approaches used to analyze electrical phenomena. This dissertation

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[20] See, for example, Peter Heering, "The Replication of the Torsion Balance Experiment: The Inverse Square Law and Its Refutation by Early 19th-Century German Physicists," in *Restaging Coulomb: Usages, Controverses et Réplications Autour la Balance de Torsion*, ed. Christine Blondel and Matthias Dörres (Florence: L.S. Olschki, 1994), 47-66; Peter Heering, "Regular Twists: Replicating Coulomb's Wire-Torsion Experiments," *Physics in Perspective* 8 (2006): 52-63; Alberto A. Martinez, "Replication of Coulomb's Torsion Balance Experiment," *Archive for History of Exact Sciences* 60 (2006): 517-563.

demonstrates that chemists and natural philosophers practicing chemistry were also deeply concerned with and invested in the study of electricity and the development of experimental science as a whole.

This work analyzes the development of electrical research in a broad context. It considers the contributions of scientists not normally included in the history of electricity because they were involved in chemical studies, such as Joseph Priestley, William Nicholson, and William Cruickshank. It also focuses mainly on British electricians for three reasons.

First, in the early to mid nineteenth century, British scientists openly lamented the sorry state of mathematical science in Britain. Charles Babbage, for example, criticized his contemporaries for adhering to outdated modes of mathematical analysis. Similarly, historians of physics often overlook late eighteenth and early nineteenth-century British natural philosophy because it did not have the same mathematical character as research being conducted elsewhere, especially in France.[21] Although British natural philosophers and chemists may not have developed sophisticated mathematical accounts of electrical phenomena, they did make significant contributions to the development of quantitative experimental methods in electrical research.[22]

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[21] Harvey Becher, "Radicals, Whigs, and Conservatives: The Middle and Lower Classes in the Analytical Revolution at Cambridge in the Age of Aristocracy," *British Journal for the History of Science* 28 (1995): 405-426; Jed Z. Buchwald, "Discrepant Measurements and Experimental Knowledge in the Early Modern Era," *Archive for History of Exact Sciences* 60 (2006): 565-649; Maurice Crosland, "A Science Empire in Napoleonic France," *History of Science* 44 (2006): 29-48; Eugene Frankel, "J.B. Biot and the Mathematization of Experimental Physics in Napoleonic France," *Historical Studies in the Physical Sciences* 8 (1977): 33-72.

[22] A notable exception to this trend was Henry Cavendish, who did develop a sophisticated and comprehensive mathematical account of electricity using similar methods as Franz Aepinus. This will be discussed further in chapter two. See, for example, Henry Cavendish, "An Attempt to Explain Some of the Principal Phenomena of Electricity, by Means of an Elastic Fluid," *Phil. Trans.* 61 (1771): 584-677.

Second, British electricians were in a unique position to study the chemical changes associated with electricity. There was a long history of examining the chemistry of airs in Britain. After Benjamin Franklin marshaled evidence demonstrating that lightning was a form of electricity in 1751, British experimentalists began to analyze the effects of electricity on gas composition. Their researches on atmospheric electricity and gas chemistry were often at the forefront of electrical science in the late eighteenth century.

Third, British electricians frequently discussed in publications and correspondence changes in continental-European natural philosophy. In an age characterized by exploration and industriousness, Priestley, Nicholson, and other members of the scientific community energetically sought out foreign scholars’ works on electricity and chemistry. Continental-European natural philosophers and chemists were similarly aware of British theories and experiments through this active correspondence network. British scientists further benefited from the close ties that electricians forged. For example, because Volta chose to announce his invention of the pile to the Royal Society, innovative British chemists like Humphry Davy were able to take the lead in electrochemical research in the early nineteenth century.

One drawback to this approach, however, is that continental-European studies of electricity are often portrayed through the eyes of British electricians. There were a number of priority disputes over instrumentation, and contested theories of electrical action. If given the opportunity to develop a book-length treatment of eighteenth-century electrical research, I hope to correct for this bias by providing a more detailed account of

German and Swedish contributions to the study of electricity, especially in the early nineteenth century.[23]

In spite of this limitation, I hope this work will aid in our understanding of the development of physics and chemistry by illuminating some of the lesser-examined aspects of electrical experimentation.

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[23] In particular, I would like to analyze the work of Jöns Jakob Berzelius, a leading figure in Swedish chemistry who devised a table of elements based on electrochemical properties, and Johann Wilhelm Ritter, an enigmatic German chemist who tried to combine Volta's contact theory of electrical action with a chemical account of current production. It is interesting to note that French natural philosophers did not fully engage in electrical research until after Davy published his award winning paper *On Some Chemical Agencies of Electricity* in 1807. (In this essay, Davy showed that elements formed consistently at either the positive or negative lead, suggesting that simple substances carried a specific charge.) Antoine César Becquerel and André-Marie Ampère, for example, made significant contributions to the study of electrochemistry and current in the 1820s. During this period, Jean Baptiste Biot and Joseph Fourier also tried to develop a mathematical account of electrical conduction. Prior to 1807, however, there were few French electricians conducting experiments on electrical phenomena. Two notable exceptions were Abbé Jean-Antoine Nollet, a contemporary of Franklin and a two-fluid theorist, and Charles-Augustin Coulomb.

Introduction: History and Historiography of Electricity

> Through the influence of electricity on the theory of chemistry, this last science has experienced a revolution, and received a greater and more important accession of influence, than it did through the doctrines of either Stahl or Lavoisier.[1]
>
> Jöns Jakob Berzelius (1814)

> …*accurate* researches on the connexion of what may be called the electro-dynamic relations of bodies to their combining masses or proportional numbers, will be the first step towards fixing chemistry on the permanent foundation of the mathematical sciences.[2]
>
> Humphry Davy (1826)

As discussed in the preface, this dissertation is about the history of experiment and, more specifically, chemical approaches to the study of electricity. In the early nineteenth century, eminent chemists such as Humphry Davy in Britain and Jöns Jakob Berzelius in Sweden promoted the field of electrochemistry. With the study of the electrodynamics of bodies, Davy hoped chemistry would become more quantitative. Berzelius less cautiously proclaimed a revolution in chemistry had occurred through electrical research.

Davy and Berzelius believed the study of electricity would advance chemistry. Ironically, within the history of science, the systematic ways in which knowledge of electricity was produced has been traditionally discussed as the pursuit of physicists and engineers. More specifically, historians of physics have placed emphasis on the development of the electromagnetic field equations by James Clerk Maxwell in the latter

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[1] Jöns Jakob Berzelius and John Black, *An Attempt to Establish a Pure Scientific System of Mineralogy, by the Application of the Electro-Chemical Theory and the Chemical Proportions* (London: R. Baldwin and W. Blackwood, 1814), 11.

[2] Humphry Davy, "The Bakerian Lecture: On the Relations of Electrical and Chemical Changes," *Phil. Trans.* 116 (1826): 383-422, 419.

half of the nineteenth century.[3] A notable exception is John Heilbron's *Electricity in the Seventeenth and Eighteenth Centuries, a Study of Early Modern Physics* (1979).[4] Heilbron and Thomas Kuhn[5] have argued that during this period experimentation in the physical sciences became quantitative, a crucial element of the discipline of modern physics.[6] They have stressed the importance of analyzing this historical development through the study of electricity. Recent historiography has also tended to focus on the contributions of certain select individuals, such as Alessandro Volta, Charles-Augustin Coulomb, and André-Marie Ampère, rather than examining the study of electricity within a broader scientific context and community.[7]

Historians of chemistry have also virtually ignored chemists' research in electricity. Recent literature on eighteenth-century chemistry has focused on re-

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[3] There is an extensive literature on Maxwell. See for example, Jed Z. Buchwald, *From Maxwell to Microphysics: Aspects of Electromagnetic Theory in the Last Quarter of the 19th Century* (Chicago: University of Chicago Press, 1985); Olivier Darrigol, *Electrodynamics from Ampere to Einstein* (New York: Oxford University Press, 2000); P.M. Harman, *The Natural Philosophy of James Clerk Maxwell* (Cambridge: Cambridge University Press, 1998); John Hendry, *James Clerk Maxwell and the Theory of the Electromagnetic Field* (Bristol: Hilger, 1986); Bruce Hunt, *The Maxwellians* (London: Cornell University Press, 1991); Basil Mahon, *The Man Who Changed Everything: The Life of James Clerk Maxwell* (Chichester: Wiley and Sons, 2003).

[4] John Heilbron, *Electricity in the 17th and 18th Centuries: A Study in Early Modern Physics [1979]* (New York: Dover Publications, 1999); Roderick Home, "The Notion of Experimental Physics in Early 18th Century France," in *Change and Progress in Modern Science*, ed. Joseph C. Pitt, *University of Western Ontario Series in Philosophy of Science* (Dordrecht: Reidel, 1985), 107-131; Roderick Home, *Electricity and Experimental Physics in 18th Century Europe* (Brookfield, VT: Ashgate Publishing, 1992).

[5] Thomas S. Kuhn, "Mathematical versus Experimental Traditions in the Development of Physical Science," *Journal of Interdisciplinary History* 7 (1976): 1-31.

[6] Heilbron is quite critical of Kuhn's 1976 work. See John Heilbron, "Analogy in Volta's Exact Natural Philosophy," *Nuova Voltiana* 1 (2000): 1-24, 4.

[7] See for example, Heering, 1994; Heering, 2006; J. R. Hoffman, *André-Marie Ampère* (Oxford: Oxford University Press, 1995); Martinez, 2006; Giuliano Pancaldi, *Volta: Science and Culture in the Age of Enlightenment* (Princeton: Princeton University Press, 2003).

examining the “chemical revolution” in which Antoine Lavoisier prominently figured.[8] Nineteenth-century studies have concentrated on the development of organic chemistry, applied chemistry (e.g. dyes and textile manufacturing), and stoichiometry, the study of quantifiable relationships between substances involved in a chemical reaction; for example that two hydrogen molecules combine with one oxygen molecule to form two molecules of water. [9]

Although Heilbron encourages scholarship on the development of electrochemistry in the epilogue to his ground breaking 1979 work, to my knowledge no comprehensive analysis has been made.[10] Only a handful of works examine the relationship between electricity and chemical change in the eighteenth and nineteenth centuries. For example, in 1979, William Sudduth wrote a dissertation on the electrical decomposition of water.[11] In celebration of the bicentennial of the invention of the voltaic

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[8] See, for example, Bernadette Bensaude-Vincent, "Lavoisier: A Scientific Revolution," in *History of Scientific Thought: Elements of a History of Science*, ed. Michel Serres (Oxford: Blackwell, 1995), 455-482; Bernadette Bensaude-Vincent, *A History of Chemistry*, trans. Deborah Van Dam (Cambridge, MA: Harvard University Press, 1996); Marco Beretta, ed., *Lavoisier in Perspective* (Munich: Deutsches Museum, 2005); Arthur Donovan, *Antoine Lavoisier: Science, Administration, and Revolution* (Cambridge, MA: Blackwell, 1993); Arthur Donovan, ed., *The Chemical Revolution: Essays in Reinterpretation*, vol. 4, *Osiris* (1988); Trevor H. Levere, "Lavoisier: Language, Instruments, and the Chemical Revolution," in *Nature, Experiment, and the Sciences: Essays on Galileo and the History of Science in Honour of Stillman Drake*, ed. Trevor H. Levere and William Shea (Dordrecht: Kluwer Academic Publishers, 1990), 207-223.

[9] See, for example, John H. Brooke, "Berzelius, the Dualistic Hypothesis, and the Rise of Organic Chemistry," in *Enlightenment Science in the Romantic Era: The Chemistry of Berzelius and Its Cultural Setting*, ed. Evan Melhado and Tore Frängsmyr (New York: Cambridge University Press, 1992), 180-221; Trevor H. Levere, *Chemists and Chemistry in Nature and Society (1770-1878)* (Brookfield, VT: Ashgate Publishing Ltd., 1994); Alan J. Rocke, *Chemical Atomism in the 19th Century: From Dalton to Cannizzaro* (Columbus: Ohio State University Press, 1984).

[10] Heilbron, 1999, 491. Heilbron includes a table outlining the “Distribution of Articles on Electricity by Field”. He states that between the years 1762/1774, 1775/1788 and 1789/1797 there were 0, 5 and 10 works respectively published addressing electrochemistry. As this dissertation shows, these figures under represent the number of natural philosophers/chemists researching the chemical effects of electricity.

[11] Gad Freudenthal, "Early Electricity between Chemistry and Physics: The Simultaneous Itineraries of Francis Hauksbee, Samuel Wall, and Pierre Polinière," *Historical Studies in the Physical Sciences* 11 (1981): 203-229; Roderick Home, "Nollet and Boerhaave: A Note on Eighteenth-Century Ideas about

pile (battery) in 2000, a new periodical was established entitled *Nuova Voltiana*. It promotes scholarship on Alessandro Volta, his contemporaries, and their science, and includes several significant articles examining episodes in the history of electricity and chemistry. For instance, Helge Kragh and Nahum Kipnis have written essays on the long-lasting debate over how electricity was produced in the pile. Their respective works, however, concentrate on the history of contact theory, Volta's fluid dynamic model of the pile's electrical action.[12] Raffaella Seligardi and Valeria Mosini have also written on the chemical applications of electricity. Seligardi argues Italian physiologists promoted the idea that electricity was a chemical element in the late eighteenth century, while Mosini contends that serious study of electricity's chemical effects began only with the pile.[13] This small, but growing body of literature indicates renewed scholarly interest in the history of electrochemistry.

Relatively few historical studies, however, broadly examine this dynamic period in the history of electricity from a chemical point of view. Historians of physics and chemistry, by projecting onto the past their modern conception of physics or chemistry,

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Electricity and Fire," *Annals of Science* 36 (1979): 171-176; and William Sudduth, "The Electrical Decomposition of Water: A Case Study in Chemical and Electrical Science, 1746-1800" *Dissertation Abstracts International* 38 (1979): 2315. He also subsequently published two articles on this topic: William Sudduth, "Eighteenth Century Identifications of Electricity with Phlogiston," *Ambix* 25 (1978): 131-147; William Sudduth, "The Voltaic Pile and Electrochemical Theory in 1800," *Ambix* 27 (1980): 26-35.

[12] Nahum Kipnis, "Debating the Nature of Voltaic Electricity, 1800-1850," *Nuova Voltiana* 3 (2001): 121-146; Nahum Kipnis, "Changing a Theory: The Case of Volta's Contact Electricity," *Nuova Voltiana* 5 (2003): 143-162; Helge Kragh, "Confusion and Controversy: Nineteenth Century Theories of the Voltaic Pile," *Nuova Voltiana* 1 (2000a): 133-157; Helge Kragh, "Volta's Apostle: Christoph Heinrich Pfaff, Champion of the Contact Theory," *Nuova Voltiana* 5 (2003): 69-82.

[13] Valeria Mosini, "When Chemistry Entered the Pile," *Nuova Voltiana* 5 (2003): 117-132; Raffaella Seligardi, "Volta and the Synthesis of Water: Some Reasons for a Missed Discovery," *Nuova Voltiana* 2 (2000): 33-48. Seligardi has also published an insightful, yet very preliminary article pertaining to electrochemistry focused in the history of medicine. See Raffaella Seligardi, "What Is Electricity? Some Chemical Answers, 1770-1815," in *Electric Bodies: Episodes in the History of Medical Electricity*, ed. Paola Bertucci and Giuliano Pancaldi (Bologna: University of Bologna Press, 2001), 181-208.

have neglected the variety of scientific approaches to the study of electricity. Today, chemists are not interested in electricity per se, but in understanding the interactions and structure of matter. The laws and behaviour of electromagnetism and circuitry are typically taught and studied in physics and engineering departments. In contrast, this dissertation demonstrates that in the eighteenth and early nineteenth centuries, the study of electricity belonged to no one discipline; electricity was thought to be a substance with unique properties and, therefore, worthy of study by a variety of methods.

A similar problem has occurred in the history of optics. Alan Shapiro, in his pioneering work on the history of colored bodies, argues historians neglected Newton's theory of color not only because it was "wrong"[14] and might detract from his other accomplishments, but also because "the explanation of the colors of bodies… gradually disappeared as a fundamental problem in physics, and historians have taken their lead from physicists." In contrast, Shapiro shows the historical importance of Newton's research into the colors of materials to developments in eighteenth-century science, such as spectroscopy and the chemistry of dyeing.[15]

Heilbron, in a recent article examining the use of analogy in early modern science, also argues historians of this period have created "pseudo problems" by falsely aligning themselves along disciplinary boundaries that did not exist in the eighteenth century. For example, he points to "the question, recently actively debated in the historical literature, whether Lavoisier was a chemist or physicist or both"? Whether

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[14] Alan E. Shapiro, *Fits, Passions, and Paroxysms: Physics, Method, and Chemistry and Newton's Theories of Colored Bodies and Fits of Easy Reflection* (Cambridge: Cambridge University Press, 1993), 3.

[15] Ibid, 5.

historians should call Lavoisier a physicist or a chemist, Heilbron argues, "is an artifact of false categories, to his contemporaries Lavoisier was a *physicien*, which should be translated 'natural philosopher', not 'physicist'." Throughout the revolutionary and Napoleonic era in France, anyone recognized as systematically studying natural phenomena was referred to by the general term *physicien*, irrespective of their subject of interest or methodology. Thus, Heilbron calls this historiographic trend quite aptly "a self-inflicted injury".[16] Whether Lavoisier should be called a physicist or a chemist detracts from the real historical problem: chemistry not only became an independent discipline over the course of the eighteenth and nineteenth centuries, but also gained an authority that it did not have in the seventeenth century. How did this transformation occur, what made it possible, and what did it consist of?[17]

Many historians of science have argued that the most transformative period in the theory and practice of chemistry occurred in the late eighteenth century. In the seventeenth century, university curricula included mathematics, which covered subjects such as astronomy, and physics or natural philosophy, which investigated the principles of motion of natural substances. This included, for example, biology and meteorology. Chemistry was included in some medical programs, but practiced mostly outside of the academy. In the late eighteenth century, natural philosophy, as it had been broadly

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[16] Heilbron, 2000, 3.

[17] This is my broad conception of the historiograpical problem. In contrast, Heilbron provides an answer to this question: "The pseudo-problem of Lavoisier's disciplinary identity has given life to the pseudo-question, whether he affected a revolution in or into chemistry. If he were a chemist, the argument runs, the revolution would be internal; if a physicist, external. The question misses the reality that both natural philosophy and chemistry (understood as the study of different combinations of matter) were revolutionized around 1770 by the discovery of the different gas types." See, Ibid, 3.

conceived, began to divide into specialized subjects and chemistry gained more acceptance and authority as a science.[18]

Chemical practitioners, in part, saw themselves as rivals to the mechanistic natural philosophers, whose focus was on the geometrical and spatial arrangement of matter – how that material was arranged determined its properties. In contrast, chemists argued that a finite number of different substances existed, each with individual properties and qualities that were too complicated to be reduced to mechanics or discussions of matter in motion.[19] Subsequently, there was an explosion of researches into the physical (volume, specific heat, etc.) and chemical (flammable, corrosive, etc.) properties of substances.[20] During this period, natural philosophers and chemists alike struggled to define the essential properties of materials, characteristics that were (hopefully) less subjective than older comparative measures such as heaviness and taste when defining a substance and its behavior.[21]

Scholars have pointed to numerous changes in the study of materials, such as new emphasis on gravimetric analyses (weights and measures), pneumatics, the development of a new chemical nomenclature and a ‘balance-sheet’ approach, examining the amount and kind of materials involved in chemical reactions.[22] Other historians support a model

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[18] Maurice Crosland, *In the Shadow of Lavoisier: The Annales De Chimie and the Establishment of a New Science* (Oxford: Alden Press, 1994), 6-10, 34-36.

[19] Shapiro, 1993, 216-225.

[20] Klein and Levfèvre, 2007.

[21] Betty-Jo Dobbs and Robert Siegfried, "Composition, a Neglected Aspect of the Chemical Revolution," *Annals of Science* 24 (1968): 275-293.

[22] See for example, Henry Guerlac, *Lavoisier: The Crucial Year* (New York: Cornell University Press, 1961); Henry Guerlac, "Chemistry as a Branch of Physics: Laplace's Collaboration with Lavoisier," *Historical Studies in the Physical Sciences* 7 (1976): 193-276; Frederick L. Holmes, *Antoine Lavoisier: The*

of gradual change over time in which chemistry came into its own through a series of slow and successive modifications. For example, Newman and Principe have shown that seventeenth century alchemists like George Starkey were engaged in the systematic study of chemical change, employing methods like the ‘balance-sheet’ approach much earlier than traditionally recognized by historians.[23]

While this dissertation makes no attempt to enter into this larger debate of whether or not there was a chemical revolution, it does demonstrate that electrical research informed the development of chemistry in important ways. More specifically, I argue that the study of electricity was a material science. Scientists practicing chemistry were actively engaged in the transformation of the study of electricity. They brought to it their own methods and modes of inquiry. They asked: what was the role of electricity in chemical processes? Did it physically interact as a material with other substances? Did it possess unique chemical properties? Did it cause chemical change? They attempted to answer these questions by rigorously examining its chemical effects and, later, the effect chemical processes had on the production of electricity.

What did it mean to be an eighteenth-century chemist? This work examines the scientific identity of practitioners and the methods they used to study electrical phenomena. For example, historians have labeled William Nicholson, a self-taught

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Next Crucial Year or Sources of His Quantitative Method in Chemistry (Princeton: Princeton University Press, 1998); Trevor H. Levere, "Gay-Lussac and the Problem of Chemical Qualities," in *Chemists and Chemistry in Nature and Society, 1770-1878* (Brookfield, VT: Ashgate Publishing Ltd., 1994), 1-11; C.E. Perrin, "Lavoisier's Thoughts on Calcination and Combustion, 1772-1773," *Isis* 77 (1986): 647-666; C.E. Perrin, "Chemistry as Peer of Physics: A Response to Donovan and Melhado on Lavoisier," *Isis* 81 (1990): 259-270; Robert Siegfried, "The Chemical Revolution in the History of Chemistry," *Osiris* 4 (1988): 34-52.

[23] See for example, J.B. Gough, "Lavoisier and the Fulfillment of the Stahlian Revolution," *Osiris* 4 (1988): 15-33; William Newman and Lawrence Principe, *Alchemy Tried in the Fire: Starkey, Boyle, and the Fate of Helmontian Chymistry* (Chicago: University of Chicago Press, 2002).

British experimentalist, editor, and publisher of scientific works, a chemist, neglecting his important contributions to the study of electricity. He did conduct chemical experiments, but he also invented electrical detectors, wrote books on natural philosophy, and made significant contributions to the study of experimental and mathematical error.[24] For instance, he argued that in a mathematical calculation involving many measurements, the answer could only be as precise as the least precise measurement.[25] Using his knowledge of electrical phenomena, Nicholson also challenged Alessandro Volta's theory of

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[24] See, for example, S. Lilley, "Nicholson's Journal (1797-1813)," *Annals of Science* 6, no. 1 (1948): 78-101; William Nicholson, *An Introduction to Natural Philosophy*, 2 vols. (London: printed for J. Johnson, 1787); William Nicholson, *The First Principles of Chemistry*, 2nd ed. (London: G.G. and J. J. Robinson, 1790). Nicholson censured Lavoisier for his inappropriate use of significant figures in Richard Kirwan, *An Essay on Phlogiston and the Constitution of Acids to Which Are Added, Notes, Exhibiting and Defending the Antiphlogistic Theory; and Annexed to the French Edition of This Work by Messrs. De Morveau, Lavoisier, De La Place, Monge, Berthollet, and De Fourcroy* trans. William Nicholson (London: J. Johnson, 1789), Nicholson's Preface. See also, Jan Golinski, *Science as Public Culture: Chemistry and Enlightenment in Britain, 1760-1820* (New York: Cambridge University Press, 1992), 141-144.

[25] John Heilbron and M. Norton Wise argue that sophisticated discussions about the nature of precision (often conflated with accuracy in the eighteenth century) began in response to economic and military concerns, "in large part derived from the need of administrators for reliable information about particular aspects of the world in order to be able to make reasonable plans [with regards to the] availability [and allocation] of human and material resources, cost estimates, tax revenues, life and annuity tables, maps, location of ships, etc." The emerging definitions of precision were of a statistical nature, e.g. did a sample set reliably and consistently represent a larger group trend. For example, Pierre Simon Laplace used data from a "partial census undertaken by the French government in 1802" to extrapolate the annual birth and death rates, and total population of France. Natural philosophers and statisticians, in addition to evaluating the rigor of computational methods, asked: what were the necessary criteria to ensure that a cross section was a truthful representation of the whole? In physics, however, the context of precision and accuracy were (and are) slightly different. As in the above example of determining population trends, there were discussions of how to minimize and estimate experimental and mathematical error. Unlike the study of demographics however, which were fraught with social and cultural complexities that were difficult to disentangle, natural philosophers increasingly tried to develop methods and instruments to reduce ambiguity and assist in the evaluation and analysis of phenomena. As a result, the term precision by the end of the nineteenth century specifically came to refer to the measurement limits of an instrument (or computation) while accuracy denoted the ability of a set of experiments (or methods or computations) to consistently produce results within an expected numerical range. Jed Buchwald has published an insightful article on this topic. His work addresses the development of the experimental-mathematical side of this story, and focuses mainly on optics. Angela Bandinelli has also recently published an interesting article on the development of quantitative experimental methods in eighteenth-century studies of heat. See, Angela Bandinelli, "The Isolated System of Quantifiable Experiences in the 1783 "Mémoire Sur La Chaleur" Of Lavoisier and Laplace," *Ambix* 54, no. 3 (2007): 274-284; Buchwald, 2006; John Heilbron, "The Measure of Enlightenment," in *The Quantifying Spirit in the 18th Century*, ed. John Heilbron, et al. (Berkeley: University of California Press, 1990), 207-242; Norton M. Wise, ed., *The Values of Precision* (Princeton: Princeton University Press, 1995), 5, 31.

electricity by emphasizing its inability to account for the pile's chemical effects.[26] Thus, this dissertation examines the contributions of scientists normally pushed to the periphery in the history of electricity because they practiced chemistry, including Nicholson, Joseph Priestley, and Humphry Davy. In doing so, it also provides a richer account of the study of natural philosophy during this period. I argue that natural philosophers, like Volta, were forced to respond to chemical practitioners' cogent experiments and criticisms. In particular, I am interested in examining their disputes over the reliability and authority of different experimental approaches to the study of electricity. I contend that these debates, more so than subject matter, helped to define physics and chemistry as independent fields of study.

This dissertation shows that chemical practitioners were deeply concerned with and invested in the study of electrical phenomena. It is fundamentally a study of eighteenth-century experimentation. It contributes to the history of scientific practice by analyzing electricians' experiments in gory detail.[27] This analysis demonstrates that analogical reasoning was a widely used and productive research method during this period. It also shows that, although natural philosophers and chemists ubiquitously used analogies to further their experimental and theoretical goals, they increasingly diverged on their approach to the study of electricity. I will first briefly discuss the history of analogical reasoning before providing an overview of changes in electrical practice and chemists' contributions to this discourse.

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[26] Sudduth, 1980.

[27] This approach was, in part, inspired by recent historiography including, but not limited to: Frederick L. Holmes et al., *Reworking the Bench: Research Notebooks in the History of Science*, ed. Jed Z. Buchwald, *Archimedes* (Dordrecht: Kluwer Academic Publishers, 2003); Pancaldi, 2003; Shapiro, 1993.

I.I Analogical Reasoning in Electrical and Chemical Experiments

> The foundations of chemical philosophy are, observation, experiment, and analogy. By observation, facts are distinctly and minutely impressed on the mind. By analogy, similar facts are connected. By experiment, new facts are discovered; and, in the progression of knowledge, observation, guided by analogy, leads to experiment, and analogy confirmed by experiment, becomes scientific truth.[28]
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> Humphry Davy (1812)

Reasoning by analogy was an important part of scientific practice in the eighteenth and nineteenth centuries. "The belief in the 'analogy of nature,' or that 'nature is ever consonant to herself,' served as a guiding maxim throughout Newton's career."[29] "Buffon [an influential French naturalist and director of the Jardin du Roi] judged that if 'experience is the foundation of all our physical and moral knowledge, analogy is its first instrument.'"[30] Thomas Young, in a series of physics lectures, also emphasized its importance[31]: "That like causes produce like effects, or, that in similar circumstances similar consequences ensue, is the most general and most important law of nature; it is the foundation of all analogical reasoning, and is collected from constant experience".[32]

Many essays written in the eighteenth and nineteenth centuries used analogy to not only draw parallels between diverse phenomena, but also to make theoretical claims about objects in Nature. For example, Etienne Geoffroy St-Hilaire, the French zoologist,

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[28] Humphry Davy, *Elements of Chemical Philosophy* (London: J. Johnson and Co. St. Paul's Churchyard, 1812), 2.

[29] Shapiro, 1993, 43-44.

[30] Jessica Riskin, *Science in the Age of Sensibility: The Sentimental Empiricists of the French Enlightenment* (Chicago: University of Chicago Press, 2002), 95.

[31] Young, in his own research, used analogy to compare sound and light waves. See Thomas Young, "Outlines of Experiments and Inquiries Respecting Sound and Light," *Phil. Trans.* 90 (1800): 106-150, 125-133.

[32] Thomas Young, *A Course of Lectures on Natural Philosophy and the Mechanical Arts* (New York: Johnson Reprint Corporation, 1971), 15.

argued similarities in form between the embryos of turtles, sheep, and humans suggested that all vertebrates were derived from a common archetype.[33] William Herschel, the English astronomer, argued that observed variations in the surfaces of the sun and planets indicated that, like the Earth, they have atmospheres.[34] Giambatista Beccaria, an Italian natural philosopher, asserted electricity was a species of common fire because of the numerous similarities in electrical and thermal effects.[35]

Chemical practitioners had also long drawn on analogy not only to demonstrate the identity of a material, but also to devise experimental stratagems for the analysis of complex substances. For instance, Newman and Principe discuss George Starkey's use of analogy in his analysis of the chemical composition of cinnabar (mercury sulfide). In particular, Starkey tried to accurately determine the identifying properties or characteristics of substances believed to be in cinnabar, like sulphur, and then looked for those attributes when analyzing it.[36]

Starkey was not alone in using analogy to further his understanding of chemical combination. Tiberius Cavallo, an Italian émigré to England, consecutively gave the Royal Society's Bakerian lecture, a prize awarded for outstanding work in "natural history" or "experimental philosophy", between 1780 and 1792. In his popular textbook,

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[33] Herve Le Guyader, *Geoffroy Saint-Hilaire: A Visionary Naturalist*, trans. Marjorie Grene (Chicago: University of Chicago Press, 2004).

[34] William Herschel, "On the Nature and Construction of the Sun and Fixed Stars," *Phil. Trans.,* 85 (1795): 46-72, 49-51.

[35] Giambatista Beccaria, *A Treatise Upon Artificial Electricity in Which Are Given Solutions of a Number of Interesting Electric Phenomena, Hitherto Unexplained: To Which Is Added an Essay on the Mild and Slow Electricity Which Prevails in the Atmosphere During Serene Weather*, trans. anonymous (London: J. Nourse, 1776). Beccaria's analogical arguments and experiments are discussed at length in chapter one.

[36] Newman and Principe, 2002, 92-135, 114.

Elements of Natural or Experimental Philosophy, he incorporated a discussion of chemistry including its tenets and methods. He noted that analogical reasoning served as a guiding principle for discerning the relationships between chemical substances, processes, and properties like weight and inflammability.[37]

Nicholson also emphasized the utility of analogical reasoning to the development of chemistry. He wrote: "It is impossible to give advice against the many casualties to which chemical experiments are liable; one general maxim is, always to endeavor, from analogy, to foresee the consequence, or probable result, of the intended process, and when that cannot be done, to observe the phenomena, and proceed with caution."[38] In other words, analogy provided a means of devising a working experimental hypothesis, based on the likelihood of previously observed events, to be either confirmed or refuted by additional experiments. This approach facilitated research. The results of an experiment could be compared to a set of known experimental outcomes with similar characteristics. If the analogy held, it increased confidence in the validity of the hypothesis. If it failed, it suggested new experimental avenues and theoretical questions to explore.

For example, the name "acid" denoted a compound that produced an agreed upon set of behavioral properties: nitrous acid like sulphuric acid caused corrosion, reacted with alkalis to form salts, and turned litmus, a plant extract, red. Lavoisier developed a sophisticated research program to further investigate the composition of acids. In addition

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[37] Tiberius Cavallo, *The Elements of Natural or Experimental Philosophy* (Philadelphia: Thomas Dobson & Son, 1819), 416-439, 418.

[38] Nicholson, 1787, xiii; Nicholson, *The First Principles of Chemistry*, 9, 21, 108, etc.

to manifesting similar effects, chemical analysis revealed that each acid consisted of an inflammable substance and oxygen. Because the form of each acid was the same, Lavoisier argued that the cause of acidity must reside in its common constituent, oxygen or the “acid-generator”. He wrote: “when, from these particular facts, the general induction is made, that oxigene is a principle common to all acids, the consequence is founded on analogy [that oxygen engenders acidity in these substances], and here it is that the theory commences. Experiments which daily become more numerous, afford an increasing probability to this theory”.[39]

Although Lavoisier’s analogy and explanation of acidity was ultimately incorrect e.g. muriatic (hydrochloric) acid does not contain oxygen, it was a productive theory. As William Henry, an influential British chemist, noted in 1800: many chemists undertook analyses of complex acids, like fluoric (hydrofluoric) and muriatic acid, to determine whether oxygen was indeed one of its components.[40] These experiments led to new discoveries, e.g. that chlorine and fluorine were elements, not compounds.[41]

The ubiquity and use of analogical reasoning has only recently become a subject of study. A few historians and philosophers have started to ask which phenomena formed a basis for comparison and how were likenesses prioritized and privileged in conceptual

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[39] Lavoisier quoted in Kirwan, *Essay on Phlogiston*, 20. Also, see Antoine Lavoisier, *Essays on the Effects Produced by Various Processes on Atmospheric Air; with a Particular View to an Investigation of the Constitution of the Acids*, trans. Thomas Henry (Warrington: W. Evans for J. Johnson, 1783), 8; Antoine Lavoisier, *Elements of Chemistry, in a New Systematic Order, Containing all the Modern Discoveries* (Edinburgh: William Creech; G.G. and J.J. Robinsons, 1790), xxix, 146, etc.

[40] William Henry, "Account of a Series of Experiments, Undertaken with the View of Decomposing the Muriatic Acid," *Phil. Trans.* 90 (1800a): 188-203, 188-189.

[41] Le Grand, 1974.

development.[42] This dissertation adds to the small, but growing number of case studies examining the role of analogy in scientific practice. I analyze how eighteenth-century scientists conceptualized electricity in light of their experiments and its similarities and/or differences to other phenomena.

What did an analogy consist of? I have identified four types of analogical arguments in use in electrical studies in the eighteenth century:

1) Similarity of Form: A resembles B physically

> For example, a bat's wing has the same number and arrangement of bones as a whale's fin; the voltaic pile has stacked, regularly alternating partitions of conducting materials like the electrical organ of the torpedo ray.

2) Similarity of Function:[43] A has the same purpose as B

> For example, a fish's heart has two chambers while the human heart has four, yet both pump blood; a series of Leyden jars and the torpedo fish produce identical weak, electrical effects.

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[42] Studies examining the role of analogy in scientific practice include: Heilbron, 2000; Mary Hesse, *Models and Analogies in Science* (Indiana: University of Notre Dame Press, 1966); Michel Janssen, "COI Stories: Explanation and Evidence in the History of Science," *Perspectives in Science* 10 (2002): 457-522; Laura Snyder, *Reforming Philosophy: A Victorian Debate on Science and Society* (Chicago: University of Chicago Press, 2006). C. Kenneth Waters argues that analogy is regarded skeptically within the philosophy of science because it relies on a set of complicated, observed relationships and a form of inductive reasoning that is difficult to accurately and generally describe. The use of analogy in science cannot be characterized by "simple inductions" because "analogical inferences are not based upon a random selection of common properties, but on properties that are associated by the relations that lead us to call systems… analogous." With the form of the argument difficult to capture, some historically minded philosophers have black-boxed analogy, examining its function after its creation. A few studies suggest that analogical reasoning acts in the context of justification, to persuade and validate a particular line of scientific thought. For example, philosophical analyses of Charles Darwin's *Origin of Species*, probably the most famous analogical argument in the history of science, contend that his likening of artificial selection to natural selection was intended to show the soundness of his belief in natural selection as a process, crudely taking the form: if a person can manipulate the characteristics of living organisms, nature can too. See, for example, Susan Sterrett, "Darwin's Analogy between Artificial and Natural Selection: How Does It Go?," *Studies in the History and Philosophy of Biological and Biomedical Sciences* 33 (2001): 151-168; Kenneth C. Waters, "Taking Analogical Inference Seriously: Darwin's Argument from Artificial Selection," *Proceedings of the Biennial Meeting of the Philosophy of Science Association* 1 (1986): 502-513.

[43] Although similarity of function and effect appear to be related, they are not. For instance, the structural differences between a human and fish heart produce different effects, e.g. the additional chambers of the human heart cause pulmonary transit. Despite this marked difference in how blood circulates, the overall biological function of each heart is identical: the organ pumps blood throughout the body.

3) Similarity of Effect: A produces B effects; C produces B effects

> A and C are (somehow) related. The same cause or mechanism manifest in A and C perhaps produced B, but not necessarily so - e.g. heat and electricity both produce fire and light; therefore they are (somehow) related.

4) Similarity of Cause: A causes B; A causes C

> B and C are (somehow) related. For example, friction generates heat and electricity; therefore heat and electricity are (somehow) related.

When drawing comparisons, eighteenth-century scientists often used the phrases: “in analogy to”, “resembles”, “imitates” or “in the same manner as” to express likeness. The use of analogy was not primarily a pedagogical or heuristic tool, but rather played a substantive role in scientific practice.[44] As Alex Levine argues, “an argument grounded in… analogy [was] rationally compelling… because it engender[ed] anticipations… of possible interactive environments.”[45] In other words, an analogy suggested a starting point for experimental and theoretical analysis. Subsequent debates over whether a set of phenomena belonged together and which properties were most important or characteristic of that group opened new fields of inquiry.

To give another brief example - chapter one shows that there was a long history of likening electricity to heat. Benjamin Franklin and Beccaria, amongst others, advocated that electricity was a form of fire. Their experiments showed that heat and electricity produced a number of similar effects, e.g. both generated sparks and light and caused the

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[44] For a specific example of its pedagogical use, see Michael Faraday, *A Course of Six Lectures on the Chemical History of a Candle* (New York: Harper and Brothers, 1861), Lecture VI: “Carbon or Charcoal – Coal Gas – Respiration and Its Analogy to a Candle”. For a discussion of its general heuristic value, see Fernand Hallyn, ed., *Metaphor and Analogy in the Sciences* (Boston: Kluwer Academic Publishers, 2000).

[45] Alex Levine, "Partition Epistemology and Arguments from Analogy," *Synthese* 166 (2009): 593-600, 599.

calcination of metal (rusting). Joseph Priestley, a well-known British natural philosopher, chemist, and proponent of Georg Stahl's theory of combustion, found it a compelling analogy. He extended Franklin and Beccaria's research by comparing the effects of electricity and heat on gas composition. Whether he exposed air to a candle's flame or a spark, he observed similar kinds of chemical change: the volume of gas diminished and the air became toxic to living organisms. Because electricity and heat shared a number of effects, Priestley argued that for any theory of heat to be successful, it also had to adequately account for electrical phenomena. In contrast, Lavoisier developed a new theoretical framework to explain thermal effects, which did not include electricity. He emphasized his experiments on heat transfer, which determined, amongst other things, specific heat – a unique measure of the amount of heat required to raise the temperature of a substance one degree. There was no analogous property to specific heat in the study of electricity. Thus, I am interested in examining how scientists likened and/or distinguished between electrical and thermal phenomena by analyzing their experiments and the evidence they marshaled to argue that electricity was a form of heat or, in Lavoisier's case, that heat was caloric, a substance distinct from electrical matter.[46]

I argue that analogical reasoning encouraged either the development of a new operational definition for a group of phenomena, i.e. a working hypothesis and set of criteria by which to compare experimental results, or a more sophisticated and nuanced understanding of their differences. In short, it promoted experimental research to substantiate why the likenesses should outweigh the differences (or vice versa) when

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[46] See chapter 1.

assessing experimental results. This dissertation demonstrates that the prevalent use of analogy was productive to the growth of electrical knowledge and discourse in the eighteenth century.

I.II Chapter Overviews: Changes in Scientific Practice

> The chemical effects produced by electricity have been for some time objects of philosophical attention; but the novelty of the phenomena, their want of analogy to known facts, and the apparent discordance of some of the results, have involved the enquiry in much obscurity. An attempt to elucidate the subject will not, I hope, be considered by the Society as unfitted to the design of the Bakerian Lecture. I shall have to detail some minute (and I fear tedious) experiments; but they were absolutely essential to the investigation.[47]
>
> Humphry Davy (1807)

This work analyzes chemical practitioners' contributions to the study of electricity and the uses of analogical reasoning in scientific practice. As discussed in the preface and introduction, it is by design a history of the theoretical conclusions drawn from experiment. Each of the following chapters roughly traces the electrical study of a different state of matter in chronological order. Chapter one discusses gases and how they were chemically changed by the presence of a spark. Chapter two examines the electrical properties of solids and how the proximity of charged bodies and different substances interacted to produce electricity. Chapter three concentrates on the electrical properties of liquids, how they affected the production of electricity, and how metals and electric current chemically altered them.

More specifically, chapter one analyzes eighteenth-century experiments indicating that electricity, like heat, caused chemical change. For example, in 1768, Priestley

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[47] Davy, 1807, 1.

showed that repeatedly discharging a point conductor through a flat piece of metal produced concentric, colored rings in that plate.[48] In 1788, Henry Cavendish, a British natural philosopher and chemist, whom James Clerk Maxwell admired as one of the greatest electricians of his generation,[49] synthesized nitrous acid by passing an electric spark through a mixture of air (atmospheric gas, mostly nitrogen and oxygen) and dephlogisticated air (oxygen).[50] Dutch chemists, Adriaan Paets van Troostwijk and Rudolph Deiman, further reported in 1789 that they had electrically decomposed water into inflammable air (hydrogen) and dephlogisticated air (oxygen).[51] These experiments form the basis of chapter one.

This chapter demonstrates that there was a long history of likening electricity to fire, e.g. both caused sparks, rusting, and other kinds of chemical change. In particular, electricians discovered that applying sparks to gases profoundly altered their composition and volume in a manner similar to heating. Natural philosophers and chemists actively debated how electricity and heat brought about chemical change: did they facilitate or participate as substances in chemical reactions?

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[48] Joseph Priestley, "An Account of Rings Consisting of All the Prismatic Colours, Made by Electrical Explosions on the Surface of Pieces of Metal," *Phil. Trans.* 58 (1768): 68-74. Priestley argued that these experiments provided additional support for Newton's theory of colored bodies. "He [Newton] also mentions the colours which arise on polished steel, by heating it; as likewise on bell-metal, and some other metalline substances, when melted and poured on the ground, where they may cool in the open air: and he ascribes these colours to the *scoriæ*, or vitrified parts of the metal…" (68). Vitrification referred to the chemical process (heating) by which a substance was converted into glass; electricity also possessed this ability.

[49] Henry Cavendish, *The Electrical Researches of the Honourable Henry Cavendish*, ed. James Clerk Maxwell (London: Frank Cass & Co. Ltd., 1967), xxvii-lxvi.

[50] Cavendish, 1788.

[51] George Pearson, "Experiments and Observations Made with a View of Ascertaining the Nature of Gaz by Passing Electric Discharges through Water, with a Description of the Apparatus and Experiments," *Nicholson's Journal* 1, Sept. (1797): 241-248, 299-305, and 349-355.

Priestley, for instance, accounted for the chemical changes caused by electricity and heat with one chemical substance. Despite differences, e.g. unlike warm bodies, charged bodies attracted and repelled objects, Priestley found their other similarities of effect compelling. He argued that electrical and thermal phenomena were both manifestations of phlogiston, Stahl's principle of inflammability.[52]

Others devised different explanations. For example, Cavendish also recognized the similarities between electricity and heat, but argued that their motion and not their substance caused chemical change.[53] I also discuss possible reasons why Lavoisier chose not to emphasize the analogy between electrical and thermal phenomena.[54] Thus, this chapter examines the way in which scientists' likened and/or distinguished between electricity and heat by analyzing their chemical experiments and theoretical conclusions.

Chapter two analyzes how changes in experimental practice, especially the study of insulated conductors and the discovery of non-frictional methods of producing sparks, affected scientists' conception of electricity. In particular, I examine the roots of the contentious turn of the nineteenth-century debate: did there exist more than one kind of electrical fluid?[55] I argue that chemical practitioners, like William Nicholson and Tiberius

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[52] See, for example, Joseph Priestley, *History and Present State of Electricity [1775]*, 3rd ed., *The Sources of Science* (London: Johnson Reprint Corporation, 1966).

[53] See, for example, Henry Cavendish, "Experiments on Air," *Phil. Trans.* 74 (1784a): 119-153.

[54] See, for example, Lavoisier, *Elements of Chemistry [1790]*, 92-93, 326-327. While Lavoisier discussed the importance of the sparking of airs to chemical analysis, he did not address how electricity brought about chemical change.

[55] This debate continued well into the nineteenth century. Michael Faraday summarized the state of electrical knowledge and the effects produced by the four different forms of electricity in 1833. See Michael Faraday, "Experimental Researches in Electricity. Third Series," *Phil. Trans.* 123 (1833): 23-54.

Cavallo contributed to this discussion through the development of electrical instruments designed to measure different types of electricity.

In the mid-eighteenth century, the standard electrical generator was a variation on handheld frictional devices used since antiquity: by rubbing a piece of glass (or wax), the glass could be encouraged to release electricity.[56] Most natural philosophers did not believe electrical fluid was created. Rather, they thought it was a ubiquitous material agitated into motion by friction. John Freke, a British physician, electrician, and fellow of the Royal Society, compared this process to "priming a pump", friction bringing to the surface of a substance its electrical fluid, evidenced by its ability to attract light objects and emit sparks. The friction machine was not just a device, but also the mechanism by which electricity was made manifest.[57]

Discoveries of non-frictional sources of electricity forced electricians to rethink their understanding of electrical phenomena and its relationship to heat. For example, in 1773, John Walsh, an English physician and friend of Benjamin Franklin, demonstrated

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[56] See for example, Francis Hauksbee, "Several Experiments Shewing the Strange Effects of the Effluvia of Glass, Produceable on the Motion and Attrition of It," *Phil. Trans.* 26 (1708-1709): 87-92.

[57] John Freke, *A Treatise on the Nature and Property of Fire in Three Essays. Part I. Shewing the Cause of Vitality and Muscular Motion, Part II. On Electricity, Part III. Shewing the Mechanical Cause of Magnetism* (London: W. Innys and J. Richardson, 1752), 84. In Freke's words: "As I have mentioned Friction, I cannot help observing how unphilosophical and unmeaning it is, for anyone to advance, that Fire is caused by Friction; when I think he may as well say, that Water is caused by Pumping." See also, Heilbron, 1999, 294-296. Heilbron, like Benjamin Martin –an instrument maker and opponent of Freke – criticizes Freke's work on electricity. Heilbron argues that Freke was not a 'physicist'. Regardless of Freke's training (medicine), his views reflected the beliefs of the majority of his contemporaries: the motions of electrical fluid, agitated into action by friction, caused electrical effects. See, for example, Benjamin Franklin, *Experiments and Observations on Electricity Made at Philadelphia in America and Communicated in Several Letters to Mr. P. Collinson* (London: E. Cave, 1751); William Watson, "Experiments and Observations, Tending to Illustrate the Nature and Properties of Electricity," *Phil. Trans.* 43 (1744-1745): 481-501.

that a fish, called the torpedo eel or ray, produced a fluid similar to electricity.[58] In 1775, Volta built the electrophore, an unorthodox electrical condenser (capacitor) made of metal and wax that seemed to 'perpetually' release electrical fluid despite having been charged only once by a friction machine.[59] In 1788, Nicholson constructed the "revolving doubler", a device that rotated metal plates in parallel planes. It also produced electricity without contact.[60] These new methods of generating sparks opened a new field of inquiry: were these unique fluids or different manifestations of the same type of electricity? How many analogies and what kind of likenesses must a fluid-behaving-like electricity possess to be identified as electrical fluid?[61]

It is interesting to note that scientists, such as Cavendish, Volta, Cavallo, and Nicholson, argued that evidence of identity must include measurement.[62] They asserted

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[58] John Walsh, "Of the Electric Property of the Torpedo," *Phil. Trans.* 63 (1773): 461-480. Many works within the history of medicine examine the historical importance of the torpedo ray to the development of physiology, specifically with respect to the nervous system. See for example, Stanley Finger, *Minds Behind the Brain: A History of the Pioneers and Their Discoveries* (Oxford: Oxford University Press, 2000), 107-118; Miriam Foccacia and Raffaella Simili, "Luigi Galvani, Physician, Surgeon, Physicist: From Animal Electricity to Electro-Physiology," in *Brain, Mind, and Medicine: Essays in Eighteenth Century Neuroscience*, ed. Stanley Finger (New York: Springer, 2007); Marco Piccolino, *The Taming of the Ray: Electric Fish Research in the Enlightenment from John Walsh to Alessandro Volta*, *Biblioteca Di Nuncius. Studi E Testi* (Florence: L.S. Olschki, 2003). In contrast, there are few historical studies examining the relationship between the torpedo ray and electricity within the history of the physical sciences. A notable exception is: Pancaldi, *2003*, Chapter 6; Marcello Pera, *The Ambiguous Frog: The Galvani-Volta Controversy on Animal Electricity* (Princeton, N.J.: Princeton University Press, 1992).

[59] Pancaldi, 2003, 73-109. Unlike many condensers, e.g. the Leyden jar, the electrophore did not use glass, and seemingly stored more electricity than it received.

[60] William Nicholson, "A Description of an Instrument Which, by the Turning of a Winch, Produces Two States of Electricity without Friction or Communication with the Earth," *Phil. Trans.* 78 (1788): 403-407. The workings of the electrophore and doubler will be discussed in detail in chapter 2, section 2.3.1 and 2.3.2.

[61] Humphry Davy, "On the Electrical Phenomena Exhibited in Vacuo," *Phil. Trans.* 112 (1822): 64-75, 64; Faraday, 1833.

[62] Jed Buchwald argues an important conceptual shift occurred over the course of the eighteenth and early nineteenth centuries. Rather than attributing variation in measurement to human (moral) deficiency, nature being precise, natural philosophers began to view numerical inconsistencies as natural within certain tolerances. Instead of reporting their "best" number, they began to publicly document their measurements,

that an electrometer capable of measuring frictional, animal, and other forms of electricity would demonstrate that these fluids were just different manifestations of one kind of electrical matter. No such instrument, however, yet existed. Animal electricity could not be measured directly with standard electrometers. This begged the question: was animal electricity something unique or was it simply too "weak" to be measured?[63]

I argue that as electricians worked to develop reliable, accurate, and more sensitive electrical detectors, they learned more about electricity. Key components of

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methods, and the conclusions they drew from that information. They began to demand "probity of measurement" and to discuss "discrepant measurements" and the use of mathematical tools, such as averaging and the least squares method, for analyzing large data sets. Although Buchwald does not specifically address their work, Nicholson, Cavendish, Cavallo, and Volta were very much a part of this movement. By the end of the eighteenth century, Cavendish, for example, was publishing the gory details of his experiments and results. He often presented his raw data in tabular form and openly discussed the sources of error in his research and how he had tried to compensate and correct for it. See, for example, Buchwald, 2006; Tiberius Cavallo, *A Complete Treatise of Electricity in Theory and Practice with Original Experiments* (London: Edward and Charles Dilly, 1777a); Henry Cavendish, "Experiments to Determine the Density of the Earth," *Phil. Trans.* 88 (1798): 469-526; Pancaldi, 2003 and Nicholson in Kirwan, *Essay on Phlogiston* and Golinski, *Science as Public Culture: Chemistry and Enlightenment in Britain, 1760-1820*, 141-144.. See also, chapter two, section 2.2.

[63] With regards to animal electricity, historians have tended to focus on the debate between Volta and Luigi Galvani. For example, Marcello Pera's analysis of this discourse focused on what he saw as the crucial and irreconcilable difference between their scientific approach to electrical research: Galvani, as a physician, favored a biological interpretation of his experiments, whereas Volta, trained in experimental physics, supported a physical explanation. More recent scholarship has begun to build on this framework and challenge aspects of this dichotomy. Marco Bresadola has argued that Galvani and Volta had more in common than Pera's study suggests. For instance, Volta conducted, albeit rudimentary, physiological experiments. Galvani also "tried to measure, even if unsuccessfully, the electricity involved in the phenomenon of contractions and performed many experiments aimed at explaining the difference in the number and intensity of contractions in various experimental arrangements." Fernando Abbri has further shown that Volta's research interests were not confined to 'physics'. He also practiced chemistry. He carried on an avid correspondence with Priestley and conducted experiments on the chemistry of airs, notably isolating methane. Guiliano Pancaldi has also demonstrated how Volta's concern for his academic position and place within the scientific community both fostered and impeded aspects of his research. By examining "some of the consequences brought about by Enlightenment values and notions", Pancaldi's biography provides the most sophisticated analysis of Volta's life and work to date. This dissertation adds to this discourse by analyzing British electricians' reception of Volta's experiments and theories. See, Ferdinando Abbri, "Volta's Chemical Theories: The First Two Phases," *Nuova Voltiana* 2 (2000): 1-14; Marco Bresadola, "Animal Electricity at the End of the Eighteenth Century: The Many Facets of a Great Scientific Controversy," *Journal of the History of the Neurosciences* 17 (2008): 8-32, 24,25; Pancaldi, *2003*, 2; Giuliano Pancaldi, "On Hybrid Objects and Their Trajectories: Beddoes, Davy, and the Battery," *Notes and Records of the Royal Society* 63 (2009): 247-262; Pera, 1992.

electrometers, like insulated conductors, often behaved in strange and unexpected ways when placed in different configurations. Volta, Nicholson, and Cavallo recorded detailed accounts of their procedures and results, conducted numerous trials with each instrument, and discussed possible sources of experimental error when using insulated conductors. They also debated how these instruments worked and what exactly they responded to and measured in a charged body. I show that the development of electrical instruments was an iterative experimental process.[64]

Natural philosophers and chemists were not only interested in measuring fluids behaving like electricity. They were also motivated by the unique anatomical structure of the torpedo ray. They tried to develop machines that not only mimicked the fish's effects, but also the structure of its so-called electrical organs. Cavendish, Nicholson, and Volta applied their knowledge of electrical devices to the study of animal electricity. For example, Cavendish created a mock-fish out of common electrical equipment, like insulated conductors, that was capable of imitating the torpedo's effects. He used his invention as proof that there existed a possible mechanism by which to account for the fish's electricity.[65] Thus, I analyze the different functions of insulated conductors in these two related contexts: as tools of experiment and measurement, and as models for the production of electricity in animals.

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[64] Historians often distinguish between instrument makers and instrument users. See, for example, Blondel, 1997; Warner, 1990. In contrast, this dissertation demonstrates that scientists were actively involved in the invention of electrical instruments in the eighteenth century.

[65] Henry Cavendish, "An Account of Some Attempts to Imitate the Effects of the Torpedo by Electricity.," *Phil. Trans.* 66 (1776): 196-225.

This rich history of analyzing the electrical properties of solids contributed to Volta's invention of the pile in 1799. The pile, which Volta christened the "artificial electrical organ" because of its similarity in form to the torpedo ray's anatomy, generated a continuous electrical discharge from the interaction of inorganic materials, such as silver, zinc, and salt water.[66] Unlike friction machines, the pile had no moving parts. Yet, its "power" was somehow derived from its material layers: not all substances or material combinations worked and those that did produced different amounts of electricity.[67] Electricians generally acknowledged that there must exist a relationship between the substances in the pile and its electrical output, but the nature of that relationship was contentious.[68]

Chapter three examines chemical theories of the pile's electrical action. Several histories of the battery contend that the pile validated Volta's theory of contact electricity.[69] In brief, Volta adopted the widespread view that all substances contain some amount of electrical fluid and argued that the contact of different conductors created a repulsive 'tension' or force, setting electrical fluid into motion. I show that the scientific community was by no means convinced by Volta's argument. Although Volta asserted that the pile was an electromotive instrument, chemists re-interpreted its electrical action

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[66] Alessandro Volta, "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds," in *Alessandro Volta and the Electric Battery*, ed. Bern Dibner (New York: F. Watts, 1964).

[67] Humphry Davy, "An Account of Some Galvanic Combinations Formed by the Arrangement of Single Metallic Plates and Fluids Analogous to the New Galvanic Apparatus of M. Volta," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839g), 182-187.

[68] Kragh, 2000a.

[69] See, for example, Joost Mertens, "Shocks and Sparks: The Voltaic Pile as a Demonstration Device," *Isis* 89, no. 2 (1998): 300-311; Pera, 1992.

and, via a series of sophisticated experiments, argued that it was primarily a chemical device.[70]

In 1797, Nicholson founded a journal dedicated to natural philosophy, chemistry, and the arts. As editor, he selected papers on topics he considered to be relevant and important to the study of electricity, even re-publishing little known essays on electrochemistry. He also used his journal to publish his experiments on the pile's chemical effects, co-authored with Anthony Carlisle, a physician and friend of Royal Society president, Joseph Banks. Their research showed that the pile's current decomposed compound liquids, e.g. water was transformed into hydrogen and oxygen gas. As a result of their studies, there was an explosion of chemical researches on the pile and its electrical action.[71]

In chapter three, I analyze British chemists' experiments with the pile. I argue that two questions framed this discourse. First, scientists were forced to revisit the problem that had plagued eighteenth-century chemical practitioners: did electricity facilitate or participate as a substance in chemical change? Davy argued that his experiments indicated that electricity was created and limited by the chemical changes taking place between the pile's layered materials. To the consternation of many of his contemporaries, he suggested that electricity might be something other than a material like oxygen or

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[70] See, for example, Humphry Davy, "Early Miscellaneous Papers," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, Co. Cornhill, 1839); William Henry, "On the Theories of the Excitement of Galvanic Electricity," *Nicholson's Journal* 35, no. August (1813): 259-271; William Nicholson and Anthony Carlisle, "Account of the New Electrical or Galvanic Apparatus of Sig. Alex. Volta, and Experiments Performed with the Same," *Nicholson's Journal* 4, no. July (1800): 179-191; William Hyde Wollaston, "Experiments on the Chemical Production and Agency of Electricity," *Phil. Trans.* 91 (1801): 427-434.

[71] Lilley, "Nicholson's Journal (1797-1813) "; Nicholson and Carlisle, 1800; Sudduth, 1980.

hydrogen. Other chemists rejected this view. William Wollaston, a British metallurgist, argued that electricity was a chemical substance, capable of being displaced by other materials and released during chemical change. I examine these two different theories in detail.

Second, did the flow of electrical fluid cause chemical change or was chemical change the cause of electricity? While natural philosophers and chemists agreed that the pile produced profound chemical alterations in substances, they disagreed on how chemical change affected electrical production. Although Davy and Wollaston devised different chemical mechanisms to account for current, they fundamentally supported a chemical theory of electricity, i.e. the pile's current was a product of chemical change. Their innovative chemical experiments with the pile, however, did not convince natural philosophers that the battery was a chemical instrument. Why?

I argue there were two important reasons for this. First, contact theorists appealed to the historical authority of natural philosophy. For over a century, electricians had not only probed the effects of electricity, but also established quantifiable relations between its attractive and repulsive characteristics.[72] Therefore, many natural philosophers deemed the measurement of electricity from the contact of metals more reliable than the often qualitative, chemical effects associated with the pile's electrical action. Secondly, although chemists believed there must exist some connection between chemical change and the production of electricity, they disagreed on the nature of that relationship. For example, rather than arguing like his contemporaries that electricity was produced by a

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[72] Heilbron's study of electricity remains the most comprehensive account of electrical research and practice from the seventeenth to mid-eighteenth century. See Heilbron, 1999.

specific chemical process, like oxygenation, Davy argued there was a general relationship between all chemical reactions and electrical effects.[73]

Thus, the following three chapters illustrate that subtle, but important distinctions emerged between eighteenth and early nineteenth-century electricians. Priestley, Nicholson, and Cavallo combined their interests in chemistry and electricity by not only studying the chemical effects of electrical fluid, but also by developing instruments to probe the physical properties of electricity. In contrast, early nineteenth-century British electrochemists often measured the amount of electricity indirectly, using chemical change as guide to electrical strength instead of an electrometer.[74] In short, chemical practitioners began to focus more on analyzing the particulars of chemical reactions, which included electricity, whereas natural philosophers increasingly used precision instruments to mediate their experience and measure of electrical phenomena, e.g. by comparing electrical properties to known calculable quantities like gravity. Fewer scientists kept a foot in both camps. Although natural philosophers and chemists acknowledged the importance of each type of research, these differences in experimental approach contributed to the debate on electrical generation: chemists arguing that

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[73] Davy supported a chemical theory of electricity throughout his career, but modified his ideas in light of new experimental findings. Between 1800 and 1802, for instance, he argued that current was somehow generated by the chemical changes occurring in the pile. In 1807, he proposed that different elements possessed different electrical energies. This explained why certain substances were consistently drawn towards either the positive or negative terminal of the battery. See for example, Davy, 1807; Davy, "Early Miscellaneous Papers."

[74] Davy argued that: "a measure of the intensity of that agency in galvanic batteries, which produced chemical changes in water, may be derived from the quantity of gas it is capable of evolving in a given time; or from the length of the fluid chain through which it can be transmitted." Humphry Davy, "A Syllabus of a Course of Lectures on Chemistry," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839k), 327-436, 408.

chemical changes preceded current while natural philosophers asserted that a percussive force, preceding chemical change, caused the flow of electricity.[75]

Whether a contact or a chemical theorist, however, all physical scientists recognized that electricity provided a powerful new means of decompounding complex substances, suggesting new theories of chemical cohesion, but what was electricity? Was it a material that entered into chemical combination with other substances to form charged bodies, or was electricity itself the product of chemical reactions?

This dissertation examines chemical practitioners' experiments with electricity and the theories they constructed to explain its effects. Michel de Certeau has argued that by understanding the evolution of concepts, historians can obtain a richer understanding of the intellectual and cultural forces at work at a particular time and location.[76] Utilizing this approach, this dissertation has two complementary goals: First, by analyzing the experimental methods used to study electricity, this work demonstrates that analogical arguments were prevalent and important to the development of eighteenth-century electrical science. Second, it demonstrates that chemical practitioners were profoundly concerned by and interested in electrical phenomena. They were actively involved in shaping electrical discourse and, in turn, their participation affected the development of their own discipline. Chemists, such as Priestley and Davy, sought to demonstrate the rigor of their methods and the validity of their claims regarding chemical processes using electricity. Their research revealed the importance of electricity to fundamental chemical

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[75] See, for example, Jean-Baptiste Biot, "Quelle Est L'influence De L'oxidation Sur L'électricité Développée Par La Colonne De Volta," *Annales de Chimie* 30 Prairial an 11, no. June (1803): 4-45.

[76] Michel Certeau, *The Writing of History*, trans. Tom Conley (New York: Columbia University Press, 1988).

reactions, like synthesis and decomposition. Thus, by analyzing how chemists conceptualized and utilized electricity, this dissertation significantly contributes to the growing body of literature challenging the traditional history that the study of electricity had been the pursuit of physicists alone.

Chapter 1: The Study of Heat and Electricity in the Eighteenth Century

> It may appear doubtful to some whether the subject of heat belongs most properly to mechanical or chemical philosophy. Its influence in chemistry is unquestionable and indispensable; but its mechanical effects are no less remarkable: it could not therefore with propriety be omitted either in a course of chemical or physical lectures…[1]
>
> Thomas Young (1807)

Introduction

As discussed in the Introduction to this dissertation, this work analyzes chemical practitioners' contributions to the study of electricity. This chapter demonstrates that eighteenth-century chemists not only investigated the relationship between electricity and heat, but also debated how these phenomena brought about chemical change.[2] As a result of this discourse, the theoretical and methodological standards of chemistry changed. Part of this transformation included a shift away from principles, for instance the belief that all combustible substances must contain an inflammable principle, to elements whose qualities did not necessarily carry over when combined with other substances.[3] Adopting the latter framework, however, made it more difficult to not only classify heat and electricity, but also to explain their respective roles in chemical processes.

It was well known that applying heat to complex substances separated materials with different melting points. Heat, however, produced other effects that were more difficult to explain. Joseph Priestley, for instance, showed that heating a pure metal in air (like zinc or copper) not only transformed its appearance (becoming whitish or greenish

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[1] Young, *A Course on Natural Philosophy*, 631.

[2] Some historians suggest the study of electricity and its relationship to chemistry only began with the invention and application of the voltaic pile in 1800. As this chapter shows, this is not true. See for example, Mosini, "When Chemistry Entered the Pile."

[3] Dobbs and Siegfried, 1968.

respectively), but also altered its physical properties like hardness. Moreover, the air was also changed by the act of heating the metal - it no longer sustained life (specifically, mice asphyxiated in the gas).[4]

To explain these results, Priestley modified the popular chemical theory of Georg Stahl, who proposed that all combustible substances contain phlogiston, a material agent necessary for burning.[5] Priestley argued that the chemical changes observed in metal and air during combustion were evidence that phlogiston was being released into the surrounding medium. Burning ceased when the surrounding medium was saturated with phlogiston, or when the material itself had released all of its phlogiston to the environment. He also asserted that phlogiston must be toxic, as evidenced by the inability of phlogisticated air to sustain respiration.[6]

A debate over the material cause of combustion broke out in the latter half of the eighteenth century.[7] Antoine Lavoisier showed that combustible materials gained weight during burning. He argued that this experimental result was incompatible with phlogiston theory: if phlogiston, a substance, was released during combustion the weight of the

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[4] Joseph Priestley, "Observations on Different Kinds of Air," *Phil. Trans.* 62 (1772): 147-264.

[5] J.R. Partington and Douglas McKie, "Historical Studies of Phlogiston Theory: Part I. The Levity of Phlogiston," *Annals of Science* 2 (1937): 361-404, 368-373.

[6] Priestley, Air 1772.

[7] There is an extensive literature on this topic, including, but not limited to: Arthur Donovan, "Lavoisier as Chemist and Experimental Physicist: A Reply to Perrin," *Isis* 81 (1990): 270-272; Donovan, ed., *1988*; Guerlac, "Chemistry as a Branch of Physics: Laplace's Collaboration with Lavoisier."; Henry Guerlac, ed., *Antoine-Laurent Lavoisier, Chemist and Revolutionary* (New York: Scribner, 1975); Holmes, "2000."; Evan Melhado, "On the Historiography of Science: A Reply to Perrin," *Isis* 81 (1990): 273-276; J.R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: Part III. Light and Heat in Combustion," *Annals of Science* 3 (1938): 337-371; J.R. Partington and Douglas McKie, "Historical Studies on Phlogiston Theory: Part IV. Last Phases of the Theory," *Annals of Science* 2 (1939): 113-149; Perrin, "1990."; Simon Schaffer, "Priestley's Questions: An Historiographic Survey," *History of Science* (1984): 151-183; Frederick Seitz, "Henry Cavendish: The Catalyst for the Chemical Revolution?," *Notes and Records of the Royal Society* 59 (2005): 175-199.

burning material should decrease. In *Elements of Chemistry* in 1789, he proposed a new chemical classification system based on elements, unique substances that could not be broken down into other materials, and introduced the oxygen theory of combustion to replace phlogiston.[8]

Oxygen theory held that two elements were required for combustion: oxygen, which is the element that the burning substance absorbed during combustion, and caloric, which is heat transmitted into the surrounding medium as a subtle fluid, a collection of tiny particles capable of permeating solid matter.[9] Within this new framework, the process of burning involved the decomposition and recombination of substances. In its simplest form, an inflammable material, denoted by *X*, possessed a high degree of affinity for oxygen. Combustion occurred when *X* was immersed in oxygen gas (a mixture of elemental oxygen and caloric), and an igniter, like a spark or flame, was present. The igniter started and/or increased the rate of burning. It facilitated the separation of oxygen gas into its constituents, making it possible for the particles of *X* to recombine with elemental oxygen particles, releasing caloric. This produced a new compound of *X* and oxygen like metal calx or rust. Caloric particles produced the accompanying sensations of warmth and light.[10]

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[8] Lavoisier, *Elements of Chemistry [1789].*

[9] Caloric was thought to be self-repulsive. This explained phase changes and differences in latent heat. For example, water and steam co-exist at 100C, yet it takes more heat to transform water into steam at 100C. Lavoisier argued that the extra caloric attached itself to the water corpuscles. Since there was more caloric in steam, and caloric repelled caloric, the water corpuscles were pushed farther apart. Thus, steam occupied more volume than water.

[10] Antoine Lavoisier and Pierre Simon LaPlace, *Memoir on Heat, Read to the Royal Academy of Sciences, June 28, 1783*, trans. Henry Guerlac (New York: Neale Watson Academic Publications, 1982).

Priestley asserted that in the process of burning, something was lost: phlogiston. In contrast, Lavoisier argued that something was gained: oxygen. By asserting that caloric was an element that entered into chemical combination with other substances, Lavoisier also reasoned that water was ‘chemically’ different from steam; the ratio of caloric to water particles increasing from liquid to gas.[11] Humphry Davy took offense to this notion.[12] He contended that the only difference between water and steam was ‘physical’, that is while the distance between the water corpuscles increased from liquid to gas, the particles themselves remained the same. Citing Count Rumford’s famous cannon-boring experiments that called into question the physicality of heat, Davy further argued that heat was an effect of matter in motion. The introduction of heat or motion to a substance modified its internal structure, aiding in chemical change.[13] Thus, over the course of the late eighteenth and early nineteenth centuries, chemists actively debated whether heat was a physical effect that could bring about chemical change or a substance with its own unique chemistry.

During this period, electricity, its relation to heat, and its role in chemical processes also became important problems worthy of debate.[14] Although heated

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[11] Lavoisier, *Elements of Chemistry [1789]*, 1-25, 175.

[12] Humphry Davy, "Essay on Heat, Light, and the Combinations of Light, with a New Theory of Respiration," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839a), 3-88, 9-23.

13 Ibid, 21; Sir Benjamin Thompson (Count Rumford), "An Inquiry Concerning the Source of Heat Which Is Excited by Friction," *Phil. Trans.* 88 (1798): 80-102.

[14] Sudduth argues that “[b]efore Beccaria’s experiments, electricity had most often been examined *qua* electricity, not *qua* an electric fire exhibiting chemical properties.” As this chapter shows, there was a long history of likening electricity to fire predating Beccaria’s research. See Sudduth, "Eighteenth Century Identifications of Electricity with Phlogiston," 132.

substances did not exhibit the same attractive powers as electrified bodies, natural philosophers and chemists noticed many similarities between electrical and thermal phenomena. Electricity like heat produced fire and light. Substances like copper transmitted both electricity and heat, while others like wood did not. While wood readily burned, it did not permit heat transfer as efficiently as copper. Similarly, it did not conduct electricity.[15] Furthermore, in 1775, Priestley demonstrated that applying static electricity to metal in atmospheric and/or dephlogisticated air (oxygen) also created calxes (metal oxides) in the same manner as heating.[16] These observations and experiments reinforced the relationship between heat and electricity.

To account for these effects, a variety of electrical theories were developed that described electricity as a fiery, material fluid related to heat, while electrical experiments focused on friction machines, which produced electricity mechanically. Like phlogiston, and later caloric, it was thought that electrical fluid interacted on a microscopic scale with matter to produce observable macroscopic effects, such as light, sparks, and tingling.[17] Towards the end of the eighteenth century, however, as chemists' conception of heat began to change and new ways of generating electricity were discovered, it became clear that drawing a simple parallel between these two phenomena no longer sufficiently accounted for electrical behavior.

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[15] Beccaria, *Artificial Electricity*, 315-316.

[16] Priestley, *HPSE 1775*, 311.

[17] For example, William Watson, Benjamin Franklin, Joseph Priestley, Giambatista Beccaria, and Henry Cavendish all described electricity as a (subtle) fluid somehow related to heat. Their research is the focus of this chapter.

In 1775, Alessandro Volta invented the electrophore, an electrical condenser (capacitor) made of metal and resin that perpetually released electrical fluid despite having been only charged once by a friction machine.[18] In 1788, William Nicholson built another instrument called a doubler, which also produced electricity without contact.[19] In 1791, Luigi Galvani discovered that placing a frog's muscle between two different metals generated an electric current,[20] and in 1799, Volta invented the voltaic pile (or battery), which also produced electricity without mechanical aids.[21]

Electricity had been hitherto generated with friction. It was the short-lived effect of a strictly mechanical process and like heat had been classified as a unique substance. These new methods of producing electricity opened a new field of inquiry within physical science: were these three electricities, frictional, animal, and voltaic, related to heat? Were they different manifestations of the same type of electricity?[22] These questions will be addressed in chapter two.

This chapter focuses on scientists' perceptions of heat and electricity, and the chemical experiments they conducted with electricity. Although chemists did not reach a consensus regarding its nature, be it a subtle fluid or an effect of matter in motion, their understanding of chemical processes changed. Late eighteenth-century chemical practitioners like Priestley argued that electricity was a form of phlogiston because it

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[18] Pancaldi, 2003, 73-109.

[19] Nicholson, 1788. The workings of the electrophore and doubler will be discussed in detail in chapter 2, section 2.3.1 and 2.3.2.

[20] Luigi Galvani, *Commentary on the Effects of Electricity on Muscular Motion [1791]*, trans. Margaret Glover (Norwalk, CT: Burndy Library, 1953).

[21] Volta, 1964.

[22] Davy, 1822, 64.

produced similar effects. As processes of combustion, however, began to be thought of as chemical reactions involving oxygen and caloric, and new non-mechanical ways of producing electricity were discovered, chemists reconsidered the relationship between heat and electricity. In evaluating the pile's electrical action, for instance, they drew on Lavoisier's theoretical account of combustion, attributing the production of electricity to the absorption of oxygen.[23] Thus, this chapter demonstrates that late eighteenth-century chemists participated in the study of electricity and its effects by drawing analogies to thermal phenomena.

1.1: The Importance of Likeness

> Franklin's chief propagandist, Priestley, agreed that "analogy is our best guide in all philosophical investigations" and hoped his *History and Present State of Electricity* would persuade electricians to follow Franklin's example in part by "deducing one thing from another by means of analogy." Franklin was indeed a bold analogist. The lightning rod is the most dramatic and successful example: thundercloud was to iron rod, Franklin surmised, as static electricity generator to bodkin.[24]

As discussed in the introduction, analogical reasoning was an important part of scientific practice in the eighteenth and nineteenth centuries. Many natural philosophers and chemists used analogy, which was generally defined as "having relations" or a "resemblance between things with regards to some circumstance or effect."[25] In specific scientific contexts, however, it had a more precise meaning. In particular, I have

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[23] See for example, Davy, "Early Miscellaneous Papers."; Wollaston, 1801.

[24] Riskin, 2002, 96.

[25] Samuel Johnson, *A Dictionary of the English Language* (London: J. Johnson, C. Dilly, G.G. and J. Robinson, et al, 1799), 62.

identified four types of analogical arguments in use in the eighteenth century: similarity of form, function, effect, and cause.[26]

This chapter demonstrates the importance of the third kind of analogy, similarity of effect, to the debates over the relationship between heat and electricity. Eighteenth-century scientists perceived that electricity and heat had much in common, e.g. they both produced light, fire, and comparable kinds of chemical change. Was electricity then a type of heat? I will analyze how electricians likened and/or distinguished between electrical and thermal phenomena, and the experimental evidence they marshaled to either support or refute the postulate that electricity was a form of heat.

1.1.1: From Electric *Fluid* to Electric *Fire*

Before examining the relationship between electricity and heat, some background information on electrical studies is required. For most of the eighteenth century, electrical research focused on mechanically produced electricity. In 1708, Francis Hauksbee, a British natural philosopher who designed public demonstrations for the Royal Society under the tutelage of Newton, developed a friction machine. This electrical apparatus consisted of a rigid wax cylinder, which could be rotated by a hand crank. As it rotated, a brush swept across its face; the resulting friction between the two surfaces produced electricity.[27] Friction was thought to agitate or enable the flow of electrical fluid, a

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[26] See Introduction, 15.

[27] Hauksbee, "Several Experiments Shewing the Strange Effects of the Effluvia of Glass, Produceable on the Motion and Attrition of It."

pervasive substance believed to be responsible for the effects collectively known as electricity.[28]

With the development of friction machines (Figure 1.1), it was possible to study the relationship between electricity and substance more extensively than in earlier periods. Unlike handheld devices, these generators allowed for the repeated firing of sparks and produced more powerful shocks. Through the application of electricity, electricians tried to charge everything and anything, taking note of its effects.

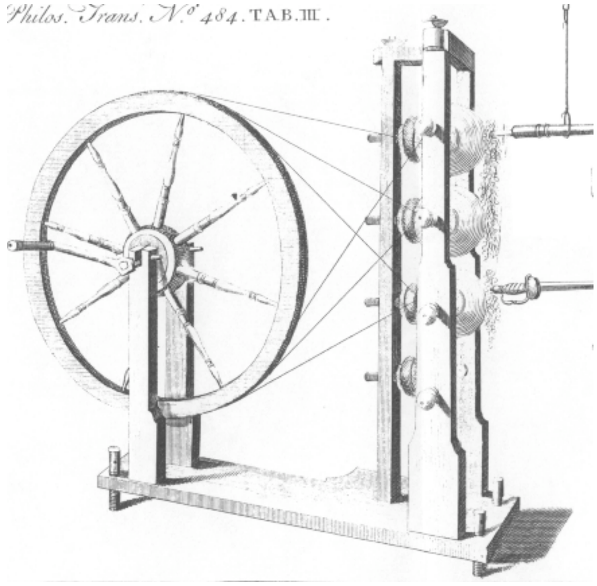

Figure 1.1: **An example of a friction machine owned by William Watson**, Benjamin Franklin's 'electrical' mentor (1746)[29]

Early experiments revealed that electricity had complex material dependencies. In 1708, Hauksbee showed that a "Hoop of Threads [held] over [an electrified wax] cylinder… were attracted and directed towards its Center", pulled taut as if by invisible hands.[30] In 1731, Stephen Gray, an English dyer turned electrician, reported an experiment in which he electrified a boy, suspended horizontally two feet above the ground from two clothes lines, thin pieces of loose, brass metal placed on a wooden platform below his head.

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[28] William Watson, "A Sequel to the Experiments and Observations Tending to Illustrate the Nature and Properties of Electricity," *Phil. Trans.* 44 (1746b): 704-749, 744. Watson wrote: "May not the electrical Machine, from its Uses, be denominated a Fire-pump, with equal Propriety as the Instrument of *Otto Guerick* and *Mr. Boyle*, that of the Air?"

[29] Ibid, 718.

[30] Francis Hauksbee, 1708-1709, 87.

"Upon the Tube's [glass] being rubbed, and held near his Feet… the Leaf-Brass was attracted by the boy's Face with much Vigour, so as to rise to the Height of eight, and sometimes ten Inches." Repeating the experiment on other days, however, produced slightly different results - the height to which the brass filings lifted noticeably varied.[31] In 1746, John Browning, a tradesman, wrote to Henry Baker, a physician interested in the therapeutic effects of electricity, of his unsuccessful attempts to electrify trees. Baker took it upon himself to try to charge "a Myrtle-tree, of between 2 or 3 Feet in Height, growing in a Pot, at the Seat of the Duke of *Montague* at *Ditton*". He reported it was a great triumph, "whenever the Hand, or other non-electric Body, was brought near the Leaves, Streams of fine purple Fire issued there from…"[32] These stunning effects, the snapping of sparks, colored lights, and the communication of a force of attraction (and repulsion) over distance without contact, captured the attention of natural philosophers and chemists alike.

Between 1730 and 1750, electrical experiments became more sophisticated. For example, Gray showed that under certain conditions metal mixtures like brass could be charged and that electrical fluid could be conveyed to an object up to 600 feet away along cords of thread.[33] Charles Francois Dufay, a talented French patrician and physicist who built significantly upon Gray's researches[34], further demonstrated that there were three

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[31] Stephen Gray, "A Letter to Cromwell Mortimer, MD Containing Several Experiments Concerning Electricity," *Phil. Trans.* 37 (1731): 18-44, 40.

[32] John Browning, "Part of a Letter from Mr. John Browning, of Bristol to Mr. Henry Baker, FRS, Dated Dec. 11, 1746, Concerning the Effect of Electricity on Vegetables," *Phil. Trans.* 44 (1747): 373-375, 375.

[33] Gray, 1731, 29.

[34] Gray, 1731; Stephen Gray, "A Letter from Stephen Gray to Dr. Mortimer, Secr. R. S. Containing a Farther Account of His Experiments Concerning Electricity " *Phil. Trans.* 37 (1731-1732a): 285-291;

classes of electrical materials: some substances produced and stored electricity (electrics); some transferred it (non-electrics or conductors), while others impeded its passage (insulators or non-conductors).[35] Table 1.1 lists substances determined to be electric, non-electric, or non-conducting.

Non-Electrics	Electrics	Non-Conductors
Water Metal (tin, iron, etc.) Animals* Plants*	Airs (Fixed Air (carbon dioxide), Nitrous Air, Dephlogisticated Air (oxygen), etc.) Glass Leather, Hair Cork, Pith Wood** Marble** Salt Fabrics (Silk, Linen, Wool) Camphor, Sulphur, Nitre Amber, Gems (Diamond, Sapphire, Amethyst, etc.) Quartz, Crystal, Talc Resin, Wax, Gums Sugar	Oil Tallow Fat Butter

Table 1.1: **Sample of Known Electrical Substances by 1769**[36]

*Animals (both dead and alive) and plants were generally thought to conduct because they contained non-electric fluids such as water, although certain animal and plant products, such as hair, fat, paper, and pith, were non-conductors.

** Certain electrics, like some types of wood and marble, only became electrified with the application of heat.

Dufay observed that conductors like copper behaved markedly different from electrics like glass or wax. A person in proximity to charged glass might witness a spark of light and experience tingling and/or numbness. Touching electrified glass with a metal rod conveyed these same sensations over the length of the conductor. While glass could maintain a charged state for a prolonged period of time, metals transmitted electrical fluid

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Stephen Gray, "Two Letters from Mr. Stephen Gray to C. Mortimer, Containing Farther Accounts of His Experiments Concerning Electricity," *Phil. Trans.* 37 (1731-1732b): 397-407; Heilbron, 1999, 250-260, 250.

[35] Roderick Home, "Fluids and Forces in Eighteenth Century Electricity," *Endeavour* 26 (2002): 55-59.

[36] Joseph Priestley, *History and Present State of Electricity with Original Experiments*, 2 ed. (London: Printed for K. Dodsley, J. Payne, and T. Cadell, 1769). See also: Cavallo, 1777a, 5-10.

virtually instantaneously. Dufay also showed that all non-conductors, including stone and wood, could be temporarily rendered electric by heating.[37] (Priestley would further show in 1770 that heating certain electrics like charcoal also briefly transformed them into conductors.)[38] These researches would later be used to support theories likening electricity and heat.

It was also qualitatively known that different electrics produced different amounts of electricity. Hauksbee had earlier noted that cylinders coated with sulphur generated less electrical fluid than those covered with “Rosin mixt with Brick-dust”.[39] Dufay further observed that electrics not only produced varying quantities of electricity, but also different kinds. He wrote, “Two Silk Ribbons rendered electrical, will repel each other; two Woollen Threads will do the like; but a Woollen Thread and a Silk Thread will mutually attract one another.”[40] Dufay argued that these simple experiments showed that two types[41] of electricity existed: one vitreous and one resinous.[42] Bodies charged by vitreous materials, such as glass, quartz, and wool, repelled similarly charged objects and

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[37] Charles Dufay, "A Letter from Mons Dufay, FRS and of the Royal Academy of Sciences at Paris, to His Grace Charles Duke of Richmond and Lenox, Concerning Electricity," *Phil. Trans.* 38 (1733): 258-266, 258; Heilbron, 1999, 252-255.

[38] Joseph Priestley, "Experiments and Observations on Charcoal," *Phil. Trans.* 60 (1770): 211-227.

[39] Hauksbee, 1708-1709, 89; Heilbron, 1999, 236: Heilbron says Hauksbee “exploited without acknowledgment hints [to this effect] first given by [Stephen] Gray.”

[40] Dufay, 1733, 264.

[41] Home, 2002, 56: Home argues that Dufay never explicitly stated whether these were two different materials, or modifications of the same substance.

[42] For a list of substances tending to be positively or negative charged, see Cavallo, 1777a, 16-18. Scholarship examining the two fluid model versus the one fluid model includes: Franz U. Aepinus, *Aepinus's Theory of Electricity and Magnetism [1759]*, ed. Roderick Home, trans. P.J. Connor (Princeton, NJ: Princeton University Press, 1979); I. Bernard Cohen, *Franklin and Newton: An Inquiry into Speculative Newtonian Experimental Science and Franklin's Work in Electricity as an Example Thereof* (Philadelphia: The American Philosophical Society, 1956); I. Bernard Cohen, *Benjamin Franklin's Science* (Cambridge, MA: Harvard University Press, 1990); Heilbron, 1999.

attracted bodies electrified by resinous substances, e.g. amber, tree sap, and silk. But, why did wool produce vitreous as opposed to resinous electricity? "[Did] it depend on the chemical character of the rubbed body?"[43]

In addition to learning there were two electricities, natural philosophers and chemists continued to explore the relationship between electrical and chemical phenomena. For example, in 1745, William Watson, an indentured servant who rose through the ranks to become a successful apothecary, fellow of the Royal Society, and winner of the prestigious Copley Medal,[44] showed that coating solid electrics with water,[45] or introducing moisture to non-conducting airs, temporarily made those substances conduct. (He found that ice behaved like an electric.)[46] He also demonstrated that electricity could set materials, like wine, oil, and gunpowder, on fire.[47]

Watson further experimented with the effects of applying sparks to gases. He combined reactive liquid and solid substances in a flask. Wetting the lip of the jar with his finger, he found that electrical fluid could be encouraged to jump from a conductor attached to a friction machine to the flask's water coating, simultaneously passing through any gases emitted from the mixture.

Watson was particularly interested in exploring the degree of inflammability of airs produced in mines, which he noted had "occasion'd many terrible Accidents".

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[43] Heilbron, 1999, 257; Home, 2002, 55-59.

[44] Heilbron, 1999, 296-301.

[45] Dufay first showed that water behaved as a conductor.

[46] William Watson, "A Continuation of a Paper Concerning Electricity," *Phil. Trans.* 44 (1746a): 695-704, 695.

[47] Watson, 1744-1745, 486-487, 489; Watson, 1746a, 697. Watson suggested that different colored sparks were the result of different "Reflextion of the electrical Fire from the Surface of the Body from which it is emitted, than to any Difference in the Fire itself." The temperature of the body remained constant.

Mixing in a glass jar "an Ounce of Filings of Iron [iron plus impurities], an Ounce of Oil of Vitriol [sulphuric acid], and four Ounces of Water… ebullition ensued". Sparks dramatically set the vapors on fire. Flames "burnt near the Top and out of the Neck of the Flask a considerable Time." He further noted that enough heat was generated by this chemical reaction to melt the remaining iron in the jar. He cautioned electricians repeating his experiments: "It has sometimes happen'd, if the [wet] Finger has been applied before the inflammable Air [hydrogen] has found a ready *Exit* from the Mouth of the Flask, that the Flash [or spark] has filled the Flask, and gone off with an Explosion equal to the Firing of a large Pistol; and sometimes indeed has burst the Flask."[48] On the basis of these experiments, Watson began to refer to electric fluid as *electric fire*.

Electricity fell into a special group of phenomena not easily represented by the traditional categories of matter. At the turn of the eighteenth century, there were three systems for describing nature. The four elements of the ancients, earth, air, fire, and water, accounted for different qualities. Water, for instance, represented fluidity, while earth embodied heaviness. In the sixteenth century, Paracelsus added three more principles, reflecting increased awareness of the complexity of matter: sulphur (inflammability), salt (fixity), and mercury (volatility). In the seventeenth century, the mechanical philosophy emerged, which described the world in terms of a single substance broken into different shapes with different motions, these variations manifesting properties such as solidity and sourness.[49] Eighteenth-century scientists

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[48] Watson, 1744-1745, 495-496.

[49] See, for example, Christoph Lüthy et al., eds., *Late Medieval and Early Modern Corpuscular Matter Theories* (Boston: Brill, 2001), 1-38; William Newman, *Atoms and Alchemy: Chymistry and the Experimental Origins of the Scientific Revolution* (Chicago: University of Chicago Press, 2006).

found flaws in all three approaches to matter: they did not adequately account for nature's diversity. More specifically, with the development of thermometers, which provided a relative measure of a body's heat, and the discovery that some chemical combinations of sulphur were non-combustible, they began to reconsider the category 'fire' and its relationship to electricity.

As an apothecary, Watson was interested in recent developments in medicine and botany, and came across the work of the Dutch physician, Herman Boerhaave. Boerhaave was professor of medicine and chemistry at the University of Leyden, most famous for his contributions to clinical practice, but also for his theory of fire, cited later in the eighteenth century by Benjamin Franklin, Lavoisier, and Priestley. Boerhaave made a distinction between "crude fire", which produced flames, and "elementary fire" (heat), which affected the density of materials.[50] He suggested that all substances were imbued with elementary fire in proportion to their volume. It was a material composed of very fine, subtle particles, capable of permeating solid matter, and characterized by warmth, "light, color, expansion of fluid or solid bodies, and burning or fusion."[51]

Electrical fluid was a substance that had hitherto defied characterization. Watson, however, immediately saw an analogy between the recently observed electrical

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[50] Cohen, 1956, 230; Rina Knoeff, *Herman Boerhaave (1668-1738): Calvinist Chemist and Physician* (Amsterdam: Koninklijke Nederlandse Akademie van Wetenschappen, 2002); Partington and McKie, "1938," 39-42; William Smeaton, "Herman Boerhaave: Physician, Botanist, and Chemist," *Endeavour* 12 (1988): 139-142. Cohen writes: "Many philosophers had confused fire 'as supported by combustible matter' with pure elementary fire. But the latter, according to Boerhaave, was quite different; for example, it might be collected in certain bodies (such as the metals) without in any way causing a destruction of them, whereas in the former 'the bodies themselves are consumed and dissipated by the action thereof, so as almost to disappear from our notice.'" Also, Boerhaave believed temperature did not affect the weight of a substance. Whether hot or cold, its weight remained unchanged. Volume, however, did have a thermal dependence as warm bodies tended to 'expand'.

[51] Cohen, 1956, 228.

phenomena and Boerhaave's[52] description of elementary fire.[53] In particular, he suggested that electrical fluid might be a type or variant of heat. Watson posed the following rhetorical questions:

> Whether or no, that, which, from its being first discover'd in Amber, we call Electricity, electrical Aether, electrical Power &c. is any other than elementary Fire?... Whether or no this Fire does not appear in different Forms, according to its different Modifications? Does it not, when diffused under a large Surface, appear to affect us as Air? When brought towards a Point, does it not become visible, as lambent Flame? When nearer still, does it not explode, and become the Object also of our Feeling as well as of our Hearing? Altho' it does not affect our Skin with the Sensation of Heat; does it not, by its lighting up inflammable Substances, shew itself to be truly Fire?"[54]

He noted that electricity, like fire, produced heat and light, as evidenced by the emission of sparks and the burning of inflammable airs. Sparks, like flames, varied in color and brightness. Metals and other substances could also be melted by electricity, their volumes altered. To explain the similarity of effects between electricity and heat, Watson suggested that electricity was a form of elementary fire.

To show precedent and support for this line of reasoning, he quoted Newton:

> …although the arguing from Experiments and Observations by Induction be no Demonstration of general Conclusions; yet it is the best Way of arguing which the Nature of Things admits of… By this Way of Analysis we may proceed from Compounds to Ingredients, and from Motions to the Forces producing them; and, in general, from Effects to their Causes …[55]

Newton advocated the rigorous study of particulars from which more general patterns of behavior or laws could hopefully be discerned. Analogy suggested a possible means for

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[52] Watson, 1746b, 745: "Does not the Power we are now Masters of, of seeing the separation of Fire from Bodies by Motion, and of seeing it restored to them again, and even after that Motion has ceased cause us rather to incline to the Opinions of *Homberg*, *Lemery* the younger, *s'Gravesand*, and *Boerhaave*".

[53] Heilbron, 1999, 300.

[54] Watson, 1746b, 744.

[55] Ibid, 749.

establishing a connection between the particulars and the general.[56] Watson argued his experiments demonstrated a strong similarity between thermal and electrical effects (the particulars). Thus, electricity had something in common with fire. Since both were substances, he proposed that they must share or contain a common material: elementary fire or heat (the general).

Watson was not alone in suggesting that the similarities between thermal and electrical phenomena indicated that electricity was a form of fire. Abbé Jean Antoine Nollet, a priest who had assisted Dufay in his research and "preferred… experimental philosophy to theology", also referred to Boerhaave's theory and used the term *electric fire*.[57]

Despite Roderick Home's studies of Nollet's contributions to the study of electricity and, more generally, experimental philosophy – Nollet having taught Lavoisier a course in experimental physics for example – history remembers him for having electrified a circle of Capuchin monks to the delight of King Louis XV. Electrical research undoubtedly had a playful side as the growing literature examining popular demonstrations of electricity and its effects attests.[58] Nollet's work, however, had a long-lasting impact on French natural philosophy. His "ideas, far from being eclipsed almost

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[56] Shapiro, 1993, 34-48, 43-45.

[57] Home, 2002, 57: "The universality of the phenomenon led Nollet and others in the 1740s to identify the matter of the electrical effluvia with the universally disseminated fiery matter that Herman Boerhaave had invoked to account for the distribution of heat in the world."

[58] See, for example, Bernadette Bensaude-Vincent and Christine Blondel, *Science and Spectacle in the European Enlightenment* (London: Ashgate Publishing, 2008); James Delbourgo, "The Electric Machine in the American Garden," in *Science and Empire in the Atlantic World* (New York: Routledge, 2008), 255-280.

overnight by those of [Benjamin Franklin], continued to dominate French discussion… well into the 1770s."[59]

Nollet adopted a Cartesian explanation of electrical phenomena. Rubbing a substance "agitated" subtle fluid "hidden within its pores", dislodging it. As this material was pushed away from the body, "a second stream of similar matter set in towards the body from its surroundings" to fill the gaps left by the exiting particles. The motion of "these two streams of matter… gave rise under appropriate circumstances to the various effects described as 'electrical'."[60]

Many natural philosophers at this time, including Nollet, attributed the property of inflammability to the presence of "sulphureous matter", which could be ignited by fire. If the two electrical streams "collide[d]… with enough force" in an inflammable substance, its sulphureous principle would be released and catch fire, sparks and heat ensuing. The motion of "this [electrical] matter, he insisted, could plainly be seen, smelled, heard and felt upon the skin, and, when brought to bear on inflammable liquors or vapours, could set them alight", just like common fire.[61]

Although heated bodies did not manifest action-at-a-distance forces, Benjamin Franklin, who viewed Watson as a "mentor" and Nollet as a rival, also adopted the term

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[59] Home, 1979, 171; Roderick Home, "The Notion of Experimental Physics in Early Eighteenth Century France," in *Electricity and Experimental Physics in 18th Century Europe* (Brookfield, VT: Ashgate Publishing, 1992a), 107-131, 107-131; Roderick Home, "Franklin's Electrical Atmospheres," in *Electricity and Experimental Physics in 18th Century Europe* (Brookfield, VT: Ashgate Publishing, 1992b), 131-151, 131-151; Roderick Home, "Electricity in France in the Post-Franklin Era," in *Electricity and Experimental Physics in 18th Century Europe* (Brookfield, VT: Ashgate Publishing, 1992c), 1-4.

[60] Home, 1979, 172.

[61] Ibid, 173.

electric fire.[62] Unlike Dufay and Nollet, he explained electrical phenomena in terms of a one-fluid model.[63] Briefly, Franklin argued that all bodies contain electrical fluid. "Friction between a non-electric and an electric per se will produce electrical fire; not by *creating*, but *collecting* it: for it is equally diffused in our walls, floors, earth, and the whole mass of common matter."[64] I.B. Cohen has shown that Franklin's views also mirrored those of Boerhaave. Electricity, like Boerhaave's elementary fire, was pervasive, and it was the distribution of these subtle fluids that caused observable secondary effects such as attraction (electricity) or temperature (elementary fire).[65]

Franklin contended that rubbing glass "collected" excess electrical fluid along its surface. This was an unnatural, induced material state. Provided with a pathway, the electrical fluid would quickly move from the glass to another lesser-charged object to restore the balance of electrical fluid in the glass to its original state.[66] Under appropriate conditions, this movement of charge manifested sparks, flames, and/or attraction. Thus, Franklin "envisaged not an excitation of this fluid, as effluvial theorists [like Nollet]

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[62] Cohen, 1956: argued that although Franklin recognized that electricity and heat had much in common, he was non-committal about their relationship. At best, electricity was related to fire, but whether it was fire was open to debate. This is an important point. Priestley, an ardent follower of Franklin, would use Franklin's electrical theory and Beccaria's experiments showing that electricity calcined metals to argue electricity was phlogiston, an inflammable principle.

[63] Heilbron 1999; Home, 1992b: have both shown, contrary to Cohen, that Franklin owed a deep intellectual debt to his contemporaries and predecessors. Perhaps Franklin's most important contribution was to bring these elements together into one coherent system.

[64] Franklin, 1751, 38.

[65] Cohen, 1956, 214-244.

[66] Franklin, 1751, 2: "The non-electric contain'd in the bottle differs when electrified from a non-electric electrified out of the bottle, in this: that the electrical fire of the latter is accumulated *on its surface*, and forms an electrical atmosphere round it of considerable extent: but the electrical fire is crouded *into the substance* of the former, the glass confining it. […] At the same time the wire and top of the bottle, &c. is electrified *positively* or *plus*, the bottom of the bottle is electrified *negatively* or *minus*, in exact proportion: *i.e.* whatever quantity of electrical fire is thrown in at top, an equal quantity goes out of the bottom."

supposed, but its redistribution" from a plus or positive state, bodies oversaturated with electricity, to a minus or negative state, objects in need of electric fire.[67]

This process of redistribution, Franklin noted, could also transform materials. Like Watson, he reported to the Royal Society experiments in which electricity altered the physical and chemical properties of substances. For example, experiments with gilded glass showed that powerful sparks could vaporize metal, e.g. applying electricity to a plate of glass coated with silver or gold removed the metal, leaving the glass stained either green or red, at times even splintering the glass.[68]

Franklin also observed that, "Electrical Fire loves water."[69] He corroborated Watson's observations that while ice did not conduct, water readily transferred electrical fluid, becoming a vapor in the process. Heat expansion suggested to scientists, like Boerhaave, Franklin, and later Lavoisier, that thermal particles were mutually repulsive.[70] They suggested that a substance was held together by the affinity of its particles for one another. As it gained more fluid fire, its density increased. Heat corpuscles were initially pushed closer together until their force of repulsion overcame the attractive properties of the substance, fracturing the material and producing a gas.[71] In Franklin's words: "[c]ommon fire, as well as electrical fire gives repulsion to the particles of water, and

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[67] Home, 2002, 58.

[68] Franklin, 1751, 66.

[69] Ibid, 36.

[70] Cohen, 1956, 228-231.

[71] Ibid, 228.

destroys their attraction of cohesion; hence fire, as well as electrical fire, assists in raising vapours."[72]

The analogies between common and electrical fire, Franklin argued, were numerous, but not conclusive. Whether they were "different modifications of the same element", fire, or two separate substances was still an open question.[73] He noted, for instance, that although heat and electricity produced repulsion as evidenced by the vaporization of metal and water, electrical bodies could also attract. Franklin asserted, however, that it was important to recognize that electricity was a natural phenomenon. It was not merely the result of deliberate human action, like rubbing glass with felt, but was produced in the natural world – lightning being the product of nature's own friction machine, as water vapor (conductors) interacted with salt and air particles (electrics) to collect excess electrical fluid from the atmosphere and transmit it to ground (the earth).[74]

Franklin's theories are well known to historians of science, but little discussed is their impact on late eighteenth-century identifications of electricity with heat, and more specifically, phlogiston. In 1753 and subsequent editions (the English version appearing in 1776), Giambatista Beccaria took up Franklin's mantle in a "career making" text, *A Treatise on Artificial Electricity*.[75] As the title suggests, this work focused on man-made electricity. In this text, Beccaria brought together the experimental results showing the

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[72] Franklin, 1751, 39.

[73] Ibid, 47.

[74] Ibid, 36-49; Secondary literature includes: Cohen, 1990; Riskin, 2002; Michael Schiffer, *Draw the Lightning Down: Benjamin Franklin and Electrical Technology in the Age of the Enlightenment* (Berkeley, CA: University of California Press, 2003); Tom Tucker, *Bolt of Fate: Benjamin Franklin and His Electric Kite Hoax* (Stroud: Sutton Publications, 2004).

[75] Beccaria, *Artificial Electricity*.

similarities between electrical and thermal effects. Heilbron argues that unlike Franklin's papers, which were published piece-meal and, at times, seemed "disorganized, parochial, unassertive and open", Beccaria's treatise was "ordered, developed, polished and generalized".[76] His writings not only disseminated Franklin's work to continental Europe, but also included novel observations on the behavior of electricity.[77]

Joseph Priestley was particularly influenced by Beccaria's researches. Priestley's first serious scientific publication on the *History and Present State of Electricity* not only drew on Franklin's work, the two having corresponded extensively about various scientific and political problems, but also used Beccaria's researches to bolster his claim that electricity was phlogiston. This identification had significant implications for Priestley's later experiments on airs, which often included eudiometry as a method of chemical analysis, a more quantitative study of the sparking of gases initiated by Watson.[78] The use of electricity as an instrument of chemical change will be discussed in the next section.[79]

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[76] Heilbron, 1999, 365.

[77] Ibid, 370: Heilbron notes that "Franklin was pleased and flattered by the defense his apparently disinterested European supporters mounted. Beccaria, he said, was a 'Master of Method,' and *Dell' elettricismo* 'one of the best pieces on the subject… in any language'."

[78] Although his article focuses on the work of Martinus van Marum, Sudduth argues that Beccaria and Franklin's association of electricity with fire was instrumental to its later identification with phlogiston by Priestley. See, Sudduth, "Eighteenth Century Identifications of Electricity with Phlogiston," 142-143.

[79] Joseph Priestley, *A Scientific Autobiography (1733-1803), with Selected Correspondence*, ed. Robert E. Schofield (Cambridge, MA: MIT Press, 1966), 36-37, 44, 74; Sudduth, "Eighteenth Century Identifications of Electricity with Phlogiston.": Although the English edition of Beccaria's text did not appear until 1776, Priestley procured a copy of the 1753 edition from Franklin sometime between Sept 1766 and April 1767. He referred to Beccaria's treatise in 1769 and all subsequent editions of *HPSE*. In 1775, his new introduction to *HSPE* stated that he had shown conclusively in his *Observations on Airs* in 1772 that electricity and phlogiston were identical. See Priestley, *Air 1775*, xxxi.

Beccaria examined the relationship between electricity and heat in more detail than his predecessors. Watson, Franklin, and Nollet's work suggested that they were related as evidenced by their use of the term *electric fire.* In particular, Watson and Franklin noted that the application of sparks to certain substances caused chemical change and vaporization in a manner consistent to heating. Was electric fluid then a form of material heat? Although Franklin recognized that their similarities of effect were compelling, he asserted that there was not enough evidence to conclusively say how their substances were connected. Beccaria's research substantially added to this discourse. In chapter five of his treatise, he persuasively argued by analogy that fire and electric fire were associated materials.[80] Table 1.2 provides an overview of the electrical phenomena he considered.

Unique to Electricity	In Common	Unique to Heat
• Tingling/Numbness • Rapidity of transfer • Quantity (capacity) proportional to surface area • Attraction • Action-at-a-distance/Force (measurable) • Induction (referred to as Vindication) • Two Types (plus and minus)	• Light • Burning • Produced by Friction • Conductivity • Calcination • Chemical Change • Color Change • State Change (only melting and vaporization) • Repulsion (theoretically postulated as a property of heat, resulting in state change) • Conservation	• Warmth • Temperature • Latent Heat (measurable) • Specific Heat (measurable (1783)) • Combustion (processes such as respiration and rusting) • Produced by Chemical Change (e.g. candle)

Table 1.2: Properties of Electricity and Heat by 1776 – Beccaria did not formally address properties unique to heat. I have included them here as a point of comparison.

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[80] Beccaria, 1776, 313-330.

More specifically, Beccaria observed that similar materials conducted both fluids, e.g. copper readily allowed both electric and heat transfer.[81] Electricity and heat also set combustible substances, like a candle's wick and alcohol, on fire. He further observed that "*heat may render such bodies* [including candle wax] *conductors of the electrical fire"*.[82] Both also produced light and "rings of prismatic colors" in metals (Priestley first observed this effect in 1768).[83]

Most importantly, Beccaria also discovered by applying sparks to metal that he could "vitrify [turn metals into glass], calcinate [create metal oxides] or metallify [remove rust from metals]… thus shew[ing], that the electric fire produced in an instant, the same alterations in bodies, which common fire only can effect gradually and slowly."[84] Indeed, he argued the most discernible difference between electricity and heat was the speed and "efficacy" at which they were communicated to neighboring bodies. He speculated that this difference "perhaps [was] owing… to its [electrical fluid] being less dense than [heat]".[85] Because of the many similarities between electrical and thermal effects, he also suggested the possibility that electric fire was related to phlogiston.

In the early eighteenth century, Georg Stahl like Boerhaave recognized that fire, the catchall element responsible for heating and inflammability (sulphur), did not adequately account for observed thermal effects. Some substances did not burn per se when exposed to a flame, but rather underwent chemical change: metal, for example,

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[81] Ibid, 315.

[82] Ibid, 313 and 321.

[83] Ibid, 314; Priestley, 1768.

[84] Beccaria, 1776, 311.

[85] Ibid, 313.

becoming calx (oxide). Generally, the release of smoke accompanied combustion and so intuitively, Stahl assumed that in the process of calcination, heating drove material out of the metal, leaving behind a simple substance, a calx. The calx, however, weighed more than the metal because it had lost phlogiston, an inflammable principle embodying lightness (and some would argue negative weight). Phlogiston, although corporeal, incorporated the ancient metaphysical notion of the "absolute levity of fire", in which fire, possessing the quality of extreme lightness, could be added to a body (in this case calx [metal oxide]) effectively lessening its weight (producing a metal). Or conversely, the burning of metals released their fiery substance making them heavier.[86] Phlogiston, however, had yet to be chemically isolated and analysed. Table 1.3 summarizes the phlogistic and anti-phlogistic views.

Antiphlogistic (ca. 1775)		**Phlogistic (ca. 1765)**[87]	
Simple	**Compound**	**Simple**	**Compound**
Metal	Metal Calx=Metal+Oxygen	Metal Calx	Metal=Metal Calx+Phlogiston
Sulphur, Carbon, Phosphorus	Acid=Base+Oxygen	Acid	Sulphur=Sulphuric Acid+ Phlogiston Carbon=Carbonic Acid+ Phlogiston, etc.

Table 1.3: Summary of the Antiphlogistic and Phlogistic views.[88]

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[86] Partington and McKie, 1937; C.E. Perrin, "Joseph Black and the Absolute Levity of Phlogiston," *Annals of Science* 40 (1983): 109-137. Aristotle, in particular, argued that combinations of the four terrestrial elements produced all physical bodies and observable phenomena on Earth. The heavens were composed of aether, a fifth unique element.

[87] The eighteenth-century conception of phlogiston underwent several modifications as natural philosophers tried to isolate it chemically. For example, Richard Kirwan, a prominent Irish chemist noted for his studies in mineralogy, argued in 1782 that phlogiston was inflammable air (hydrogen), while Pierre Joseph Macquer, a French chemist who wrote one of the first dictionaries of chemistry, suggested in 1778 that it was light. See, Partington and McKie, 1937; Partington and McKie, 1938.

[88] This is a slightly modified version of table 10.1 in Klein and Levfèvre, 2007, 184.

Like many of his contemporaries, Beccaria was a phlogistonist. He explained the changes observed in heated metal by the movement of phlogiston. He observed that heating and electrifying metals caused the same kinds of chemical change. His experiments demonstrated that calcined metals did not transmit electricity and/or heat well. Calxes were also chemically changed by repeated exposure to sparks or flames: over time they slowly returned to their metallic state. Once revivified, the metal would again conduct electrical fluid and/or heat.

Metals were thought to be compounds of calx (oxide) and phlogiston. Because calxes did not readily allow the transmission of electricity and/or heat, Beccaria proposed that what made metals conduct was phlogiston. He suggested that electricity like fire must somehow restore the metal calxes' natural amount of phlogiston, making it once more "capable of conducting."[89]

He noted: if it could be established that the presence of phlogiston was required for the transmission of electrical fluid, as his experiments suggested, this would indicate a strong material dependency between electricity and heat, and possibly even their identity. At this stage, however, all that could be said with certainty was that there existed a number of compelling similarities between electrical and thermal effects. On the basis of his experiments, Beccaria advocated using the term *electric fire*, but like Franklin expressed caution in assigning its material cause.

The work of Gray, Dufay, Watson, Franklin, and Beccaria demonstrated that there was a relationship between the chemistry of a substance and the type of electrical effects

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[89] Beccaria, 1776, 7

it produced. Their researches also indicated a connection between electrical and thermal phenomena, many natural philosophers adopting the term *electric fire* in deference to this relationship.[90] Beccaria made the most cogent survey of the effects they held in common, extending it to well-known chemical processes such as calcination, vitrification, and revivification. Furthermore, he suggested that these experiments indicated that the property of conductivity was owing to the presence of phlogiston, Stahl's principle of inflammability. Metal, a compound of calx (oxide) and phlogiston, allowed for the transmission of electrical fluid, whereas calx alone did not. It was, however, the sparking of airs and the discovery that electrical fluid calcinated metals that had the greatest impact on chemists' studies of electrical behavior in the late eighteenth century.

1.1.2: The Sparking of Airs

> Hitherto philosophy has been chiefly conversant about the more sensible properties of bodies; electricity, together with chymistry, and the doctrine of light and colours, seems to be giving us an inlet into their internal structure, on which all their sensible properties depend.[91]
>
> Joseph Priestley (1769)

Chemical change occurred three ways: spontaneously (by combining reactive materials), by applying heat, or passing electricity through substance(s). Beccaria studied how the repeated delivery of electric sparks to conductors affected their physical and chemical properties. Drawing on the accepted chemical philosophy of the time, he invoked phlogiston to account for certain electrical effects, such as conductivity and the calcination of metal.

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[90] Approximately 20% of all articles relating to electricity and printed in English in the *Philosophical Transactions* between 1740 and 1799 used the term *electric fire*.

[91] Priestley, HPSE 1769, xi.

Watson's research suggested that electricity also affected the chemistry of airs. In the mid to late eighteenth century, the study of gases became more systematic. Stephen Hales, an English parson interested in the circulatory systems of plants and animals, designed the pneumatic trough in 1727. This simple, but revolutionary device consisted of a glass vial inverted in a vat of water or mercury with gases trapped inside above the surface of the liquid (see Figure 1.2). This design was quickly improved upon, using a graduated cylinder to measure changes in gas volume and the addition of tubes to extract and insert known amounts of specific airs. Priestley and Volta further modified the trough to create the first eudiometers, instruments designed to "spark airs" (see Figure 1.3).[92]

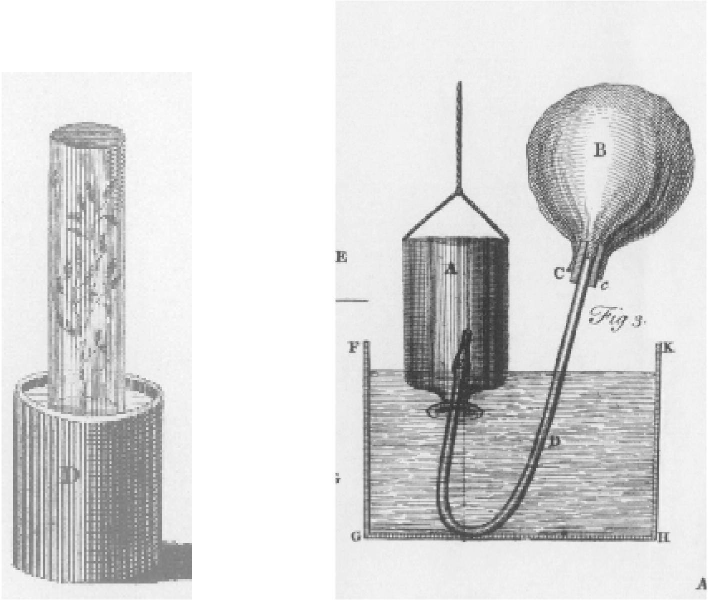

Figure 1.2: **Two pneumatic troughs.** The left hand image depicts one of Priestley's experiments. A plant has been placed in water: its roots immersed in the liquid, its leaves above the surface in the trapped air. (By experimenting with different airs, Priestley discovered that plants flourish in mice exhalations or fixed air (carbon dioxide), and that plants emit dephlogisticated air (oxygen)). The image on the right depicts one of Henry Cavendish's apparatuses for studying airs. It shows the transfer of gas from a bladder, B, to an inverted glass chamber, A, by a bent glass tube.[93]

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[92] Frederick L. Holmes, "Phlogiston in the Air," *Nuova Voltiana* 2 (2000): 73-112; Pancaldi, 2003, 110-111; Priestley, Air 1772, 381.

[93] Henry Cavendish, "Three Papers, Containing Experiments on Factitious Air," *Phil. Trans.* 56 (1766): 141-184, 141; Priestley, Air 1772, 192-195, 252.

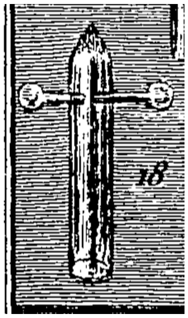

Figure 1.3: **The glass chamber of an eudiometer designed for sparking gases.** This image is from Priestley's *Experiments and Observations on Different Kinds of Airs* (1775).[94]

An eudiometer, literally meaning a measure of "good weather", was a pneumatic trough with two metal contacts implanted on opposite sides of a glass vial. By connecting one metal contact to a friction machine and the opposite to ground, an electric spark could be encouraged to jump from one side of the cylinder to the other, passing through the gas. Unlike Watson's experiments in which sparks jumped across the openings of jars, this instrument allowed for the containment of airs modified by electricity. These gases could then be subjected to a variety of physical and chemical tests.

Physical analyses included measuring the volume, weight, and temperature changes associated with chemical reactions. In 1772 Priestley designed the 'nitrous air test', a measure of air quality.[95] He discovered that combining nitrous air (nitrogen monoxide) with dephlogisticated air (oxygen) produced a reddish-brown gas (nitrogen dioxide) soluble in water.[96]

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[94] Priestley, Air 1775, 325.

[95] Holmes, 2000, 741: As Holmes notes, Franklin suggested Priestley study the chemistry of air by seeing how well a candle burned in "mephitic" air (nitrogen).

[96] Priestley, Air 1772, 211-231: In modern terms, $2NO + O_2 \rightarrow 2NO_2$

Henry Cavendish, a reclusive, but highly regarded British experimental philosopher,[97] who corresponded with Priestley about the chemistry of airs, hypothesized:

> …when nitrous [nitrogen monoxide] and common air are mixed together, the nitrous air is robbed of part of its phlogiston [forming nitrogen dioxide], and is thereby turned into phlogisticated nitrous acid, and is absorbed by the water in that state [creating nitrous acid, HNO_2], and besides that, the common air is phlogisticated [has its oxygen removed], and thereby diminished.[98]

Stahl suggested that sulphur was a compound of vitriolic (sulphuric) acid and phlogiston. This explained why some sulphureous mixtures were incombustible; they had lost their principle of inflammability.[99] Similarly, Cavendish proposed nitrous air was a compound of nitrous acid and phlogiston. Common air contained (approximately twenty percent by volume) dephlogisticated air (oxygen), which had a stronger affinity for phlogiston than nitrous air. Consequently, it separated nitrous acid from its phlogiston. The nitrous acid, now heavier, was absorbed in the water, leaving in the gaseous state, phlogisticated common air. Phlogisticating gases made them lighter, due to the increase in their total phlogiston, and reduced their elasticity, creating a subsequent reduction in volume.[100] This measurable change in volume was a physical indication of the extent of the chemical reaction.

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[97] Cavendish corresponded with William Herschel, John Hunter, Joseph Priestley, Martinus Van Marum, Jean-Andre Mongez, Benjamin Franklin, amongst others. His work was cited by the most eminent natural philosophers of his day, including Thomas Young, Humphry Davy, Antoine Lavoisier, and Alessandro Volta. See Christa Jungnickel and Russell McCormmach, *Cavendish: The Experimental Life* (Cranburn, NJ: Bucknell, 1999).

[98] Cavendish, 1783, 119.

[99] Cavendish, 1766, 145-146; Cavendish, 1784a, 135-136; Partington and McKie, 1938.

[100] Cavendish, 1783; Cavendish, 1784a, 141; Priestley, Air 1772, 232-234.

It was, therefore, possible to not only determine if an unknown gas contained dephlogisticated air (oxygen), but how much.[101] The diminution of air volume was proportional to the amount of nitrous air converted by dephlogisticated air into nitrous acid. This required meticulous volume measurements of all the gases involved, both before and after the chemical reaction.[102] This quantitative, physical test of chemical change marked an improvement over traditional, qualitative measures of breathability in which small animals, like mice or birds, were placed in a sealed container with an unknown gas, their lifespan timed.

Chemical analyses, on the other hand, included testing for changes in various behavioral traits such as inflammability, acidity, and reactivity. For example, adding litmus to a liquid caused a color change if the solution contained an acid (red) or a base (blue). In 1781 Priestley showed: "when the electric spark was made to pass through common air, [over] a solution of litmus, the solution acquired a red colour, and the air was diminished."[103] Thus, the 'litmus test' showed that the sparking of atmospheric air produced a soluble acid and volumetric tests revealed a reduction in gas volume.[104]

With further chemical analysis, Cavendish identified the unknown soluble acid in this experiment as nitrous acid.[105] It was well known that phlogisticated air (nitrogen)

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[101] Priestley observed that approximately 1/3 of a unit of nitrous combined with 2/3 of a measure of common air. See Priestley, Air 1775, 111-113.

[102] Cavendish showed that the quality of water also affected the experimental results. Distilled water absorbed more nitrous acid, for example, than bath water, maximizing volume reduction.

[103] Henry Cavendish, "Experiments on Air," *Phil. Trans.* 75 (1785): 372-384, 374; Joseph Priestley, *Experiments and Observations on Different Kinds of Air* (London: J. Johnson, 1781), 184-186.

[104] Cavendish, 1785, 374.

[105] Passing electricity through atmospheric air caused its molecules to break apart and recombine, forming a soluble acid: $2N_2 + O_2 \rightarrow 2NO_2$

comprised approximately eighty percent of common air and that it had many derivatives.[106] Lavoisier, for example, listed four different compounds of nitrogen and oxygen, and Claude Louis Berthollet, one of the first chemists in France to adopt (with some qualifications) the anti-phlogistic theory[107], showed that it was also a key component in ammonia.[108] Since it was likely that the sparking of common air had produced a compound containing nitrogen, Cavendish tried combining the unknown acid with materials known to respond to nitrogen-based substances.

In 1772, Priestley had christened spirit of niter, a component of saltpeter, nitrous acid to reflect its origins. Accordingly, Cavendish repeated the experiment with the known bases of niter (potassium nitrate).[109] He sparked atmospheric air in a pneumatic trough filled with water and soaplees (potassium hydroxide, a base used in the production of soap and gunpowder). He found that the soaplees had been modified.[110] It "seemed to be perfectly neutralized" by the unknown acid. A salt formed. This residue produced no color change in plant materials (in this case, "paper tinged with the juice of blue flowers") and when "evaporated to dryness, [it] left a small quantity of salt [which was] equal in weight to the nitre [potassium nitrate] which that quantity of soap-lees would

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[106] Cavendish substantially added to natural philosophers' understanding of phlogisticated airs. He estimated the ratio of dephlogisticated air to phlogisticated air in the atmosphere to be 1:4. See Cavendish, 1785, 376.

[107] Klein and Levfèvre, 2007, 88.

[108] Ibid; Lavoisier, *Elements of Chemistry [1789]*, 124-128, 125.

[109] Many chemists engaged in saltpeter research in an attempt to produce a more versatile gunpowder that could be used in humid climates. For example, Lavoisier was a member of the Gunpowder Association. He used the military applications of his research to defend (unsuccessfully) his life during the Reign of Terror.

[110] John Ingenhousz, "An Account of a New Kind of Inflammable Air or Gas, Which can be Made in a Moment without Apparatus, and is as Fit for Explosions as Other Inflammable Gasses in use for that Purpose; Together with a New Theory of Gun-Powder," *Phil. Trans.* 69 (1779): 376-418, 396.

have afforded if saturated with nitrous acid." Furthermore, the "salt was found, by the manner in which paper dipped into a solution of it burned, to be true nitre." Thus, the unknown acid, produced by the sparking of air, reacted with soaplees to produce a neutral salt (lacking either acidity or alkalinity), exhibiting the known weight and combustible traits of a niter composed of nitrous acid and soaplees.[111] Cavendish concluded: applying electricity to common air produced nitrous acid.[112]

Measuring changes in weight and volume, and drawing on the behavioral traits of (known) substances allowed chemists to isolate materials and (indirectly) learn more about chemical change. Electricity facilitated their research. Substances normally inert, like common air, suddenly changed when exposed to an electrical discharge, their components forming different compounds with different properties.

Scientists studied the chemistry of a variety of gases and liquids using electricity. Table 1.4 provides an overview of some of their experiments and results.

Chemist	Substance Sparked	Product
Cavendish	Inflammable and Common Airs	Dew (pure water) and Phlogisticated Air
	Dephlogisticated (derived from metal oxides) and Inflammable Airs	Nitrous acid
	Dephlogisticated (derived from plants) and Inflammable Airs	Pure water
	Phlogisticated and Dephlogisticated Airs	Nitrous acid and phlogisticated Air
	Dephlogisticated Air	Dephlogisticated Air
	Phlogisticated Air	Phlogisticated Air[113]

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[111] Cavendish, 1785, 377.

[112] Cavendish, 1788, 261, 263, 271; Jungnickel and McCormmach, 1999, 366-370.: Martinus Van Marum and Antoine Lavoisier could not reproduce Cavendish's results. In 1788, Cavendish repeated these experiments in front of witnesses, including Watson and, future president of the Royal Society, Joseph Banks to support his experimental findings.

[113] Cavendish, 1784a, 128-129, 131, 132; David Phillip Miller, *Discovering Water: James Watt, Henry Cavendish, and the Nineteenth Century 'Water Controversy'* (Burlington, VT: Ashgate, 2004); Cavendish, 1785, 375, 379.

Henry	Carbonated hydrogenous gas and oxygen	Carbonic acid and Azotic gas
	Muriatic acid gas	Hydrogen and a white deposit[114]
Lavoisier	Hydrogen and oxygen	Water[115]
Nicholson	Vitriolic acid	Vital Air[116]
Pearson; Troostwijk	Water	Hydrogen and Oxygen[117]
Priestley	Fixed Air	White sparks, soluble acid
	Inflammable Air	Red/Purple sparks
	Alkaline Air	Red sparks
	Vitriolic acid Air	“Deep brown or black matter”
	Common Air	Nitrous acid and phlogisticated Air
	Oil (including oil of olives, turpentine, mint and ether); spirit of wine; volatile spirit of sal ammoniac	Inflammable Air
	Beer	Fixed Air (and unknown airs)[118]

Table 1.4: **A Sample of Experiments involving the Sparking of Airs and Liquids in the Late Eighteenth Century.**

Cavendish and Priestley did extensive experiments with the sparking of airs. The focal point of their research was common air and its constituents: dephlogisticated (oxygen), phlogisticated (nitrogen), fixed (carbon dioxide), and inflammable (hydrogen) airs. They sought to understand why passing electricity through gases caused a diminution in the volume of air and often produced a soluble acid. They both found slightly different answers in Stahl’s theory of phlogiston.

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[114] William Henry, "Experiments on Carbonated Hydrogenous Gas; with a View to Determine Whether Carbon Be a Simple or a Compound Substance.," *Phil. Trans.* 87 (1797): 401-415, 405-406; Henry, 1800a, 188-189.

[115] Lavoisier, *Elements of Chemistry [1789]*, 93-94.

[116] Nicholson, *The First Principles of Chemistry*, 140.

[117] George Pearson, "Experiments and Observations, Made with the View of Ascertaining the Nature of the Gaz Produced by Passing Electric Discharges through Water," *Phil. Trans.* 87 (1797): 142-158; Joseph Priestley, *The Doctrine of Phlogiston Established and That of the Composition of Water Refuted* (Northumberland, PA: A. Kennedy, 1800).

[118] Priestley, Air 1772, 175; Priestley, Air 1781, 175-176; Priestley, Air 1784, Vol. 2, 209; Priestley, Air 1775, 242-245; Priestley, HPSE 1775, 364.

Priestley was strongly influenced by his research on electricity. Throughout his scientific career, he conducted research on electricity and airs. Traditionally, historians have analyzed these works separately, but for Priestley, they were intimately connected. His writings on airs referred to his electrical researches and his electrical texts cited his pneumatic studies.

In *History and Present State of Electricity* (*HPSE*) in 1769, Priestley recounted Beccaria's experiments on the calcination and revivification of metal by electricity and his suggestion that electric fire was somehow conducted by and, therefore, related to phlogiston. Priestley argued, at that time, that the source of phlogiston responsible for revivifying calx (oxide) did not come from electric fire per se, but rather was carried from metal conductors to the calx by electrical fluid. The repeated passage of electricity through metal often produced a black sooty substance. (Beccaria also observed this phenomenon.) Priestley suggested, "the phlogiston which revivified the calces was in that black dust." Electricity transported and carried this phlogiston from external, metal conductors to the calx, 'encouraging' it to chemically combine with the oxide to produce a pure metal.[119]

In 1775, however, Priestley reversed his position in *Experiments and Observations on Different Kinds of Air* and in the third edition of *HPSE*. Priestley declared his research on gas chemistry convinced him that Beccaria's intuition had been

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[119] Priestley, HPSE 1769, 645-646; Sudduth, "Eighteenth Century Identifications of Electricity with Phlogiston."

correct all along. Unlike Beccaria, however, Priestley made a much stronger claim: electricity was (a form of) phlogiston.[120]

Like many of his contemporaries, Priestley was interested in the composition of respirable air and the effects other substances had on its quality. For example, he used a "burning lens" to focus the sun's heat on metals, like lead or tin, resting on a wooden platform suspended in a standard pneumatic trough filled with common air, to see what vapors (if any) it emitted. Over time, the surface of the lead became white and flaky, and the gas volume decreased from "four ounce measures of air to three". Further tests on the gas revealed it had been phlogisticated; it now consisted (primarily) of phlogisticated gas (nitrogen) and no longer supported respiration.[121]

Like Beccaria's electrical experiments, Priestley's research demonstrated that the application of heat to metal in air caused calcination and also made gases, like dephlogisticated air (oxygen), noxious. Furthermore, he observed that sparking gases caused a reduction in gas volume and reduced the quality of air as well. Priestley noted "air… diminished by electricity makes no effervescence with, and is no farther diminished by [the addition of] a mixture of nitrous air [as in the nitrous air test]; so that it must have been in the highest degree noxious [lacking any dephlogisticated air], exactly like air diminished by any other process." Thus, in the same fashion as heating, sparking substances not only caused calcination, revivification, and vitrification, but also the diminution of air volume and increased gas toxicity. Priestley's experiments showed

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[120] Priestley, Air 1775, 282-284; Joseph Priestley, *History and Present State of Electricity, with Original Experiments* (London: C. Bathurst, and T. Lowndes, in Fleet-Street; J. Rivington, and J. Johnson, in St. Paul's Church-Yard, etc, 1775e), xxiv.

[121] Priestley, Air 1772, 228-229.

that electricity and heat had even more effects in common than previously realized. He concluded: “From these experiments it pretty clearly follows, that the electric matter either is, or contains phlogiston; since it does the very same thing that phlogiston does.”[122]

Beccaria, like most of his contemporaries, attributed electrical phenomena to the presence and motion of a special, yet unidentified fluid, which produced many similar effects to fire. Although he ubiquitously used the term *electric fire*, he was more cautious than Priestley in assigning material cause. Priestley boldly concluded from similarity of effect that electricity and heat had a common basis: phlogiston. Unlike Beccaria, who did not comment on scientific methodology, Priestley described and privileged the role of analogy in theory development. He wrote, “Human abilities are chiefly conspicuous in adapting means to ends, and in deducing one thing from another by the method of analogy”.[123] Thus, for Priestley, analogy was not just a form of justification, but also an important aspect of scientific reasoning.

While Priestley emphasized the similarities between electrical and thermal phenomena, identifying electricity with phlogiston, Cavendish drew clear distinctions between cause and effect in experimentation. He did not view electricity as an “imponderable” fluid. It was something that could be studied, the laws governing its behavior discerned, but he was cautious in attributing to it the property of phlogistication.

Although he thought electricity might be a form of phlogiston, he did not think it was the cause of the reduction in air volume in sparking experiments. Cavendish often

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[122] Priestley, 1781, 186.

[123] Priestley, HPSE 1769, iv.

chided Priestley for drawing conclusions about chemical processes without carefully reflecting on experimental operations.[124] Like Beccaria, he noted that a spark involved the rapid movement of electrical fluid from one body to another. Cavendish questioned whether or not there was enough time for the electric fire to release an appreciable amount of phlogiston into the air. He thought it more likely that, like heat, it "assisted" in chemical change by beginning the process of decomposition in which an acid and its phlogiston were separated.[125]

He noted, "phlogisticated air [nitrogen] is nothing else than nitrous acid united to phlogiston."[126] A mixture of phlogisticated and dephlogisticated airs (oxygen), as found in common air, was inert. Sparking either phlogisticated or dephlogisticated air alone had no effect on the gas. In contrast, applying electricity to a mixture of the two airs produced nitrous acid and a diminution in gas volume. Electricity, he argued, decomposed phlogisticated air into its constituents: nitrous acid and phlogiston. The dephlogisticated air, a gas with a strong affinity for phlogiston, was able to combine with the now free phlogiston, leaving behind nitrous acid. These experiments, he concluded showed that "the phlogisticated air was enabled, by means of the electrical spark, to unite to, or form a chemical combination with, the dephlogisticated air".[127]

Heat and electricity played similar roles in Cavendish's understanding of chemical change. Although he was a devout phlogistonist, believing there existed a

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[124] See, for example, Priestley, *Correspondence 1966*, 231-234. Despite their disagreements over airs, Cavendish and Priestley shared mutual respect for one another. See Jungnickel and McCormmach, 1999, 161, 518.

[125] Cavendish, 1785, 380.

[126] Ibid, 378-379.

[127] Ibid, 379.

perceptible material principle of inflammability, he thought heat like electricity only facilitated chemical reactions. He made a distinction between the act of heating, a mechanical process, in which "heat consists in the internal motion of the particles of bodies", and phlogiston, the material of combustibility.[128]

For instance, in *On Factitious Airs*, published in 1766, Cavendish observed that "tin dissolves slowly in strong spirit of salt [hydrochloric acid] while cold: with the assistance of heat it dissolves moderately fast."[129] Analyses conducted on the gases emitted by its dissolution showed inflammable air (hydrogen) had been released. Cavendish postulated that in the mixing of tin and spirit of salt, the tin's "phlogiston flies off, without having its nature changed by the acid, and forms the inflammable air".[130] Whether the reaction occurred hot or cold, the outcome was the same: the acid dissolved the metal, producing inflammable air. The only difference, he noted, was the speed at which the chemical reaction was completed.

In his study of electricity in 1771, Cavendish drew similar conclusions. Although he recognized that electricity produced chemical change, he suggested a mechanistic interpretation of its action on fluids. He wrote:

> …when the electric fluid is made to pass through water, in the form of a spark… I imagine that the water, by the rapid motion of the electric fluid through it, is turned into an elastic fluid, and so much rarefied as to make very little opposition to its motion: and when stones are burst or thrown out from buildings struck by lightning, in all probability that effect is caused by the moisture in the stone, or some of the stone itself, being turned into an elastic fluid.[131]

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[128] Cavendish as quoted in Jungnickel and McCormmach, 1999, 400.

[129] Cavendish, 1766, 144.

[130] Ibid, 145.

[131] Cavendish, 1967, 62.

Franklin first showed that electricity vaporized substances. Cavendish argued this occurred because electricity, itself an elastic fluid, imparted to the conducting substance, in this case water, some of its motion. Its volatizing nature caused materials to expand, making it easier for chemical reactions to occur.

Through the heating and sparking of airs, chemical practitioners like Priestley and Cavendish came to recognize the usefulness of electricity in studying chemical change. Priestley built on earlier studies, which suggested that heat and electricity were related. He showed that applying heat to metals caused calcination and affected the quality of ambient airs in the same fashion as the passage of electrical fluid. He and Cavendish also demonstrated by sparking airs that electricity chemically transformed gases, often producing a soluble acid and phlogisticated air. While Priestley identified electricity with phlogiston, because of the numerous effects they had in common, Cavendish pondered how the transmission of these fluids brought about chemical change.

1.2: The Importance of Difference

> A distinction is sometimes made, in experimental Science, between men of theory [Lavoisier] and men of fact [Priestley]. We are but too apt to run into extremes. The men of theory consider general results as the great and dignified objects of Science, and estimate the importance of facts according to their respective rank among the illustrations of their general theorems. The men of fact, on the contrary, are disposed to attach a high value to the practical department and are much more attentive to register one incident after another, than to generalize and explain the operations they behold. The enlightened cultivators of Science will be neither of these exclusively or rather he will be both.
>
> William Nicholson (1795)[132]

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[132] Nicholson, 1795, Vol. 1, v.

Antoine Lavoisier is a well-known historical figure surrounded by triumph and tragedy. Numerous biographies and studies examine his contributions to eighteenth century science and French society. Although he is most famous for his researches in chemistry, he also studied law, becoming an effective administrator (e.g. tax farmer and chairman of the Gunpowder Association) and defender of the Academy of Sciences during the French Revolution. Despite his years of public service, scientific achievements, and the protests of his colleagues, his association with Old Regime agencies led to his imprisonment in 1793 and execution by guillotine in 1794. He was then fifty years old.[133]

While Lavoisier was in prison for crimes against the state that he ardently denied, Joseph Priestley and his family were in hiding in England. Priestley, in addition to studying chemistry, was a minister and prolific writer, conveying not only his scientific experiments in print, but also his political and religious views. He was an outspoken reformer who advocated equal rights for Dissenters, helped to establish the Unitarian church, and vocally supported both the American and French revolutions. Few in England were sympathetic to his impassioned cries for reformation. In 1791, rioters destroyed his home, laboratory and church in Birmingham. In 1793, France declared war against Britain heightening public anger towards those who supported the French

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[133] There is an extensive literature on Lavoisier's life and science. See, for example, Bensaude-Vincent and Abbri, eds., *Lavoisier in European Context: Negotiating a New Language for Chemistry*; Marco Beretta, "Chemists in the Storm: Lavoisier, Priestley and the French Revolution," *Nuncius* 8, no. 1 (1993): 75-104; Beretta, ed., *Lavoisier in Perspective*; Donovan, *1993*; Guerlac, ed., *Antoine-Laurent Lavoisier, Chemist and Revolutionary*.

revolution. In 1794, under increasing threat of violence, Priestley emigrated to the United States.[134]

Historically, Lavoisier and Priestley have been viewed as the opposing champions of the two predominant views of combustion. Many historians argue Lavoisier, by applying quantitative methods gleaned from experimental physics to the study of the states of matter, revolutionized or at the very least re-oriented chemical theory.[135] Priestley, on the other hand, while praised for his ability to design and conduct chemical experiments, is often criticized for not "seeing" the theoretical implications of his own researches, a foil to the progressive French chemistry.[136]

Priestley and Lavoisier, however, often spoke at cross-purposes. While Lavoisier focused on the measurable properties of heat, Priestley reflected (in part) on the chemical effects of electricity and their relation to thermal phenomena. More specifically, building on the work of Dufay, Watson, and Beccaria, Priestley's researches showed that heating non-conducting substances, like charcoal, rendered them conductors. He further demonstrated that electricity could calcify, revivify, and vitrify metals, while sparking gases produced a diminution in air volume and increased toxicity. Applying heat to these

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[134] Maurice Crosland, "Priestley Memorial Lecture: A Practical Perspective on Joseph Priestley as a Pneumatic Chemist," *British Journal for the History of Science* 3, no. Nov. (1983): 223-238; Schaffer, "1984," 151-183; Robert Schofield, *The Enlightened Joseph Priestley: A Study of His Life and Work from 1773 to 1804* (University Park, PA: The Pennsylvania State University Press, 2004), 320. Although Priestley protested his treatment by the mob, he received little support, King George III reportedly saying: "I cannot but feel better pleased that Priestley is the sufferer for the doctrines he and his party have instilled, and that the people see them in their true light."

[135] Donovan, 1990; Guerlac, *Lavoisier: The Crucial Year*; Holmes, *Antoine Lavoisier: The Next Crucial Year or Sources of His Quantitative Method in Chemistry*; Holmes, 2000; Melhado, 1990; Perrin, 1990.

[136] Schaffer, 1984, 151-183; Schofield, 2004, 193: With only a few exceptions, Robert Schofield, Priestley's biographer, characterizes the historiography as promoting the view that "before Lavoisier, Priestley was a brilliant experimenter, afterward a bumbler".

materials produced the same effects. This led Priestley to argue that electricity was a form of phlogiston.

Like most of his contemporaries, Lavoisier was also intrigued by electrical phenomena. He recognized the importance of sparking airs, citing Volta's eudiometer as a useful tool with which to learn about the chemical behaviors of gases.[137] He sat on several committees vetting various publications on electricity, had taken classes with Nollet (once a leader in French electrical studies), was a friend of Benjamin Franklin, and owned a number of electrical instruments, including a friction machine, various Leyden jars, and a sparking apparatus.[138] Lavoisier also conducted experiments investigating whether measurable changes in electricity accompanied chemical reactions with Volta and Pierre-Simon Laplace, the leading French natural philosopher during the Napoleonic era. In a letter to the Royal Society in 1782, Volta reported that they had obtained "unequivocal signs of electricity from the evaporation of water, from the simple combustion of coals, and from the effervescence of iron fillings in diluted vitriolic acid."[139] These experiments will be further discussed in the next chapter.

It is interesting to note that, while some of his colleagues included electricity as a simple substance in their translation of his seminal text, *Elements of Chemistry*, Lavoisier did not.[140] Marco Beretta argues that, although "Lavoisier was convinced that electricity played an important role in the understanding of the structure of matter and the dynamic

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[137] Lavoisier, *Elements of Chemistry [1789]*, 404-405.

[138] Donovan, 1993, 48-52, 183-185.

[139] Alessandro Volta, "Del Modo Di Render Sensibilissima La Piu Debole Elettricita Sia Naturale, Sia Artificiale," *Phil. Trans.* 72 (1782): 237-xxxiii, xxix.

[140] Seligardi, "What Is Electricity? Some Chemical Answers, 1770-1815."

of gas reactions, … he was unable to find the experimental means to transform this intuition in a coherent theory.” Moreover, electricity was, for many natural philosophers, closely allied with phlogiston, the very model Lavoisier was challenging with his oxygen theory of combustion.[141]

In the 1770s, Lavoisier began to experiment and publish on thermal processes. He proposed a convincing, alternative interpretation to the generally accepted theory of combustion. Priestley’s research demonstrated the importance of dephlogisticated air to life. He argued that the heating of metal released its phlogiston, forming a calx, and phlogisticated the surrounding air, making it toxic to living organisms. In contrast to Priestley, who emphasized the loss of phlogiston in the calcination of metal, Lavoisier asserted that something had been gained. As the metal burned it chemically combined with (or absorbed) the surrounding dephlogisticated air (oxygen), reducing the gas volume, making it noxious, and causing the metal to become measurably heavier.

Lavoisier recognized that the process of burning (including animal respiration and rusting, which he argued were forms of combustion) required the presence of dephlogisticated air (oxygen). Priestley himself had shown that candles would not burn in just any gas, the vapor had to contain dephlogisticated air. Cavendish also noted that heating and sparking gases diminished air volume and increased gas toxicity. For example, he demonstrated that sparking common air (a mixture of phlogisticated (nitrogen) and dephlogisticated airs) over water produced nitrous acid and phlogisticated air. He argued electricity decomposed phlogisticated air into nitrous acid and phlogiston.

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[141] Marco Beretta, "From Nollet to Volta: Lavoisier and Electricity," *Revue Histoire des Sciences* 54 (2001): 29-52, 30.

The nitrous acid, he showed, was dissolved in water, while its phlogiston combined with dephlogisticated air, making it noxious. Lavoisier, on the other hand, suggested heating made it possible for dephlogisticated air to directly combine with phlogisticated air, producing nitrous acid. The reduction in gas volume and increase in toxicity was, therefore, not from the decomposition of phlogisticated air, but rather from the removal of dephlogisticated air, as it chemically united with nitrogen to produce a soluble acid. Lavoisier subsequently renamed dephlogisticated air, oxygen, to reflect its acid-generating properties.[142]

Although he denied the existence of phlogiston, Lavoisier also proposed, contrary to Cavendish, that the act of heating had a material cause. He and Laplace conducted quantitative researches into heat transfer.[143] Crucial to their studies was the notion of latent heat, introduced in 1761 by Joseph Black, a professor of medicine at the University of Glasgow.[144]

Black noticed both water and ice could co-exist at zero degrees Celsius, and postulated that every substance required a certain amount of heat in order to convert it from a solid to a liquid or from a liquid to a gas. This amount of heat did not affect its temperature, but rather went into melting or vaporizing the substance.[145] Black called this

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[142] Lavoisier, *Elements of Chemistry [1789]*, 255-263.

[143] On Lavoisier and Laplace’s scientific partnership, see Guerlac, "Chemistry as a Branch of Physics: Laplace's Collaboration with Lavoisier."

[144] Robert G. Anderson, "Boerhaave to Black: The Evolution of Chemistry Teaching," *Ambix* 53 (2006): 237-254; Perrin, 1983.

[145] Angela Bandinelli, "The Isolated System of Quantifiable Experiences in the 1783 "Mémoire Sur La Chaleur" Of Lavoisier and Laplace," *Ambix,* 54, no. 3 (2007): 274-284, 276-277.

heat, latent, meaning: “hidden; concealed; [or] secret”.[146] (Cavendish tremendously disliked this terminology. He saw it as being biased towards a material interpretation of heat.[147])

Using this concept, Lavoisier and Laplace designed the calorimeter, an instrument that could be used to measure a material’s latent heat (Figure 1.4). They discovered:

Figure 1.4: A view of the calorimeter. The left hand image shows a cross section of its interior. The right hand illustration depicts its outer casing. The middle images, from upper to lower, show the apparatus from above and at an angle.[148]

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[146] Johnson, *A Dictionary of the English Language*, Vol. 2, 13; Thomas Thomson, *A System of Chemistry, from the Fifth London Edition, with Notes, by Thomas Cooper*, Fifth ed., 4 vols. (Philadelphia: Abraham Small, No. 112 Chestnut Street, 1818), 94-97.

[147] Jungnickel and McCormmach, 1999, 400-401.

[148] Over the course of the eighteenth century, natural philosophers increasingly developed experimental methods and instruments to reduce error in measurement and clarify the source(s) of information for analysis. For example, Angela Bandinelli argues Lavoisier and Laplace’s calorimeter experiments “inaugurated the study of a new unit of experimentation, the *isolated system* of quantifiable experiences.” The calorimeter was designed to eliminate external sources of heat, so that the amount and direction of heat transfer for a particular chemical reaction could be determined and measured. By controlling environmental conditions, they were able to show that the heat absorbed (or lost) by a material was a linear function of its weight, initial and final temperature, and specific heat capacity, assumed to be constant at atmospheric

> …that the heat necessary to melt a pound of ice could raise the temperature of a pound of water 60 degrees, so that if you mix together a pound of ice at zero and a pound of water at 60 degrees, you will have two pounds of water at zero. It follows that ice absorbs 60 degrees of heat on becoming a liquid.[149]

With this information, they could also determine a substance's specific heat, the amount of heat required to raise the temperature of a material by one degree. Through systematic study, they found the amount of heat a warm body lost in a cold room was proportional to its weight and change in temperature, both measurable quantities. They expressed this mathematically as $Q = m\,q\,(a-b)$, in which Q represented the total amount of heat lost; m, the weight of the substance; q, the material's specific heat; a, its initial temperature; and b, its final temperature. As the substance lost heat, the surroundings absorbed it. (It is interesting to note that although Lavoisier adopted the view that heat was a material like oxygen or iron, he wrote that "the conservation of free heat, in the simple mixture of bodies, [was] independent of any hypothesis about the nature of heat," whether it be the effect of matter in motion or itself a substance.[150]) Therefore, "q" could not be absolutely determined, but it could be expressed as a ratio. In other words, $m\,q\,(a-b) = m'\,q'\,(b-c)$, in which m' represented the weight of the absorbing substance (usually water); q', its specific heat (typically normalized to 1.0); b, the final temperature of the mixture; and c, its starting temperature. Thus, the ratio of a substance's specific heat to that of the

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pressure. See, Bandinelli, 2007, 274; Buchwald, 2006; Lavoisier, *Elements of Chemistry [1790]*, 343-356, plate vi. In contrast, Lissa Roberts argues that the calorimeter experiments were "an emblem of the new chemistry's explanatory power". Although natural philosophers questioned the veracity of some of Lavoisier and Laplace's results, it nonetheless illustrated the advantages of adopting caloric as a material form of heat, bestowing additional authority to Lavoisier's theory of combustion after the fact. See, T. H. Lodwig and William A. Smeaton, "The Ice Calorimeter of Lavoisier and Laplace and Some of Its Critics," *Annals of Science* 31 (1974): 1-18; Lissa Roberts, "A Word and the World: The Significance of Naming the Calorimeter," *Isis* 82 (1991): 198-222, 221.

[149] Lavoisier and LaPlace, *Heat*, 15.

[150] Ibid, 5

absorbing material could be determined by the following equation: $q/q' = m' q' (b-c) / m q (a-b)$.[151]

The determination of specific heat provided another tool of chemical analysis. An unknown, isolated substance could have its specific heat compared with known materials. These measurements also allowed for the comparison of different amounts of heat given off by different chemical processes, often measured in gross units of melted ice.[152]

For instance, igniting “an ounce of saltpeter with an ounce of flowers of sulphur” melted “2 pounds of ice”.[153] They also found burning “an ounce of phosphorus absorbed… 65.62 ounces of oxygen gas” and “melt[ed] 6 pounds, 4 ounces, 48 grains of ice”.[154] A live guinea pig was placed in the calorimeter, “in a little basket lined with cotton, whose temperature was zero”. Its body heat melted seven ounces of ice in “5 hours and 36 minutes”.[155] “The formation of fixed air can melt 26.692 ounces of ice”[156], whereas burning an ounce of carbon in oxygen gas produced six pounds, two ounces of water.[157]

Through the systematic study of (mostly exothermic) chemical reactions, Lavoisier and Laplace observed, “the [amount of] heat given off in chemical reactions is not the result of an unequal temperature of the substances that react together”.[158] Rather,

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[151] Ibid, 8

[152] Ibid, 32-34.

[153] Ibid, 18.

[154] Ibid, 32-33.

[155] Ibid, 19.

[156] Ibid, 32.

[157] Ibid, 18.

[158] Ibid, 21.

it had something to do with the invisible processes of decomposition and recombination occurring amongst materials at microscopic scales. For example, they noted that "the heat given off by oxygen gas, when [one ounce of] it is absorbed by… phosphorus, is approximately two and one third times greater than when [one ounce] is changed into fixed air [carbon dioxide]."[159] Why did the chemical combination of phosphorus and oxygen release more heat than a chemical reaction involving charcoal and oxygen? Why did substances release different amounts of heat during chemical change?

Although these results did not preclude the idea that heat was a form of internal motion, Lavoisier argued it was conceptually useful to consider heat to be a substance.[160] He named this "matter of fire" caloric. Like Franklin's account of how electricity (and heat) caused vaporization, Lavoisier attributed to caloric the force of self-repulsion. As the amount of caloric in a substance increased, the force of repulsion between the caloric particles increased. Once a certain heat density had been reached, the material splintered – the force of attraction between its own particles overcome – and the substance became a liquid or a gas. Caloric could, therefore, exist in different ratios in different substances at the same temperature because each material had its own unique cohesive force. In

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[159] Ibid, 33.

[160] Nicholson deftly argued that heat could not be the result of matter in motion alone: "The chief advantage which the opinion that heat is caused by mere vibration possesses, is its great simplicity. It is highly probable that all heated bodies have an intestine motion or vibration of their parts; and it is certain that percussion, friction, and other methods of agitating the minute parts of bodies will likewise increase their temperature. Why, then, it is demanded, should we multiple causes, by supposing the existence of an unknown fluid, when the mere vibration of parts, which is known to obtain, may be applied to explain the phenomena? To this it is answered, that mere motion will not apply to the phenomena: for, among other facts, water at 32° contains more heat than ice at 32°, and ought therefore to possess more vibration, yet it does not communicate more to the thermometer. A part of its motion must consequently be latent, or incommunicable [to the thermometer], which is an absurdity. A happy explanation of the manner in which the temperature of a body is raised by friction or percussion, has been given on the supposition that heat is matter." See, Nicholson, 1787, Vol. 2, 121.

other words, each substance could absorb a definite amount of heat before experiencing a state change. Water, for example, could absorb up to 100 degrees of heat and then some before becoming a gas. Moreover, as Lavoisier's research with Laplace had shown, these properties were measurable and, he argued, served as (an indirect) confirmation of the existence of caloric.

Historians, by emphasizing Lavoisier's "discovery" that combustion (often) involved oxygen absorption, have inadvertently downplayed the importance of his thermal studies to the development of his chemical philosophy.[161] Lavoisier's research suggested that heat transfer accompanied most, if not all, chemical changes. He noted, "as we live in a system to the matter of which caloric has a very strong adhesion, we are never able to obtain it in the state of absolute freedom."[162] The study of heat was, therefore, not only important for understanding why things burn, but also for explaining why certain material changes occurred. Indeed, Lavoisier saw the measurement of heat as a way to quantitatively determine the force of attraction between the particles of a material at a specific temperature and, consequently, its affinity, a measure of the likelihood of it combining with another substance. He wrote:

> Hence it is distinguished, that when two bodies are combined together, their action is absolutely different according to the degree of heat in which the combination is made. If they be both concrete, as for example, lead and tin, they have no action upon each other, because the attraction of their respective parts amongst themselves is stronger than the mutual action which the molecules of the two metals can exercise upon each other; so that it becomes a chemical axiom *corpora non agunt nisi sint soluta* [bodies do not react

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[161] See, for example, Guerlac, *Lavoisier: The Crucial Year*; Holmes, 2000.

[162] Lavoisier, *Elements of Chemistry [1789]*, 67.

> unless fluid[163]]: but when by a stronger action of heat the molecules of one of the two metals have separated; where their attraction or affinity of aggregation has been diminished, then they act on each other, and combination takes place between the metals.
>
> A table of affinities cannot therefore present true results but at a certain degree of heat. Mercury affords the most striking instance of this. Let this metal be heated to such a degree as to make it boil; it will then decompose vital air, and seize the oxigenous principle, which is one of its constituent parts, and will by that means be calcined, and become converted into the red calx of mercury.[164]

Within Lavoisier's framework, the study of heat was vital to understanding and quantifying chemical change.[165] Caloric was the material cause of the decomposition of a substance. Once a substance was separated into its aggregates (or made fluid), it was able to recombine with other materials for which it had a stronger affinity. Therefore, Lavoisier's theory of combustion had two important and related parts: it not only involved the absorption of oxygen, but also the movement and action of caloric.

Let me return briefly to an earlier example of a shared thermal and electrical effect: rusting. Beccaria and Priestley observed through the application of heat and sparks that metal calcined. Because metal calxes were non-conductors, they asserted that the metal must have lost something, phlogiston, in the process of rusting. Although Lavoisier did not address electrical phenomena, he described the process of calcination by heating differently. He wrote:

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[163] The usefulness and limits of this adage are still being discussed in modern chemistry. See, Christian Reichardt "Solvents and Solvent Effects: An Introduction" *Organic Process Research and Development* 11 (2007): 105-113; 106

[164] Lavoisier in Kirwan, *Essay on Phlogiston*, 47.

[165] Nicholson picked up on this point, and included it in his writings on chemistry and natural philosophy. For example, he wrote: "… among the actions of the minute parts of bodies, the cohesive attraction and the energy of heat are in continual opposition, and are concerned in every process of change in their peculiar properties." See Nicholson, 1795, 371-382, 379.

> Oxygen has a stronger affinity with metals heated to a certain degree than with caloric; in consequence of which, all metallic bodies, excepting gold, silver, and platina, have the property of decomposing oxygen gas, by attracting its base from the caloric with which it was combined. […] The use of the heat employed in these operations is to separate the particles of the metal from each other, and to diminish their attraction of cohesion or aggregation, or, what is the same thing, their mutual attraction for each other.[166]

Caloric, unlike phlogiston, played a substantive role in chemical change. The presence or absence of phlogiston accounted for differences in a material's properties, e.g. a metal conducted, whereas a metal calx did not. But, for Lavoisier, heating – the imparting of caloric to a substance – separated the particles of the material, making chemical change possible. It was a vehicle for explaining why chemical reactions occurred. In the above example, the act of heating a metal diminished its self-cohesion, making manifest its strong affinity for oxygen particles in the atmosphere. This attraction was stronger than the oxygen particles adhesion to caloric in the gaseous state. Thus, as the heated metal absorbed elemental oxygen from the air, it freed the gas's caloric. The release of these extra caloric particles caused the accompanying sensation of warmth as the metal "burned".[167]

Priestley was unmoved by Lavoisier's arguments, both with regards to combustion and, more generally, his views on chemical change. Unlike Cavendish and

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[166] Lavoisier, *Elements of Chemistry [1789]*, 78

[167] To further clarify any misunderstanding, Lavoisier wrote in a note to Kirwan: "It is therefore necessary to distinguish in every species of gas, the caloric which performs the office of a solvent, and the substance which is united to it, and serves as a base. Vital air therefore has its base, and it is to this base that we give the name *oxigene*. In the same manner we distinguish the base of inflammable gas, and call it by the name of *hydrogene*. We do not therefore affirm, that vital air combines with metals to form metallic calces, because this manner of enunciating would not be sufficiently accurate: but we say, when a metal is heated to a certain temperature, and when its particles are separated from each other is sufficiently diminished, it becomes capable of decomposing vital air, from which it seizes the base, namely *oxigene*, and sets the other principle, namely the *caloric*, at liberty." See, Lavoisier in Kirwan, *Essay on Phlogiston*, 12-13.

Lavoisier, he made no claims as to how heat and electricity brought about chemical change. His focus was on isolating and determining the identity of substances and their individual properties. If theory helped to discover materials and their function, so be it, but he thought there was a danger in developing general schemas. More specifically, he thought that Lavoisier's theory did not account for all of the facts. To do away with phlogiston required more than just an accounting of combustion. It also necessitated an explanation of the electrical effects held in common with heat. Table 1.5 provides an overview of the phenomena Lavoisier and Priestley considered for ease of comparison.

Priestley		**Lavoisier**	
Combustion			
Burning Respiration Rusting	Release of Phlogiston into Dephlogisticated Air (a gas capable of absorbing phlogiston)	Burning Respiration Rusting	Separation of the heated material's particles; Absorption of Oxygen; and Release of Caloric
Electricity		**Heat Transfer**	
Electricity (Conductivity)	Presence of Phlogiston	Specific heat Latent heat	Addition of Caloric (amount correlated to a substance's self-cohesion)
Heating and Sparking of Airs			
Diminution of air volume	Gas loses elasticity due to increase in phlogiston	Diminution of Air Volume	Loss of Oxygen
Increase in gas toxicity	Increase in phlogiston	Increase in gas toxicity	Loss of Oxygen
The Sensation of Heat	Particle Motion	**The Sensation of Heat**	Caloric
State Change	Particle Motion	**State Change**	Increase in caloric in a substance

Table 1.5: **Summary of the phenomena under consideration by Priestley and Lavoisier and their causes.**

Priestley frequently referred to electricity in his defense of phlogiston. Priestley (reluctantly) agreed with Cavendish "that *heat* has no more proper connexion with phlogiston than it has with water or any other constituent part of bodies… and probably (as the English philosophers in general have supposed) the heated state of bodies may consist of a subtle vibratory motion of their parts."[168] Although he conceded that heat might be the effect of matter of motion, he argued that this view did not preclude the existence or usefulness of phlogiston. He argued that it was "a *real something*", whose:

> presence or absence… makes so remarkable a difference in bodies, as that of *metallic calces* and *metals*, *oil of vitriol* [sulphuric acid] and *brimstone* [sulphur], etc. and which may be transferred from one substance to another, according to certain known laws […] It is certainly hard to conceive how any thing that answers this description can be only a mere *quality*, or mode of bodies, and not a *substance* itself.[169]

As further evidence of its existence, he reiterated his and Beccaria's experiments, which showed that "while metals have phlogiston they conduct electricity, but when they are deprived of it [becoming a metal calx] they conduct no longer."[170] He wrote: "I do not see how we can avoid inferring from the fact, that some *substance* is necessary to conduct electricity". If, as Lavoisier argued, nothing was lost in the calcination of metal, why did metal calx (oxide) not conduct? Why did the addition of heat to some substances, like charcoal, transform them into conductors? Priestley suggested that the "characteristic distinction between conducting and non-conducting substances" was that conductors "contain phlogiston intimately united with some base".[171] He also referred back to his earlier publications, such as *Observations on Different Kinds of Air*. He asserted that these published experiments: "demonstrated that the electric matter is, or contains

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[168] Priestley, Air 1781, 281

[169] Ibid, 282.

[170] Ibid, 284.

[171] Ibid, 284-285.

phlogiston; by shewing that it affects all kinds of air as phlogiston does; particularly diminishing common air one fourth, and making it noxious, so as to make no effervescence with nitrous air."[172] Thus, electricity, like phlogiston, caused comparable kinds of chemical change.

Although Priestley emphasized the importance of similarity of effect, he was aware that Lavoisier's theory (indirectly) underscored the differences between heat and electricity. There was nothing obviously analogous to the properties of specific or latent heat in the study of electricity. He also recognized the strength of Lavoisier's arguments, writing: "the experiments that Mr. Lavoisier made… are so specious, that I own I was myself much inclined to adopt it". Priestley urged caution. "If we could content ourselves with the bare knowledge of new *facts*, and suspend our judgment with respect to their *causes*, till by analogy, we were led to the discovery of more facts, of a similar nature, we should be in a much surer state of real knowledge."[173] Rather than abandon phlogiston, and the likenesses between electrical and thermal effects, Priestley appealed to his contemporaries to wait until further experiments could be performed and analogical reasoning provided an explanation for the now seemingly disparate set of phenomena.

Lavoisier did not wait. He simply did not address electrical phenomena in his theory of heat. Beretta argues he avoided it (in part) because Priestley and many other natural philosophers associated it with phlogiston.[174] It was not unusual, however, for

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[172] Joseph Priestley, *History and Present State of Electricity, with Original Experiments*, Fifth ed. (London: J. Johnson, and F. and C. Rivington, etc., 1794), xxiv.

[173] Joseph Priestley, *Experiments and Observations on Different Kinds of Air, and Other Branches of Natural Philosophy, Connected with the Subject* (London: Thomas Pearson, and J. Johnson, St. Paul's Church Yard, 1790), xxix-xxx, 249.

[174] Beretta, 2001.

natural philosophers to demote or exclude a set of incommensurable data. For instance, in 1543, Nicolaus Copernicus argued for heliocentrism although his theory at its basic level could not account for the orbit of Mars.[175] In 1628, William Harvey argued that blood circulated in the body although he could not explain what happened to blood as it passed through various organs, such as the lungs. While important, it was not necessary to make the case for circulation.[176] Similarly, Lavoisier's theory of combustion did not have to account for electrical phenomena to be compelling. Electrical effects were not wholly consistent with thermal phenomena, e.g. electricity produced an attractive force not manifest with heat. Thus, for Lavoisier's theory to be successful (and it was), he had to clearly define the boundaries of the phenomena under consideration. He explicitly addressed only thermal phenomena. Lavoisier, by ignoring electricity, implicitly argued that the differences between electrical and thermal effects out weighed their likenesses.

1.3: Conclusion: Electricity as Fire, Phlogiston, or a Unique Substance

> The chemical effects produced by electricity have been for some time objects of philosophical attention; but the novelty of the phenomena, their want of analogy to known facts, and the apparent discordance of some of the results, have involved the enquiry in much obscurity.[177]
>
> Humphry Davy (1806)

Analogical reasoning shaped the study of electricity in the eighteenth century. Using analogy, natural philosophers likened electricity and heat. For example, both caused fire and light, and were transmitted (or blocked) by similar materials. Applying

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[175] Janssen, "2002."; Noel M. Swerdlow, "On Establishing the Text Of "De Revolutionibus"," *Journal of the History of Astronomy* 12 (1981): 35-46.

[176] Jole Shackelford, *William Harvey and the Mechanics of the Heart* (New York: Oxford University Press, 2003).

[177] Davy, "1807," 1.

them to metals also chemically changed those substances in analogous ways, producing a non-conducting calx or oxide. Electricians tried to develop a theory that encompassed these phenomena. They described electricity as a special fluid; some arguing that it was electric fire, a variant of common or ordinary fire, while others more specifically tried to relate it to phlogiston.

In the late eighteenth century, however, Lavoisier excluded electricity from his theory of heat. He emphasized the importance of oxygen to fundamental chemical processes, such as combustion and the formation of acids, and caloric, the material manifestation of heat that made chemical change possible. His theory, which accounted well for thermal phenomena like specific heat and the expansion of fluids, came to supplant phlogiston. Despite Priestley's protests, chemists conceded that Lavoisier's theory was simpler and more quantitative. With the adoption of the oxygen theory of combustion, the relationship between electricity and heat became murky. For example, the sparking of gases, which had figured so prominently in the work of Priestley and Cavendish, was relegated to "interesting phenomena" as it was no longer clear how electricity brought about chemical change.[178]

Electricity as a form of heat disappeared from the natural philosophic consciousness in France and Britain in the 1790s only to re-emerge with the invention of the voltaic pile in 1800. The pile, the focus of the next two chapters, consisted of layers of silver, zinc, and salt water, and produced a non-mechanical, continuous electrical discharge. Chemists immediately noticed reactions taking place at points of intersection

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[178] Nicholson, 1795, Preface, 371-382.

between its plates and wet-conductor. For example, over prolonged use, the zinc plates became coated with a whitish film. Further experiments showed the zinc had undergone calcination (or oxygenation), similar to that observed with heating. This led some chemists to suggest a chemical reaction had occurred: oxygen from the salt solution united with the zinc, to form zinc oxide, displacing or freeing electricity. This explanation paralleled Lavoisier's own theoretical account of combustion. The pile also produced significant amounts of heat, re-opening the original enquiry: how were electricity and heat related?

Chapter 2: Instruments, Organisms, and the Debates Over Different Kinds of Electricity

> We are under no necessity of explaining electric motions by certain indeterminate kinds of attractions, or repulsions, as Sir Isaac Newton has been obliged to do with respect to the phænomena of the universal gravity. No mechanic principle of gravity has yet been discovered by our senses; and all those which men have hitherto imagined in order to explain this phænomenon, have been found insufficient, nay repugnant to the evidence of facts: but in regard to electric motions, we manifestly perceive them to be owing to a most active element, to the *inequilibration* of which electric motions exactly correspond, with respect both to their existence, and to their quantity and quality.[1]
>
> Giambatista Beccaria (1776)

Introduction

The previous chapter dealt exclusively with the relationship between heat and electricity. As we have seen, although electricity exhibited effects not wholly consistent with heat, such as attraction and the ability to "shock" living organisms, many eighteenth-century natural philosophers and chemists argued that thermal and electrical phenomena were related. Both produced sparks. They were transmitted (and blocked) by similar materials and caused comparable kinds of chemical change, such as the revivification and calcination of metals. Thus, electricians described electricity as a special fluid. Some argued it was a type or modification of ordinary fire, while others tried to relate it to phlogiston, Stahl's principle of inflammability.

A series of observations and experiments made in the late eighteenth century further complicated the relationship between heat and electricity. Lavoisier showed it was possible to measure the amount of heat involved in chemical change and defined a new physical property, specific heat, which had no obvious relation to electricity. There were

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[1] Beccaria, *Artificial Electricity*, 381-382.

also significant discoveries in the study of electricity. John Walsh, an English physician and friend of Benjamin Franklin, demonstrated that a fish, called the torpedo eel or ray, produced a fluid behaving like electricity.[2] Also, it was discovered that certain combinations of materials generated electricity without friction. For instance, in 1775, Alessandro Volta, the famous Italian natural philosopher and friend of Joseph Priestley, built the electrophorus, an electrical condenser (capacitor) made by layering metal and wax that seemed to 'perpetually' release electrical fluid.[3] In 1788, William Nicholson, a self-taught British chemist, editor, and publisher of scientific works, constructed the "revolving doubler", a device that rotated metal plates in parallel planes. It also produced electricity without contact.[4]

As the study of heat became more sophisticated and new methods of generating electricity were found, electricians questioned whether there existed more than one kind of electrical matter.[5] Two general questions framed this discourse: what kind of likenesses and how many characteristics must two things share to warrant the conclusion of identity? Although Priestley felt the analogy between thermal and electrical phenomena merited identifying phlogiston with electricity, many of his contemporaries

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[2] Walsh, 1773. There is a large literature examining the importance of studies of the torpedo eel to the development of physiology, and more specifically, the nervous system. See for example, Finger, *Minds Behind the Brain: A History of the Pioneers and Their Discoveries*, 107-118; Foccacia and Simili, "Luigi Galvani, Physician, Surgeon, Physicist: From Animal Electricity to Electro-Physiology."; Piccolino, *2003*. In contrast, only a few studies examine the relationship between the torpedo eel and electricity within the history of the physical sciences. See for example, Pancaldi, *2003*, chapter 6; Pera, 1992.

[3] For a discussion of Volta's invention of the electrophore and the resulting priority dispute, see Pancaldi, 2003, 73-109.

[4] Nicholson, 1788.

[5] In 1833, Michael Faraday listed five forms of electricity: thermal, magnetic, common, voltaic, and animal. See Faraday, 1833, 48.

questioned whether they were the same substance. With the discoveries of animal and other non-mechanical forms of electricity, scientists asked how these fluids were related to friction-based electricity. Did there exist many species of electricity or were they different manifestations of the same fluid?

Central to resolving this issue was the ability to detect and compare different kinds of fluids. For example, while a human felt the torpedo's shock, Lane's electrometer, a device used to measure the strength of an electrical discharge, could not.[6] If the fluid produced by the torpedo was too small to be detected by ordinary instruments, how could one determine with certainty whether it was electrical? The development of more sensitive electrometers was important not only for investigating animal electricity, but also for the general study of materials, such as the ability of a substance to conduct, store, and generate electricity.[7]

Research into other forms of electricity also influenced the development of the pile, invented by Volta in 1799. "[C]onstructed… in its form to the *natural electric organ* of the Torpedo or the electric eel, &c. [rather] than to the Leyden flask [or jar]", it was made by alternating two pairs of dissimilar metals, such as zinc and silver, and a third conductor, such as salt water.[8] It is interesting to note that its electrical actions were viewed as evidence that animal electricity was identical to friction-based electricity. This

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[6] Thomas Lane, "Description of an Electrometer Invented by Mr. Lane; with an Account of Some Experiments Made by Him with It, in a Letter to Benjamin Franklin," *Phil. Trans.* 57 (1767): 451-460, 453-454.

[7] See for example, Abraham Bennet, "Description of a New Electrometer in a Letter from the Rev. Abraham Bennet to Rev. Joseph Priestley," *Phil. Trans.* 77 (1787a): 26-31; Tiberius Cavallo, "An Account of Some New Experiments in Electricity, with the Description and Use of Two New Electrical Instruments," *Phil. Trans.* 70 (1780): 15-29; Cavendish, 1771; Pancaldi, 2003, 129-145.

[8] Volta, 1964, 112.

will be discussed in more detail in chapter three. Unlike friction machines, however, the pile had no moving parts. Its 'power', like that of the electrophorus and the torpedo ray, appeared to be substance dependent: not all material combinations worked and those that did produced different amounts of electricity. Electricians generally acknowledged that there must exist a relationship between the substances in the pile and its electrical output, but the nature of that relationship was contentious.

Loosely speaking, two camps emerged. Contact theorists, such as Volta and Jean-Baptiste Biot, a French physicist best known for his research in magnetism, adopted the widespread view that all substances contain some amount of electrical fluid and argued that the contact of different metals imparted a 'tension' or force, setting that electrical fluid into motion. On the other side, chemical theorists, such as Davy and William Wollaston, an English physician who isolated two new elements (rhodium and palladium), argued that the pile's electricity was caused by chemical changes occurring between the metals and the third conductor. While contact theorists appealed to concepts from mechanics to explain the flow of electricity, chemical theorists pointed to a growing number of experiments, which suggested that electricity was somehow created and limited by the chemical interaction of substances. A debate ensued between these two groups.[9]

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[9] Kipnis argues that the debate was temporarily resolved in 1807 when Davy "reconciled" the two views in his prize-winning paper *On Some Chemical Agencies of Electricity*. In contrast, Kragh, in an overview of the debate, suggests that the controversy did not abate until the end of the nineteenth-century when Walther Nernst, a physical chemist who built on the work of Heinrich Helmholtz, published his "theory of the cell". Sudduth's work, which also examines the relationship between the physical and chemical interpretations of the pile, focuses mainly on two important protagonists in the debate: Volta, cast as a physicist, and Nicholson, as a chemist. More specifically, he argues that the pile's chemical effects called into question the caloric theory of heat. As chapter three demonstrates, however, many chemists tried to develop a

Experiments conducted by chemists did not convince natural philosophers that the pile chemically generated electricity.[10] Their innovative experiments did demonstrate that the application of electricity to external substances produced profound chemical changes in those materials.[11] That electricity caused chemical change was far more palatable to the natural philosophic community than the idea that chemical change caused electricity.

I argue there were two important reasons for this. First, contact theorists appealed to the historical authority of natural philosophy. For over a century, electricians not only probed the effects of electricity, but also established quantifiable relations between its attractive and repulsive characteristics.[12] Thus, many natural philosophers deemed the measurement of electricity from the contact of metals more reliable than the often qualitative, chemical effects associated with the pile's electrical action. Second, although chemists believed there must exist some connection between chemical change and the production of electricity, they disagreed on the nature of that relationship. For example, rather than arguing like his contemporaries that electricity was produced by a specific chemical process, like oxygenation, Davy argued there was a general relationship between all chemical reactions and electrical effects.[13] Thus, focusing on the methods and arguments put forward by both sides, the following two chapters elucidate why contact theory was preferable to the chemical theory in the early nineteenth century. I am most

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chemical explanation of the pile consistent with the tenets of Lavoisian chemistry. See Kipnis, 2001, 130; Kragh, 2000a, 153; Sudduth, 1980, 30.

[10] See for example, Biot, 1803.

[11] Young, *A Course on Natural Philosophy*, 684.

[12] Heilbron 1979 remains the most comprehensive account of the study of electricity from the early to mid-eighteenth century. See Heilbron, 1999.

[13] See for example, Davy, 1807; Giovanni Fabbroni, "On the Chemical Action of Different Metals on Each Other at the Common Temperature of the Atmosphere," *Nicholson's Journal* 3, no. Oct (1799): 308-310.

interested in this epistemological debate because this discourse, more so than subject matter, helped to inform and define physics and chemistry as disciplines.

More specifically, this chapter analyzes the “physics” side of the story and the development of contact theory. Chapter three focuses on chemical explanations of electricity in Britain, especially the effects produced by the pile’s electrical action. It also examines the controversy over whether electricity was a fluid or a chemical effect. During this period, there were active debates over the appropriateness of using particular methods to study electricity. Natural philosophers and chemists questioned the exactness and reliability of new instruments and experimental procedures, and asked what their measurements physically corresponded to. This chapter demonstrates the importance of the study of insulated conductors to this discourse and to the question: did there exist more than one form of electricity?

2.1: A Brief Note on Eighteenth-Century Experimental Practice and Identity

> Chemistry is the science which endeavours to ascertain the number, the quantities, and the properties of the constituent principles of all natural bodies.[14]
>
> Tiberius Cavallo (1819)

As discussed in the introduction, this work examines chemists’ contributions to electrical research. Why then does this chapter focus on the “physics” of electricity? Before analyzing other types of electrical experiments, I will first briefly address the lack of disciplinary identity in the eighteenth century and its importance to this work. Although this chapter is nominally about “physics”, it shows that chemical practitioners such as William Nicholson, Henry Cavendish, Joseph Priestley, and Tiberius Cavallo

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[14] Cavallo, *The Elements of Natural or Experimental Philosophy*, 416.

were very much engaged in both types of research. They were, in the broadest sense of the term, natural philosophers.

All four men were engaged in chemistry: performing experiments in laboratories, mixing substances, heating and distilling and titrating materials, using glass crucibles, beakers and tubing to transfer substances from one vessel to another. They also built instruments to measure electricity, temperature, and pressure. They emphasized the importance of measurement and documenting procedure, and discussed possible sources of experimental error in their work.[15] Their broad interest in natural phenomena was reflected in the diversity of their research and publications. Cavendish, for example, published extensive articles not only on the chemistry of airs, as discussed in the last chapter, but also wrote a mathematical analysis of electricity as a fluid and an article outlining a set of experiments with a torsion balance to determine the earth's density. Similarly, Priestley published accounts of his chemical experiments on airs and, more

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[15] As discussed in the introduction, Jed Buchwald argues that natural philosophers began to openly address and mathematically analyze "discrepant measurements". For example, Alan Shapiro has demonstrated that Newton's private practice substantially differed from his public presentation of his experimental methods. In the course of his optical research, Newton took many measurements, e.g. of the diameters of concentric colored rings produced by light in thin films (interference patterns), and calculated the average diameter for each ring, using the mean in subsequent investigations. "Newton, however, would suppress all use of averages in his published work." As Buchwald notes, Shapiro postulates that Newton chose "to publish summary rather than real experimental results" because the use of averages "was not yet either mathematically or philosophically justified or an accepted scientific practice." Buchwald demonstrates that, in contrast to Newton and his contemporaries, many late eighteenth-century natural philosophers, engaged in the study of optics, publicly documented their measurements, mathematical methods, and the conclusions they drew from that information, indicating a significant change in scientific approach. This chapter supports Buchwald's findings. For example, Cavendish often openly discussed his data and the sources of experimental and mathematical error in his research. As Jungnickel and McCormmach argue "[Cavenidsh] saw the harm that secrecy caused his colleagues, who became embittered over accusations of stolen ideas." He advocated "complete openness" in science (and business). Although their analyses were not as mathematically sophisticated as Cavendish's, Nicholson and Cavallo adopted a similar attitude towards experimentation and publishing. See, for example, Buchwald, 2006; Cavallo, 1777a; Cavendish, 1798; Jungnickel and McCormmach, 1999, 308-309; Kirwan, *Essay on Phlogiston*, Nicholson's preface; Alan E. Shapiro, "Newton's Optical Notebooks: Public Versus Private Data," in *Reworking the Bench*, ed. Frederick L. Holmes, et al., *Archimedes* (Dordrecht: Kluwer Academic Publishers, 2003), 43-66, 50, 59.

generally, electrical phenomena, while Cavallo and Nicholson wrote texts on natural philosophy, chemistry, experimentation, and instrumentation. These men were, in short, experimentalists.[16] Practice mattered just as much, if not more so, than theory.[17]

Electrical research in the eighteenth century was intimately connected to the study of material properties.[18] The vast majority of electricians believed that electricity was a substance. It is perhaps not surprising that chemical practitioners were also interested in investigating aspects of its behavior. For example, how did electricity bring about

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[16] See, for example, Cavallo, 1780; Tiberius Cavallo, "Magnetical Experiments and Observations," *Phil. Trans.* 76 (1786): 62-80; Tiberius Cavallo, "Of the Methods of Manifesting the Presence, and Ascertaining the Quality, of Small Quantities of Natural or Artificial Electricity," *Phil. Trans.* 78 (1788a): 1-22; Tiberius Cavallo, *Description and Use of the Telescopical Mother-of-Pearl Micrometer* (London: C. Dilly, 1793); Cavendish, 1766; Henry Cavendish, "An Account of the Meteorological Instruments Used at the Royal Society's House," *Phil. Trans.* 66 (1776b): 375-401; Henry Cavendish, "An Account of a New Eudiometer," *Phil. Trans.* 73 (1783): 106-135; Cavendish, 1788; Nicholson, 1787; William Nicholson, "Experiments and Observations on Electricity," *Phil. Trans.* 79 (1789): 265-288; Nicholson, *The First Principles of Chemistry*; Priestley, 1768; Priestley, Air 1772; Priestley, *HPSE 1775*.

[17] As mentioned briefly in the last chapter, Nicholson noted that: "A distinction [was] sometimes made, in experimental Science, between men of theory and men of fact." He argued that there was, particularly in studies of heat, a propensity "to run into extremes". He wrote: "The men of theory consider general results as the great and dignified objects of Science, and estimate the importance of facts according to their respective rank among the illustrations of their general theorems. The men of fact, on the contrary, are disposed to attach a high value to the practical department and are much more attentive to register one incident after another, than to generalize and explain the operations they behold. The enlightened cultivators of Science will be neither of these exclusively or rather he will be both." Nicholson advocated that theoreticians and experimentalists find middle ground. Priestley, in contrast, asserted that natural philosophers were "to much in haste to *understand*… the appearances that present themselves". He argued for the continued pursuit of experimental philosophy, "[f]or when a sufficient number of new facts shall be discovered… a more *general theory* will soon present itself." Cavallo also noted that there were a number of conceptual problems with the theories of electricity and heat. He wrote that "[t]he scattered materials [were] numerous for want of a theory; but neither can a theory be formed, nor even farther investigation be instituted, without a comprehensive view of all that has been done concerning the present experiments." In short, Cavallo advocated experiment-based theory. See, Tiberius Cavallo, *A Complete Treatise on Electricity in Theory and Practice, with Original Experiments*, 4 ed., vol. 3 (London: Printed for Charles Dilly, 1795), vol.1, 2; Nicholson, 1795, vol. 1, v; Priestley, 1790, vol.1, xxix, xliii.

[18] Heilbron's groundbreaking analysis of electrical studies from the seventeenth to mid-eighteenth century illustrates the importance of experimentation and matter theory to the development of physics. Chapter one of this dissertation significantly adds to Heilbron's work. It demonstrates, in contrast to the historical literature, that electricians also used chemical methods to investigate the properties of electrical fluid and its relationship to various substances. While chapter one focused on the electrical properties of gases and the chemical changes associated with the sparking of airs, this chapter examines experiments conducted on solids.

chemical change? What governed its attractive and repulsive characteristics? Why did certain materials become charged while others remained impervious to electrical fluid? What made a substance a conductor? Did it depend on the chemical properties of the material? Cavallo, Cavendish, Priestley, and Nicholson were all interested in investigating these questions.

It was common for eighteenth-century electricians to combine practices. Nicholson and Cavendish experimented with the sparking of airs and also invented electrometers, devices designed to measure the amount of electricity on a charged body. Similarly, Volta performed chemical experiments in the vicinity of his condenser, a device used to magnify the presence of weak electrical fluid, to determine if chemical reactions produced measurable changes in ambient electricity.[19]

Something began to change, however, between the late eighteenth and early nineteenth centuries. Humphry Davy, whose experiments form the basis of chapter three, was a different kind of scientist than his predecessors. He wrote that his practice combined natural philosophic approaches with chemical methods, but his experiments and the types of questions he asked were of a different nature. For instance, in stark contrast to Nicholson and Volta, Davy used the amount and type of chemical change produced by current as a measure of electrical strength instead of an electrometer. While Volta investigated how much electrical fluid was contained in different metals, Davy

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[19] See, for example, Cavendish, 1784a; Cavendish, 1785; Nicholson, 1789; Nicholson, *The First Principles of Chemistry*; Volta, 1782. Volta was no stranger to chemistry. Although typically cast as an experimental physicist, he also studied pneumatic chemistry, notably isolating methane. See Abbri, "Volta's Chemical Theories: The First Two Phases."

asked under what chemical conditions did combining metals produce electricity.[20] Thus, the following two chapters tease out some of these emerging differences in experimental practice by examining the types of research questions electricians asked, and the methods they used to study electrical phenomena.

Experiments were designed to examine various aspects of electricity: how its presence chemically changed materials and how the strength and duration of its effects varied with the amount and kind of electricity. As discussed in chapter one, Priestley believed that he had made a compelling case for identifying electricity with phlogiston. This chapter examines electrical research conducted in tandem to Priestley and Cavendish's "sparking of airs". More specifically, it focuses on experiments with non-frictional forms of electricity and instrumentation, e.g. how did electrometers work and what did they measure? I then briefly discuss the invention of the voltaic pile and Volta's explanation of its electrical action. Chapter three examines novel chemical studies of the

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[20] Davy, "Early Miscellaneous Papers"; Davy, 1839k, 408. Many eighteenth-century chemical practitioners argued that chemistry was an integral part of natural philosophy. Cavallo, for example, included a discussion of chemistry in *Elements of Natural or Experimental Philosophy*. It was the investigation of "the number, the quantities, and the properties of the constituent principles of all natural bodies," and therefore, properly belonged with studies of matter and its motion. Nicholson further noted that chemistry: "As a science, its object is to estimate and account for the changes produced in bodies by [the] motions of their parts, which are too minute to affect the senses individually. As an art, it consists in the application of bodies to each other in such situations as are best calculated to produce those changes." Priestley further asserted that chemistry was vital to material science, shedding light on fundamental natural processes like combustion and lightning. Davy also thought that natural philosophy and chemistry should work together, but unlike Cavallo, Priestley, and Nicholson, he made a sharper distinction between the two sciences. For instance, he wrote: "Mechanical philosophy, regarded as the science of the motions of the masses of matter, in its theories and practices, is to a certain extent, dependent upon chemical laws. How in fact can the mechanic calculate with accuracy upon the powers of solids, liquids, or gases, in communicating motion to each other, unless he is previously acquainted with their particular chemical affinities, or propensities to remain disunited, or to combine? It is to chemistry that he is indebted for the knowledge of the nature and properties of the substances he employs; and he is obliged to that science for the artificial production of the most powerful and most useful of his agents [heat and electricity]. See, Cavallo, *The Elements of Natural or Experimental Philosophy*, 416; Davy, "Early Miscellaneous Papers," 312; Nicholson, *The First Principles of Chemistry*, 1; Priestley, 1790, vi-vii.

battery. The questions raised in chapter one continue to guide this discourse: Did there exist a unique electrical fluid? Did electricity facilitate or participate as a substance in chemical change? What kinds of analogies and likenesses did electricity manifest with respect to other phenomena?

2.2: Electricity Without Friction, A Study of Fish and its Analogical Model

> Some weeks ago, a sea-faring man brought to this city [Philadelphia] a large eel that had been caught in the province of Guiana, a little to the westward of Surinam. It had the extraordinary power of communicating a painful sensation, like that of an electrical shock, to people who touched it, and of killing its prey at a distance.[21]
>
> Hugh Williamson (1773)

As discussed in chapter one, eighteenth-century scientists believed in material causes. It was difficult for them to conceive of a world in which actions propagated without substance. Electricity produced action-at-a-distance effects. Stephen Gray showed that small, lightweight objects such as brass fillings or silk threads were attracted to charged bodies, drawn through space as if by invisible hands. To account for this, Benjamin Franklin proposed that a rarefied atmosphere surrounded all electrical particles. These low-density clouds were imperceptible and communicated an object's electric virtue to neighboring bodies. Although electricity's attractive and repulsive characteristics appeared to be action-at-a distance forces, they had a material basis.[22]

Electric fluid, like other substances, could also be manipulated. William Watson asserted that the friction machine "from its Uses, [ought to] be denominated a Fire-pump, with equal Propriety as the Instrument [called the air pump] of *Otto Guerick* and *Mr.*

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[21] Hugh Williamson, "Experiments and Observations on the Gymnotus Electricus or Electrical Eel," *Phil. Trans.* 65 (1775): 94-101, 95.

[22] Cohen, 1956, 388-389; Franklin, 1751, 54-59.

Boyle" because it moved electric fire from one region to another, either increasing or decreasing its local concentration.[23] Franklin further argued electricity flowed from areas of high electrical density to low. Sparks, for instance, only jumped between differently charged objects. Friction machines, thus, aided natural philosophers in their electrical research by creating artificial imbalances in the electrical fluid of ambient matter. Within this framework, friction did not create electricity, but rather agitated it into motion so that it could be studied.[24]

Discoveries of non-mechanical forms of electricity called this view into question in the latter half of the eighteenth century. In particular, this section focuses on analyses of animal electricity. How did it relate to friction-based electricity? Were they identical fluids with different causes, or two unique substances coincidentally manifesting similar effects?

Edward Bancroft, a physician who supported Franklin in his negotiations with France during the American Revolution while acting as a double agent, wrote an essay on his experiences with "torporific eels" in Guiana, South America in 1769.[25] (Figure 2.1) Named for its "torpor" or numbing effect when touched, this fish behaved like the torpedo ray found in North Atlantic waters.[26] Bancroft suggested the unique abilities of

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[23] Watson, 1746b, 744.

[24] Cohen, *1990*, 20-27; Home, "Fluids and Forces in Eighteenth Century Electricity."

[25] Stanley Finger, "Edward Bancroft's "Torporific Eels"," *Perspectives in Biology and Medicine* 52, no. 1 (2009): 61-79; Piccolino, 2003, 12-14.

[26] The torpedo's ability to stun animals in direct contact and at-a-distance fascinated both physicians and natural philosophers since antiquity. Many seventeenth and early eighteenth-century physicians, applying Cartesian philosophy to living organisms, developed mechanical explanations for the torpedo's effects. For example, in 1678 Stefano Lorenzini suggested that when the fish's muscles contracted, a large number of particles were released into the local environment and interacted with other bodies. Similarly, in 1717,

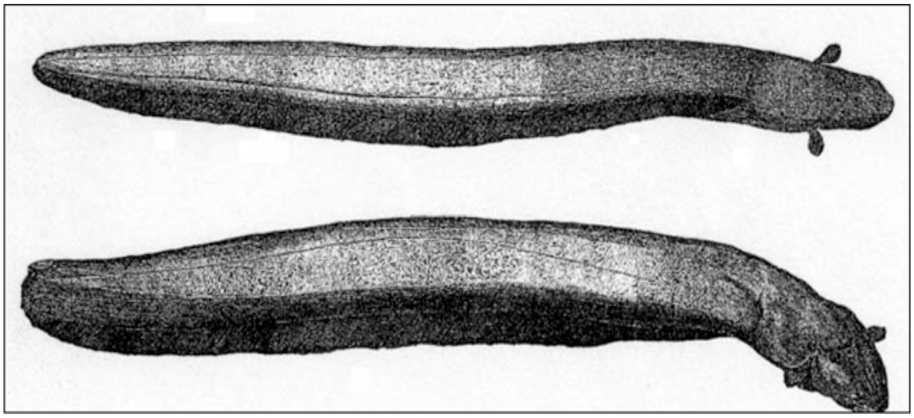

Figure 2.1: An engraving depicting the back and stomach of a torporific or electric eel (actually a knifefish) by John Hunter (1775).[27]

these fish were electrical in origin. (For instance, he dismissed alternative theories claiming that the fish's power to numb organisms was due to a toxin, because the indigenous population ate (dead) torporific eels raw.)[28]

John Walsh, an acquaintance of Bancroft and Franklin, was also a physician interested in electrical phenomena. Inspired by Bancroft's account, he traveled to La Rochelle, France to study the torpedo ray in more detail. Writing to Franklin in 1773, he conveyed a series of experiments conducted on the fish, which he argued confirmed Bancroft's suspicion: the animal produced electricity.[29] This account was followed by a detailed anatomical study of the torpedo's internal organs by the talented English physician and anatomist, John Hunter.[30] Walsh correctly predicted that their research on

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René-Antoine Ferchault de Reaumur theorized that the torpedo emitted a set of "vibrating" corpuscles, which intermingled with solid bodies to produce numbness. See Piccolino, 2003, 5-15.

[27] John Hunter, "An Account of the Gymnotus Electricus," *Phil. Trans.* 65 (1775): 395-407.

[28] Stanley Finger and et al, eds., *Brain, Mind, and Medicine: Essays in Eighteenth Century Neuroscience* (New York: Springer, 2007), 69-71.

[29] Marco Piccolino and Marco Bresadola, "Drawing a Spark from Darkness: John Walsh and Electric Fish," *Endeavour* 26 (2002): 19-26; Walsh, 1773.

[30] John Hunter, "Anatomical Observations on the Torpedo," *Phil. Trans.* 63 (1773): 481-489.

the torpedo would be of interest "both to the electrician in his walk of physics, and to all who consider, particularly or generally, the animal œconomy."[31]

As discussed in chapter one, analogical arguments were widely used in experiment, and the making of scientific claims in the eighteenth century. Walsh, like many of his contemporaries, also appealed to analogy to show that the torpedo (and electric eel) produced electricity. More specifically, using similarity of effect, he argued that the torpedo's effects were consistent with those produced by Leyden jars and therefore, like the Leyden jar, the fish emitted electrical fluid.

Invented in 1746 by a lawyer and amateur electrician, Andreas Cunaeus, and reported to the scientific community by Peter Musschenbroek, a professor of experimental natural philosophy in Holland, the Leyden jar (or phial) was designed to

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[31] There was widespread interest in Walsh's report. For example, in 1774 Alexander Garden, a physician in Charlestown, South Carolina, wrote of his attempts to examine a 'live' electrical eel brought by ship from Surinam, but found the experience too painful as the metal surgical instruments transferred the powerful shocks of the fish. Hugh Williamson, a physician in Philadelphia, also conveyed his studies of the *gymnotus electricus* to Walsh. As Williamson noted, contact with the electrical eel produced numbing and tingling sensations like the torpedo, but unlike the ray, the South American eel could kill prey with its electricity. In 1777, a trio of physicians even wrote a poem in honor of the electrical eel. In 1812, John Todd also wrote a series of articles on torpedoes caught off the coast of the Cape of Good Hope, in South Africa. These accounts added to the growing literature and sustained interest in the behavior of electric animals well into the nineteenth-century. See John Davy, "An Account of Some Experiments and Observations on the Torpedo (Raia Torpedo, Linn.)," *Phil. Trans.* 122 (1832): 259-278; John Davy, "Observations on the Torpedo, with an Account of Some Additional Experiments on Its Electricity," *Phil. Trans.* 124 (1834): 531-550; Alexander Garden, "An Account of the Gymnotus Electricus or Electrical Eel," *Phil. Trans.* 65 (1775): 102-110; Francis Gotch, "The Electromotive Properties of the Electrical Organ of Torpedo Marmorata," *Phil. Trans. B* 178, no. 487-537 (1887); John Hunter et al., *The Torpedo: A Poem to the Electrical Eel, Addressed to Mr. John Hunter, Surgeon, and Dedicated to the Right Honourable Lord Cholmondely* (London: Printed, and Sold by All the Booksellers in London and Westminster, 1777); John Ingenhousz and Mr Walsh, "Extract of a Letter Containing Some Experiments on the Torpedo, Made at Leghorn, January 1, 1773 (after Having Been Informed of Those by Mr. Walsh). Dated Saltzburg, March 27, 1773," *Phil. Trans.* 65 (1775): 1-4; Carlo Matteucci, "Electro-Physiological Researches, Sixth Series. Laws of the Electric Discharge of the Torpedo and Other Electric Fishes, and the Theory of the Production of Electricity in These Animals," *Phil. Trans.* 137 (1847): 239-241; John T. Todd, "Some Observations and Experiments Made on the Torpedo of the Cape of Good Hope in the Year 1812," *Phil. Trans.* 106 (1816): 120-126; Walsh, 1773, 416; Williamson, "Experiments and Observations on the Gymnotus Electricus or Electrical Eel."

store electrical fluid generated by friction machines. (Figure 2.2) It consisted of, from outside in: metal (a hollow cylinder made out of sheet metal), glass (a jar), water (or air), and metal (a rod suspended from the lid of the jar).[32]

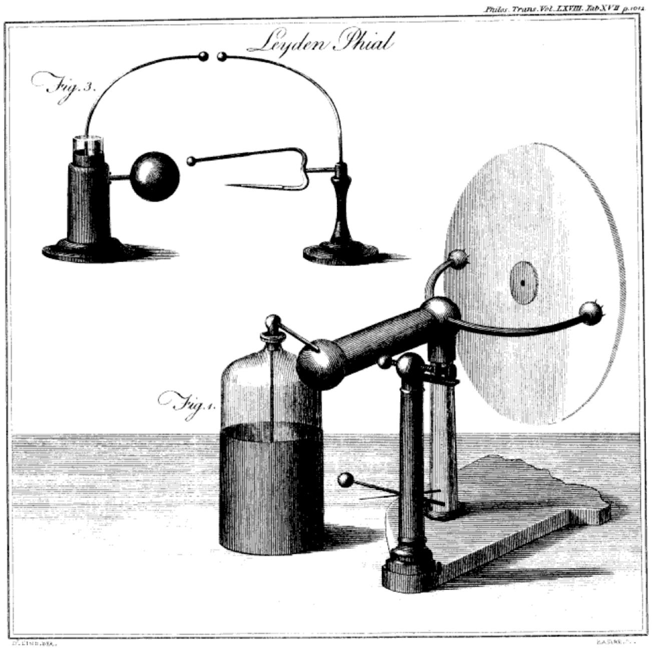

Figure 2.2: Two Leyden jars. In the upper left hand corner, the recessed image shows that the inside metal layer of the phial is attached to the outer by a fixed gap of air. (The distance a spark would travel through air served as a relative measure of the amount of electrical fluid contained within the jar.) In the right foreground image, a standard friction machine charges the jar.[33]

Walsh wrote that "[n]ot only the shock, but the numbing sensation which the animal sometimes dispenses […] may be exactly imitated with the Phial." Although a person readily experienced a shock by touching the fish, its discharge was not visible to the naked eye because it was too small to measure with "pith balls" and "seldom sensible beyond the touching finger".[34] He noted that Cavendish had recently shown "that a shock could be received from a charge [from a series of Leyden jars] which was unable to force a passage through the least space of air" also with no discernable sparks. Walsh postulated that the larger, combined "surfaces [of the Leyden

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[32] Heilbron, 1999, 312-314.

[33] Benjamin Wilson et al., "New Experiments Upon the Leyden Phial, Respecting the Termination of Conductors," *Phil. Trans.* 68 (1778): 999-1012.

[34] Walsh, 1773, 463.

jars,] together an area 400 times larger than that of [a single] Phial", diminished or weakened the electrical discharge in a similar way to the torpedo's rather large "electrical" organ.[35]

More importantly, Walsh observed that "the back and the breast of the animal [were] in different states" like the rod and cylinder of the Leyden jar. A fisherman touching a point on the torpedo's back (or stomach) experienced no effect, whereas simultaneous contact with both its back and stomach communicated a shock. Moreover, the "same conductors" used in electrical research, such as saltwater and metal, could transmit these sensations from the fish to a person and could be "intercepted" or blocked "by the same non-conductors, for instance glass and sealing-wax."[36] On the basis of similarity of effect, Walsh concluded that the torpedo emitted (a type of) weak electrical fluid like that produced by a series of Leyden jars.[37]

Hunter, convinced by Walsh's arguments and at his behest, undertook a detailed anatomical study of the torpedo.[38] (He also later studied and reported on the anatomy of the electric eel.[39]) He discovered in either 'wing' of the ray a large organ constructed "wholly of perpendicular columns, reaching from the upper to the under surface of the

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[35] Ibid, 475.

[36] Ibid, 462.

[37] Ibid, 476; Cavendish, 1771.

[38] See, Stephen J. Cross, "John Hunter, the Animal Oeconomy, and Late 18th Century Physiological Discourse," *Studies in History of Biology* 5 (1981): 1-110; Piccolino, *2003*; Piccolino and Bresadola, "Drawing a Spark from Darkness: John Walsh and Electric Fish."

[39] Hunter, 1775.

Figure 2.3: **An engraving of the torpedo ray by John Walsh (1773).** The upper image depicts a top-down view of the fish's back with the skin and upper layer of the electrical organ removed. It shows that the columns are close packed. The bottom figure shows a cross-section of the fish with its columns' partitions stacked vertically. The vertical scale of the organ: 150 hexagonal partitions per inch.[41]

body, and varying in their lengths, according to the thickness of the parts of the body" in which they were located (Figure 2.3).[40]

Unlike the Leyden jar, which was typically constructed of metal and glass, the torpedo's electrical organ had columns made of alternating "horizontal partitions" containing "membranes" and "fluids" connected by "blood vessels". Carefully counting "the number of partitions", Hunter found that "a column of one inch in length" had approximately "one hundred and fifty" segments. Additional study of the columns further suggested that "the increase in the length of a column, during the growth of the animal, does not enlarge the distance between each partition in proportion to that growth: but that new partitions are formed, and added to the extremity of the column from the fascia."[42]

The electrical organ of the torpedo, as described and illustrated by Hunter and

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[40] Hunter, 1773, 483.

[41] Ibid, 485.

[42] Ibid, 485; John Walsh, "Of Torpedoes Found on the Coast of England," *Phil. Trans.* 64 (1774): 464-473.

Walsh, was more complicated than an individual Leyden jar. Franklin had proposed the generally accepted explanation of the phial in 1751. As Franklin realized, the Leyden jar was, in its simplest form, a piece of glass sandwiched between two metals, sometimes referred to as a “Franklin square”. (Figure 2.4) Touching the metal plate, denoted *A*, to a friction machine transferred and distributed fluid charge from the generator through the metal plate to the surface, labeled *AA*, of the glass plate. As discussed in chapter one, glass was defined by Dufay and Franklin to be an electric, meaning that it could hold or “collect” charge along its surfaces, but it could not conduct or transmit electrical fluid through its material body. Metals, in contrast, were non-electric; while they readily allowed the transmission or passage of electrical fluid through their material body, they did not retain any appreciable amount of the moving fluid. Based on his experiments with the Leyden jar, Franklin also postulated that the electrical fluid present in any substance was conserved; in other words the surface labeled *BB* of the glass plate lost electrical fluid in proportion to the increase in electrical fluid on its *AA* surface. Thus, while the total amount of charge present in the glass plate remained the same, its surfaces contained different amounts of electrical fluid. This was an unnatural, induced material state. Provided with a pathway, the electrical fluid would quickly move from one surface to the other to restore the balance of electrical fluid in the glass plate to its natural state.[43]

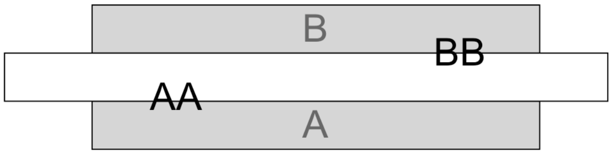

Figure 2.4: **A Schematic of a Franklin Square.**

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[43] Franklin, 1751, 1-4.

There was no obvious, analogous structure in the torpedo's electrical organ or its columns. One could not say with confidence that a particular column or partition acted like the conducting metals or fluid-collecting glass plate of the Leyden jar. The phial also received its charge from a friction machine, which relied on inorganic substances and moving parts to draw electrical fluid out of materials and transfer it to the phial. The fish had no clear mechanical system producing electrical fluid. How then did the torpedo generate electricity?

Despite the apparent lack of structural or material similarity, Cavendish also described the torpedo as a living-Leyden jar in 1776. Although he rarely made his results public, Cavendish energetically pursued the study of electricity in addition to the chemistry of airs.[44] For example, in 1771, he published a lengthy article on his electrical research in which he indicated that he had independently pursued a similar line of inquiry as Franz Aepinus, a Russian natural philosopher who had mathematized Franklin's qualitative theory in 1759.[45] Both Cavendish and Aepinus conducted experiments to see if there existed a relationship between the amount of electricity and the resistivity of a substance to the flow of electrical fluid. Based on their experimental data, both tried to determine if there existed a mathematical dependence between variables such as the force of electricity, the distance between charged objects, and the amount of electrical fluid.[46] Cavendish was also notably among the first to abandon Franklin's notion of an electrical

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[44] Cavendish had in his possession many unfinished manuscripts on a variety of topics. See Jungnickel and McCormmach, 1999, 8-9.

[45] Cavendish, 1771, 582.

[46] Aepinus, *Aepinus's Theory of Electricity and Magnetism [1759]*, 124-127.

atmosphere, adopting a more abstract concept of force not unlike gravity.[47] Additionally, he experimented with the capacity of Leyden jars to store electricity and studied how connecting multiple jars (in different ways) affected observed electrical phenomena.[48] Although he lacked Walsh's biological and anatomical knowledge, he was much better acquainted with the experimental physical sciences and the Leyden jar. Drawing on his strengths, Cavendish set out to quantitatively test Walsh's claims.

More specifically, Cavendish took one of Walsh's observations as a starting point for re-examining the relationship between the phial and the fish:

> …the torpedo is not constantly electrical, but hath a power of throwing at pleasure a great quantity of electrical fluid from one surface of those parts which he [Walsh] calls the electrical organs to the other; that is, from the upper surface to the lower, or from the lower to the upper, the experiments do not determine which; by which means a shock is produced in the body of a person who makes any part of the circuit which the fluid takes in its motion to restore the equilibrium.[49]

Charging one side of a Franklin-square affected the movement of fluid on its opposite face. When its two opposing plates were connected via a third conductor (such as a person), electricity flowed from one side to the other until equilibrium was reached. As Cavendish noted, Walsh's experiments with the torpedo suggested that, like the Leyden jar, its back and stomach were in different electrical states. When a fisherman grasped its upper and lower surfaces simultaneously, electrical fluid flowed "to restore equilibrium". This suggested to Cavendish a possible mechanism for explaining the torpedo's electrical action: the top and bottom of the fish were organic equivalents to the upper and lower

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[47] Jungnickel and McCormmach, 1999, 230-235; Pancaldi, 2003, 120.

[48] Cavendish, 1967, 56-63.

[49] Henry Cavendish, "An Account of Some Attempts to Imitate the Effects of the Torpedo by Electricity," *Phil. Trans.* 66 (1776a): 196-225, 196; Piccolino, 2003, 134-140.

surface of a charged phial, with something complicated in between.

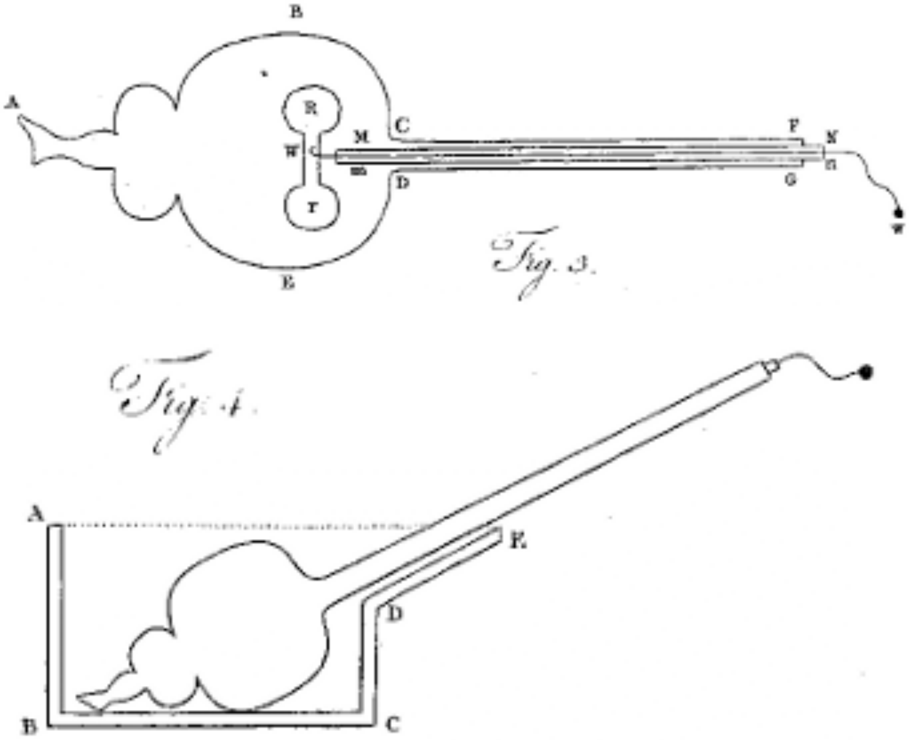

Figure 2.5: **Two Images of Cavendish's Mock Fish.** In the top illustration, a wire, running W to w, charges Leyden jars located at points R and r. The bottom picture shows the artificial torpedo immersed in water.[50]

Cavendish further investigated this possibility by constructing a 'working' model of the torpedo. (Figure 2.5) He created this mock fish using a series of Franklin-squares mounted in a wooden frame and covered in leather (sheep's skin). He weakly charged the device and immersed this "artificial Torpedo" in salt water.[51] He then repeated Walsh's experiments, touching various parts of the leather apparatus with his hands, wires, and electricity detectors.

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[50] Ibid, 222-223.

[51] Cavendish, 1776, 205.

Cavendish modified Lane's electrometer in order to detect smaller amounts of charge. Conveyed to the Royal Society by Franklin in 1767, Lane's electrometer was a common instrument used for detecting and measuring the amount of electricity present in a charged object. This apparatus has been simplified and schematically represented in Figure 2.6. Thomas Lane recognized that a spark would only pass through the air from point *E* to *F* if it were "strong" enough. Therefore, adjusting the distance between *E* and *F* until a discharge was observed was a way of measuring the relative amount of electrical fluid present in an object, the distance correlating to the power of the difference in electrical fluid between points *B* (attached to a charged object) and *C* (connected to a non-electrified object).[52] Instead of measuring the distance the electrical fluid traveled through air, Cavendish attached to either end of the spark gap "cork balls about 0.25 of an inch in diameter". Small amounts of electrical fluid, too weak to jump from E to F, would flow into the first cork ball. The second sphere having less charge was attracted to it and moved towards the first ball, eventually touching it. Upon contact,

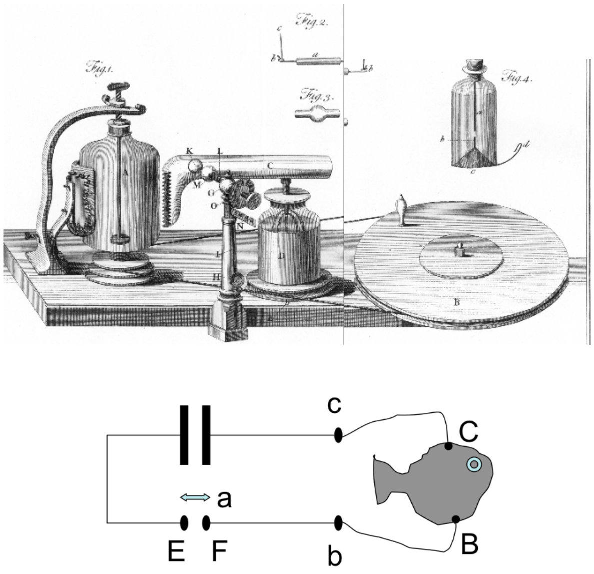

Figure 2.6: **Lane's Electrometer.** The top image depicts his electrometer as presented to the Royal Society in 1767. The bottom illustration shows a simplified schematic version of this instrument, using modern conventions.

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[52] Lane, 1767, 453-454.

excess fluid would be transferred from one sphere to the other. Both balls now contained electrical fluid. Subsequently, the spheres moved apart, repelled by their mutual fluid charge. Cavendish then "estimated the divergence of these balls" as a measure of the amount of electrical fluid present.[53]

Using this detector, Cavendish observed that electrical fluid traveled across the leather from the positive (or plus) plate located on the mock fish's back to the negative (or minus) plate of its stomach. As Walsh had suggested, Cavendish found that he could mimic the properties and behavior of the torpedo with a combination of metal and glass plates. Cavendish argued his experiments demonstrated that "the effects of this artificial Torpedo agree very well with those of the natural one"; therefore, the fish must produce electricity.[54]

Although he acknowledged that it was "perhaps… not necessary that there should be any thing analogous to a battery [a series of Leyden jars] within [the Torpedo]" the manner and behavior of the Torpedo suggested otherwise:

> …if we suppose, that the fluid is gradually transferred through the electrical organs, from one side to the other at the same time that it is returning back over the surface [of the fish or through an external circuit], and through the substance of the rest of the body; so that the quantity of fluid on either side is during the whole time very little greater or less than what is naturally contained in it: then it is possible, that a very great quantity of fluid may be transferred from one side to the other, and yet the force with which it is impelled be not sufficient to force it through a single interval of the links of a chain.[55]

Cavendish reasoned that there must be enough electrical fluid in the fish to produce the

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[53] Cavendish, 1776, 202.

[54] Ibid, 205, 216: He used four Leyden jars in series.

[55] Ibid, 223.

sensation of shock, but not enough fluid traveling along its surface at any given time to spontaneously travel through the air or along a short metallic "chain" to a lesser charged object. This suggested that the fish contained a battery or series of Leyden jars, which allowed for differences in the amount of electrical fluid (within the electric) while retaining its total charge. Cavendish conceded this meant that either the electric organ's substance behaved as an imperfect electric, allowing electrical fluid to slowly seep from its edge through its material body, or that electricity was conducted slowly through the organ via the complicated network of fibers connecting the partitions, the partitions somehow regulating the flow of electrical fluid. Neither option, however, was impossible. When connected to an external circuit, such as its own skin or a fisherman in contact with its body, the electrical fluid would flow from one side (i.e. the fish's back) to the other (its stomach).[56]

Walsh had suggested that the partitions in the torpedo's electrical organ might act in combination to produce a larger surface area over which electrical fluid could be stored. Cavendish noted that each partition in the fish's organ was connected to its neighbors via various types of connecting tissues. He measured the effect of surface area on the amount of transmitted electrical fluid in Leyden jars of differing size. Using Hunter's estimated size and description of the torpedo's partitions, Cavendish estimated that "the sum of the areas of all the partitions is about 3700 square inches." He calculated that "3700 square inches of coated glass 1/150 of an inch thick will receive […] 2 ¼ times as much [electricity] as [the] battery [used in the construction of the artificial

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[56] Ibid, 223.

Torpedo], supposing both to be electrified by the same conductor".[57] Cavendish concluded that a Leyden jar made of similar thickness to a partition and with an equivalent surface area to all the partitions, stored more than enough electrical fluid to behave like the torpedo.[58] He asserted that his device was not incompatible with the actual electric organ of the fish. Cavendish's model implicitly reduced the torpedo to a Leyden jar: the organic tissue of the partitions collected electrical fluid like glass[59] while the subcutaneous tissue transmitted the fluid like metal plates to the skin and/or external circuit.

Walsh and Cavendish's respective researches used different approaches to show that the torpedo generated electricity.[60] Walsh argued from experience that its ability to shock other animals was consistent with physiological responses to common electrical fluid; human 'detectors' in both cases experiencing tingling and numbness. Hunter's anatomical analysis also showed that the torpedo possessed a unique organ, responsible for its effects. While Walsh theorized about the relationship between the Leyden jar and torpedo, Cavendish expanded the argument by experimenting with actual combinations of Leyden jars, constructed in size and dimension to the electrical organ of the fish, and measuring their electrical output. This inorganic representation also produced similar phenomena to the fish, further reinforcing the analogy between the two. This led

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[57] Ibid, 223-224.

[58] Ibid, 224.

[59] Cavendish conceded that this view suggested that either the partition's substance behaved as an imperfect electric.

[60] Jungnickel and McCormmach, 1999, 248: "So that others could experience his artificial torpedo, Cavendish invited into his laboratory a number of interested persons: the torpedo anatomist Hunter; Lane, whose electrometer Cavendish was using; Nairne, whose battery and coated glass plates he was using; Priestley, who was in London on a visit; and Thomas Ronayne… a skeptic [of Walsh's claims]."

Cavendish to speculate on the relationship between the parts of the Leyden jar and the structure and function of the fish's electrical organ. On the basis of similarity of effect, both Walsh and Cavendish concluded that the torpedo produced electricity.

If the torpedo stored and emitted electricity, as Cavendish proposed, where did its electrical fluid come from? Cavendish recognized that neither he nor Walsh had adequately explained the origins of the animal's "invisible" generator. Priestley suggested that organisms chemically created their own electrical fluid out of phlogiston in their internal organs. As discussed in chapter one, Priestley identified electricity with phlogiston, the material manifestation of heat, because of the numerous chemical effects electricity and heat had in common, such as vitrification and calcination.

Like Cavendish, Priestley conducted extensive electrical research prior to his more famous work on the chemistry of airs. In the late 1760s, he began to write *History and Present State of Electricity*, a lengthy book published in two volumes. It provided an overview of the history of electrical studies, and Priestley's own original experiments on the subject. As discussed in the first section, Priestley had a diverse set of interests, exemplified by the scope of phenomena addressed in this text. For example, he not only wrote about the chemical changes associated with electricity, but he also compared the different methods used to determine whether an object was positively or negatively charged. He related experiments on electrical explosions, showing that the length of a conductor affected the force of an emitted spark, and examined, like Cavendish, how the type and size of an electric affected its electrical output. He further discussed how heating affected electrical measurements and conductivity, and wrote about the effects of applying electricity to animals. It became a popular and widely read text.[61]

Priestley drew on this research to suggest that the torpedo ray processed phlogiston and emitted electrical fluid, as Walsh and Cavendish advocated. Writing to Watson in 1766, he noted that "dischar[ing] 37 square feet of coated glass through the head and tail of a cat" caused "universal convulsions" and "quick breathing".[62] Priestley further noted that Beccaria's experiments on animal responses to electricity had also showed that "electric matter directed through the body of any muscle forces it to contract… and occasions a proper *convulsion*".[63] He, thus, associated electricity with the nervous system and nervous fluid because it caused muscle spasms.[64]

His experiments with plants further convinced him that living organisms contained preferentially conducting conduits. He observed that if a person placed their finger near a conductor receiving a spark, they experienced the sensation of "a stroke, as of something pushing against [their] finger". He attempted to determine the extent of a spark's "lateral force" or "concussion" by seeing how and what kinds of objects were affected by it, including cork, cabbage leaves, glass, metal filings, etc. He noted that "[i]f pieces of cork, powder of any kind, or any light bodies whatever, be placed near the explosion of a jar or battery, they will not fail to be moved out of their places, upon the instant of the discharge." Discharging a Leyden jar through a cabbage leaf, he further

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[61] Priestley's *History and Present State of Electricity with Original Experiments,* first published in 1767, received wide circulation; five English editions and three translations (French, German and Dutch) were issued during his lifetime alone.

[62] Priestley, *Correspondence 1966*, 35.

[63] Beccaria, *Artificial Electricity*, 269, 273; Priestley, Air 1775, 276.

[64] Newton had also proposed that nervous fluid might be electrical fluid. Pancaldi, 2003, 192.

observed that "[t]he electric matter had… been evidently attracted by the veins of the cabbage leaf" as evidenced by changes in the color and texture of the leaf. He tried other configurations of objects. He placed "a piece of common window glass [on top of a cabbage leaf] on the [conducting] path, pressed by a weight of six ounces; but [when sparked] it [the glass] was shattered to pieces, and totally dispersed, together with the leaf on which it lay. Placing the black side of a piece of cork wood upon it [another cabbage leaf], pressed by a weight of a half a pound," he found that "the leaf was not rent, but the cork was furrowed all the way, a trench being made in it, about half an inch in breadth, and a quarter of an inch in depth."[65]

He also varied the shape and length of the conducting path. For instance, he cut the cabbage leaf at right angles. He also experimented with bent metal wires, placing at the far end a small amount of gunpowder. He noted changes in the color and texture of the leaf and metal, and to what extent the gunpowder had burned. In each case, he found that the shape of the conductor produced no discernible variation in the electrical fluid's "*momentum*". He did observe, however, that the length of the conducting path affected his experimental results. For example, he connected a brass wire to a fixed length of iron wire wrapped around a nail. On top of the nail, he again placed a small amount of gunpowder. Using "twenty-two yards" of brass, he found that "the wire was not melted, nor the gun powder exploded". In contrast, he noted that when he shortened the brass wire, a discharge from "the same battery was able to melt more than nine inches of [the] iron wire" and the gunpowder "was easily fired". Priestley asserted that sparks could

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[65] Priestley, HPSE 1775, 666-667.

travel through veins of leaves and oddly shaped conductors with equal efficacy, but that "the diminution of force [exhibited in his latest experiments] must have been owing to the length of the circuit."[66] (Volta would later quantitatively confirm Priestley's experiments, comparing how different lengths of metals affected the measured amount of electrical fluid. This will be further discussed in section 2.3.)

These experimental results, in conjunction with his research on the chemistry of sparked airs, encouraged Priestley to consider the causes of animal electricity. In *Experiments and Observations on Different Kinds of Air* in 1775, he included a section entitled: *Speculations arising from the consideration of the similarity of the electric matter and phlogiston*, in which he discussed the torpedo ray's abilities.[67]

It had long been held that "the source and materials of all muscular motion must be derived" from diet. Priestley argued, "nothing will nourish that does not contain phlogiston, and probably in such a state as to be easily separated from it by the animal functions."[68] For instance, he pointed out that liquor, a highly flammable substance, which contains large amounts of phlogiston, "brace[s] and strengthen[s] the whole nervous and muscular system." Also, water, an essential material to life and a conductor, was thought to be a compound of dephlogisticated air (oxygen) and phlogiston. Furthermore, Priestley asserted his "conjecture" that bodies contained large amounts of phlogiston was additionally "favoured by [his] observation, that respiration and putrefaction affect common air in the same manner in which all other processes diminish

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[66] Ibid, 666-672, 668.

[67] Priestley, Air 1775, 274-286.

[68] Ibid, 276.

air and make it noxious, and which agree in nothing but the emission of [excess] phlogiston [from the body]."[69] In other words, like the sparking and heating of airs, the processes of breathing and decay caused a reduction in air volume and increase in gas toxicity. Priestley speculated:

> these facts [suggest]… that animals [like the torpedo] have a power of converting phlogiston, from the state in which they receive their nutriment, into that state in which it is called the electrical fluid; that the brain, besides its other proper uses, is the great laboratory and repository for this purpose; that by means of the nerves this great principle, thus exalted, is directed into the muscles, and forces them to act, in the same manner as they are forced into action when the electric fluid is thrown into them [from an external source like a friction machine]…[70]

Priestley was not alone in suggesting that nervous fluid was electrical fluid. Luigi Galvani, an Italian physician interested in the therapeutic applications of electricity, argued that there also existed a form of animal electricity. More specifically, his experiments focused on the material and structural composition of muscles and nerves. While Walsh and Cavendish sought to reify the torpedo's electrical action by emphasizing its similarity to Leyden jar phenomena and artificial or friction-based electricity, Galvani argued that muscle and nerves were an organic Leyden jar, storing a unique electrical fluid that was, as Priestley speculated, produced in the brain.[71]

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[69] Ibid, 277.

[70] Ibid, 278.

[71] Galvani, 1953. There is a large literature examining Galvani's work. See, for example, Marco Bresadola, "At Play with Nature: Luigi Galvani's Experimenta; Approach to Muscular Physiology," in *Reworking the Bench*, ed. Frederick L. Holmes, et al., *Archimedes* (Dordrecht: Kluwer Academic Publishers, 2003), 67-92; Marco Bresadola and Giuliano Pancaldi, eds., *Luigi Galvani International Workshop Proceedings: Bologna, 9 October 1998* (Bologna: Centro Internazionale per la Storia della Università e della Scienza, 1999); Nahum Kipnis, "Luigi Galvani and the Debate on Animal Electricity, 1791-1800," *Annals of Science* 44 (1987): 107-142; Pera, 1992.

Galvani showed in a series of four treatises published in 1791 that changes in ambient electricity,[72] created either by a friction machine or a storm, produced muscle contractions in both living and dead frogs. For example, he "separate[d] the nerve from the surrounding [muscle] tissue" in the "upper thigh" of a live frog. He then "attach[ed] it [the nerve] to a conductor. When a spark was discharged [into the air from a nearby electrical machine], the limb reacted by contractions".[73] He also discovered that connecting nerve to muscle with a metallic arc produced similar spasms:

> when I brought the animal [a frog] into a closed room, placed it on an iron plate, and began to press the [metal] hook which was fastened in the [frog's] spinal cord against the plate, behold!, the same contractions and movements as before. I immediately repeated the experiment in different places with different metals and at different hours of the day. The results were the same except that the contractions varied with the metals used; that is, they were more violent with some and weaker with others.[74]

Thus, by isolating and connecting the nerve with a metal conductor to muscle mounted on an iron plate, the muscle still contracted. Why did the muscle move? Repeating the experiment with non-conductors, such as "glass", "resin" and "wood", gave a null result: the muscle did not contract.[75] Since there was no external source of electrical fluid, Galvani argued there must be an internal source of electricity responsible for the muscle's contraction. He suggested that when a conductor[76] connected nerve to muscle, a special

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[72] Galvani, 1953, 47.

[73] Galvani also tried these experiments on "warm-blooded animals like chickens and sheep" and found that "the results were substantially the same for both kinds of animals". Ibid, 55.

[74] Ibid, 59.

[75] Ibid, 59-60.

[76] Ibid, 66. Galvani also commented on the effects of connecting tissues with different materials: "Of the metals, it is conducted far more easily through gold and silver and less successfully through lead and iron (especially when rusted). […] After investigating the conducting power of solid bodies, we likewise looked

type of electrical fluid flowed from the nerves to the muscle through the conductor back to the nerves (and so on) causing spasms.

Muscles, Galvani noted, consisted of stringy fibers interlaced with channels or fine nerves. If nerves did carry electrical fluid to muscles producing movement: "how then can they retain the animal electric fluid… so that it is not diffused and spread to adjacent parts, with a greater diminution of muscular contractions [over time]?" Anatomical study of nerves showed that they were "hollow", while chemical analysis (distillation of boiled nerve tissue) demonstrated that they contained an "oily" substance and "a greater amount of inflammable air [hydrogen]… than was ever derived from any other part of the animal."[77]

Oils were known to inhibit the transmission of electric fluid. Also, many chemists, like Richard Kirwan, an Irish academic who engaged in a highly publicized debate with Lavoisier over combustion, argued inflammable air was a form of phlogiston.[78] Galvani was also a phlogistonist. Thus, he argued that "such a structure and composition of the nerves" demonstrated that nerves conducted electricity. The elevated amount of inflammable air was indicative of the presence of phlogiston, and Priestley's experiments suggested that electricity was itself a form of phlogiston. This implied that

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into the same property of fluids, and the result was practically the same. We discovered that animal electricity makes its way most successfully through aqueous fluids but is delayed and virtually stopped by oily fluids."

[77] Ibid, 76.

[78] Kirwan, *Essay on Phlogiston*. See also, Michael Akeroyd, "The Lavoisier-Kirwan Debate and Approaches to the Evaluation of Theories," *Annals of the New York Academy of Sciences* 988 (2003): 293-301; Victor Boantza, "The Phlogistic Role of Heat in the Chemical Revolution and the Origins of Kirwan's "Ingenious Modifications... Into the Theory of Phlogiston"," *Annals of Science* 65 (2008): 309-338; Cavendish, 1788; Joseph Priestley, "Objections to the Experiments and Observations Relating to the Principle of Acidity, the Composition of Water, and Phlogiston, Considered; with Farther Experiments and Observations on the Same Subject," *Phil. Trans.* 79 (1789): 7-20.

the nerves likely contained electrical fluid while "at the same time, [its outer layers] prevent[ed] its [the electric fluid's] dissipation" because the nerve's "pipe" was made of a non-conducting material, oil.[79]

While nerves behaved like insulated conductors, Galvani postulated that muscle acted like an "elastic" electric. Glass, due to its rigidity, retained its shape, whereas muscle fibers could easily tighten and expand. Since all materials contained some electricity, including muscle, the muscle responded to the charge moving through the nerves[80] just like the surface of a glass plate responded to changes in the amount of electrical fluid present on its opposing surface.[81] Therefore, the movement of (negative) electrical fluid through (positively charged) muscle tissue caused its "fibres" to "shorten" as the "particles [were] drawn closer to one another", producing contractions.[82]

Galvani, like many of his contemporaries, adopted a two-fluid model of electricity. Although Franklin's theory relied on one fluid, experiments conducted in the latter half of the eighteenth century supported Dufay and Nollet's two-fluid system: one positive (in Franklin's theory a state of "plus" or an excess amount of electrical fluid) and one negative (a state of "minus" or a lack of electrical fluid). For example, poking a rod through a piece of paper caused the paper to furl outwards in the direction of motion

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[79] See chapter 1, especially section 1.1.2 and Galvani, 1953, 76.

[80] Galvani refers to this as "nervo-electric" fluid.

[81] Galvani, 1953, 80.

[82] Galvani noted that: "It was also possible that contractions "occur… in some other manner that is not yet known." As Bernardi has noted, the "controversy" began first between physicians; those who advocated that muscle contractions were caused by muscle-irritation, such as Albrecht von Haller, and those who supported animal electricity, such as Galvani and later his nephew Giovanni Aldini. See Walter Bernardi, "The Controversy on Animal Electricity in Eighteenth-Century Italy: Galvani, Volta, and Others," *Nuova Voltiana* 1 (2000): 101-114; Galvani, 1953, 79.

through which the rod passed through the paper. Similarly, Musschenbroek conducted a simple experiment in which an electric discharge was directed through a piece of paper. The paper furled in both directions.[83] This suggested that there were two simultaneous discharges, traveling in opposite directions through the paper. This experiment was easily repeated and confirmed.[84]

Based on these experiments, Galvani concluded that muscle tissue acted like "a small Leyden jar… with a twofold and opposite electricity."[85] His arguments represented a sharp break from those of Walsh and Cavendish. While they tried to emphasize the similarity of effects produced by fish and friction machines, Galvani sought to make animal electricity distinct from friction-based electricity because they had different causes. Galvani, like Priestley, asserted that nervous fluid was electrical fluid, and that it was likely produced in the brain. This suggested that animal electricity was somehow manufactured in the organism, either chemically separated from or made out of bodily materials, like food, air, and blood. Despite this marked difference, the Leyden jar figured prominently in Galvani's theory of animal electricity as the mechanism by which

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[83] David Knight, *Ideas in Chemistry* (New Brunswick, NJ: Rutgers University Press, 1992), 58.

[84] With the assistance of Brian Anderson (Physics Laboratory Technician) and L. Andrew Helton (an astronomy graduate student and experimental physicist), I replicated this experiment using an electrostatic generator and various types of paper. It is interesting to note that, while papers made with cotton or linen, did visibly furl in both directions, papers made of wood pulp did not. Scholarship examining the two fluid model versus the one fluid model includes: Aepinus, *Aepinus's Theory of Electricity and Magnetism [1759]*; Cohen, *1956*; Heilbron, *1999*; Home, *Electricity and Experimental Physics in 18th Century Europe*; Home, "Fluids and Forces in Eighteenth Century Electricity."

[85] Galvani appealed to analogy to show that muscle to contain both positive and negative electricity: "Finally, if one, even briefly, has considered the mineral, tourmaline, which embodies a two-fold and opposite electricity, as the investigations of contemporary experimenters seem to indicate, he has come upon a new argument based on analogy which renders a hypothesis of this kind not at all improbable." Galvani, 1953, 74. See also Roderick Home, "Aepinus, the Tourmaline Crystal, and the Theory of Electricity and Magnetism," *Isis* 67 (1976): 21-30.

electrical fluid induced muscles to contract. While Galvani used similarity of form and function to argue that muscles were organic Leyden jars, Walsh and Cavendish used similarity of effect to argue that animal and artificial electricity were identical fluids.

2.3: The Instrument Makers

> It is a truism that progress in any branch of Science is conditioned by the invention and improvement of instruments.[86]
>
> W. Cameron Walker (1936)

Using different approaches, Walsh and Cavendish sought to show that the torpedo ray emitted an electrical fluid not unlike that produced by friction machines. Galvani also contended that animals generated electricity, but asserted that their electrical fluid was unique to living organisms, distinct from mechanically produced sparks. Each used the physics of the Leyden jar to bolster their arguments.

Did there exist distinct forms of electricity? Many natural philosophers and chemists, like Priestley and Cavendish, came to the study of animal electricity through their interest in weak electrical phenomena. In order to show that fluids were in fact electric, it was imperative to be able to compare and measure minute quantities of electricity. Scientists asked: if everything was imbued with electricity, was there a way to measure the amount of electrical fluid in a material, even if it existed in only small quantities? Was it possible to measure the amount of fluid flow between objects? If so, could the type and source of electricity within an object or organism be conclusively determined?[87]

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[86] W. Cameron Walker, "The Detection and Estimation of Electric Charges in the Eighteenth Century," *Annals of Science* 1 (1936): 66-100, 66.

[87] See for example, Bennet, 1787a; Cavallo, 1788a; Cavendish, 1776.

With the discovery of animal electricity and the chemical effects wrought by the passage of electrical fluid, electricians readily acknowledged the need for more consistent and precise methods of detecting and measuring weak electricity. Research into electrical detectors, however, revealed other sources of non-frictional electricity. Instrument makers discovered that the relative motion of electrified bodies and the combination of certain substances produced or intensified the presence of electrical fluid. This not only made the manufacture of reliable electrometers challenging, but also necessitated a better understanding of how non-frictional forms of electricity were made manifest.

This section focuses on physical theories of non-frictional electricity, including animal electricity. Chemical accounts are discussed in the next chapter. Since the development and debate over instrumentation was an essential component of research into non-mechanical forms of electricity, I will briefly describe some of the changes in electrical technology. I will discuss a few of the conceptual problems these instruments posed and the physics developed to explain their function. Many purported chemists also participated in this discussion. This section will conclude with an examination of how these theories were extended to apply to animal electricity.[88]

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[88] In 1980, Derek de Solla Price lamented that few histories of physics address the complex relationship between instrumentation, experiment, and conceptual development. He wrote: “It is unfortunate that so many historians of science and virtually all of the philosophers of science are born-again theoreticians instead of bench scientists.” Almost thirty years later, only a handful of histories on the study of electricity in the eighteenth century directly address the interplay between practice and theory, and the role electrical instrumentation played in changing natural philosophers’ understanding of electrical phenomena. See for example, Cohen, *1990*; Heilbron, *1999*; Home, *Electricity and Experimental Physics in 18th Century Europe*; Pancaldi, *2003*; Friedrich Steinle, "The Practice of Studying Practice: Analyzing Research Records of Ampere and Faraday," in *Reworking the Bench*, ed. Frederick L. Holmes, et al., *Archimedes* (Dordrecht: Kluwer Academic Publishers, 2003), 93-118.

2.3.1: The Study of Insulated Conductors

> If a homogeneous body be presented to the excited [or charged] tube, so as to receive electricity from it, and the electricity remain at or near the end or part presented, without being communicated to the rest of the body, it is called a non-conductor or electric. But if, on the contrary, the electricity be thus communicated to every part, the body is called a conductor, or non-electric. In the usual temperature of the atmosphere, metallic substances, charcoal, and water are conductors; most other bodies are non-conductors.
>
> A conductor cannot be electrified while it communicates with the earth, either by direct contact or by the interposition of other conductors, because the electricity is immediately conveyed away to the earth. But if a conductor be supported by an electric, so as not to communicate with the earth, it is said to be insulated.[89]
>
> William Nicholson (1787)

In order to facilitate the measurement of electrical charges, a series of detectors were designed and modified with varying degrees of success. In the mid-eighteenth century, the strength of an electrical discharge was often measured in terms of the minimum distance it would travel through air and correlated to the number of rotations of a friction machine.[90] This technique required multiple measurements of identical and often difficult to reproduce sparks in order to determine the shortest distance. Therefore, it only provided an approximate measure of the strength of an electrical discharge.[91] By experimenting with different Leyden jars, Cavendish also demonstrated that there existed forms of electricity too weak to pass through air, which could not be measured using this method.

The most common "weak electricity" detectors focused on repulsion, using the amount of divergence between two similarly charged objects as a measure of electrical

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[89] Nicholson, 1787, 302.

[90] See for example, Lane, 1767.

[91] Changes in weather, and the ability to visually witness sparks and exactly replicate the experimental conditions, often played havoc with results.

strength. For example, in 1753 John Canton, a British schoolteacher and natural philosopher who gained international recognition for showing that water was a compressible fluid, developed a prototype for many electricity detectors called a cork electrometer. This simple apparatus consisted of "two cork-balls, each about the bigness of a small pea… suspended by linen threads of eight or nine inches in length, so as to be in contact with each other." He noted, if one brought an "excited glass tube" near the cork, the spheres "separated". The closer the charged object was to the cork balls, the greater their divergence.[92]

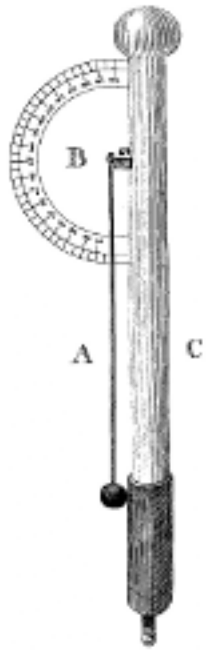

Figure 2.7: **Henly's Electrometer.**

In 1772 William Henly, a British electrician and correspondent of Priestley,[93] invented a more sophisticated version of Canton's apparatus called a graduated electrometer, depicted in Figure 2.7. It consisted of two thin, parallel rods of wood. Attached to one pole was a cork or pith ball. This rod was half the length of the other and mounted such that it was able to pivot 180 degrees relative to the longer pole. The other rod was coated at one end with brass such that, when uncharged, the pith ball rested on the metal. Touching the brass with an electrified object transferred electrical fluid to the metal and lighter pith ball. Subsequently, the ball experienced a repulsive force and was displaced a number of measurable degrees from

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[92] John Canton, "Electrical Experiments, with an Attempt to Account for Their Several Phænomena; Together with Some Observations on Thunder-Clouds," *Phil. Trans.* 48 (1754): 350-358, 350; Heilbron, 1999, 373-380.

[93] Heilbron, 1999, 451.

the brass rod. While Canton's apparatus provided visual clues as to the strength of a charged body, Henly's instrument provided a more exact angular measurement and an easier means of comparing electrified objects. It was also light, portable, inexpensive to make, and easily constructed. Subsequently, it became a standard piece of laboratory equipment with some slight modifications.

Volta recognized the importance of making the pivoting rod as light as possible so that the force of gravity would not overcome or counteract weak electrical forces.[94] Rather than using ivory or wood, as Priestley had suggested, Volta successfully made the electrometer out of straw. Furthermore, Priestley noted that this apparatus behaved more reliably if it was slightly "baked" in between experiments. Heating materials (often) increased their conductivity, making it easier for charge to be transferred out of a substance. This helped to remove any lingering or residual electricity from the detector. (As Priestley remarked, however, if too much heat was applied, parts of the detector could undergo chemical change, e.g. the metal rod might be oxidized and lose its ability to receive and transfer charges. This could potentially damage the instrument.) In spite of these adjustments, however, Henly's electrometer was still not as efficient as 'human detectors' in sensing weak electricity.[95]

Abraham Bennet was a minister whose electrical research was supported by Priestley, Erasmus Darwin, a prominent English physician and Charles Darwin's

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[94] Pancaldi, 2003, 129-137, 140-141.

[95] Priestley in William Henly, "An Account of a New Electrometer, Contrived by Mr. Henly, and of Several Electrical Experiments Made by Him, in a Letter from Joseph Priestley to Dr. Franklin," *Phil. Trans.* 62 (1772): 359-364, 360-361.

grandfather,[96] and other members of the industrious Lunar Society.[97] He invented the gold-leaf electrometer in 1787, depicted in Figure 2.8.[98] Also a modified version of Canton’s cork detector, this device “consist[ed] of two slips of leaf gold… suspended [parallel] in a glass [cylinder].”

The glass was mounted in a “foot” of “wood or metal”. Its “cap” was made of flat metal, such “that plates, books, evaporating water, or other things to be electrified, [could] be conveniently placed upon it.” The relative displacement of the leaves again stood as a measure of the strength of weak electrical fluids. Figure 2.9 illustrates some of Bennet’s experiments.

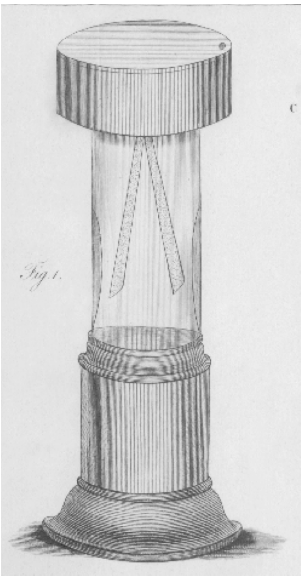

Figure 2.8: **Bennet’s gold-leaf electrometer**

Unlike Henly’s detector, which was designed to come into direct contact with an electrified object, Bennet’s device could be used in a variety of mediums, e.g. to detect the presence of electricity in gases. For instance, placing

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[96] Darwin, a physician, was interested in examining animal electricity. See Erasmus Darwin, *Zoonomia, or the Laws of Organic Life* (New York: T. & J. Swords, 1796), 73-77.

[97] Josiah Wedgwood was also interested in Bennet’s images of electricity, made by discharging a spark underneath a plate dusted with powder (iron fillings). Wedgwood hoped to transfer these figures onto cups, plates, etc., to create an interesting "natural" pattern and to capitalize on the popularity of late eighteenth-century electrical studies. Tiberius Cavallo also noted: “those impressions are very beautiful ornaments, and as such, it is not unlikely, that they may be hereafter be introduced in various manufactures.” See Cavallo, 1795, 141; Paul Elliot, "Abraham Bennet: A Provincial Electrician in Eighteenth Century England," *Notes and Records of the Royal Society* 53 (1999): 59-78, 69-70. For information on the Lunar Society see, Robert Schofield, *The Lunar Society of Birmingham: A Social History on Provincial Science and Industry in Eighteenth Century England* (Oxford: Clarendon Press, 1963); Jennifer Uglow, *The Lunar Men: Five Friends Whose Curiousity Changed the World* (New York: Farrar, Straus, and Giroux, 2002).

[98] Abraham Bennet, "Appendix to the Description of a New Electrometer," *Phil. Trans.* 77 (1787b): 32-34, 34.

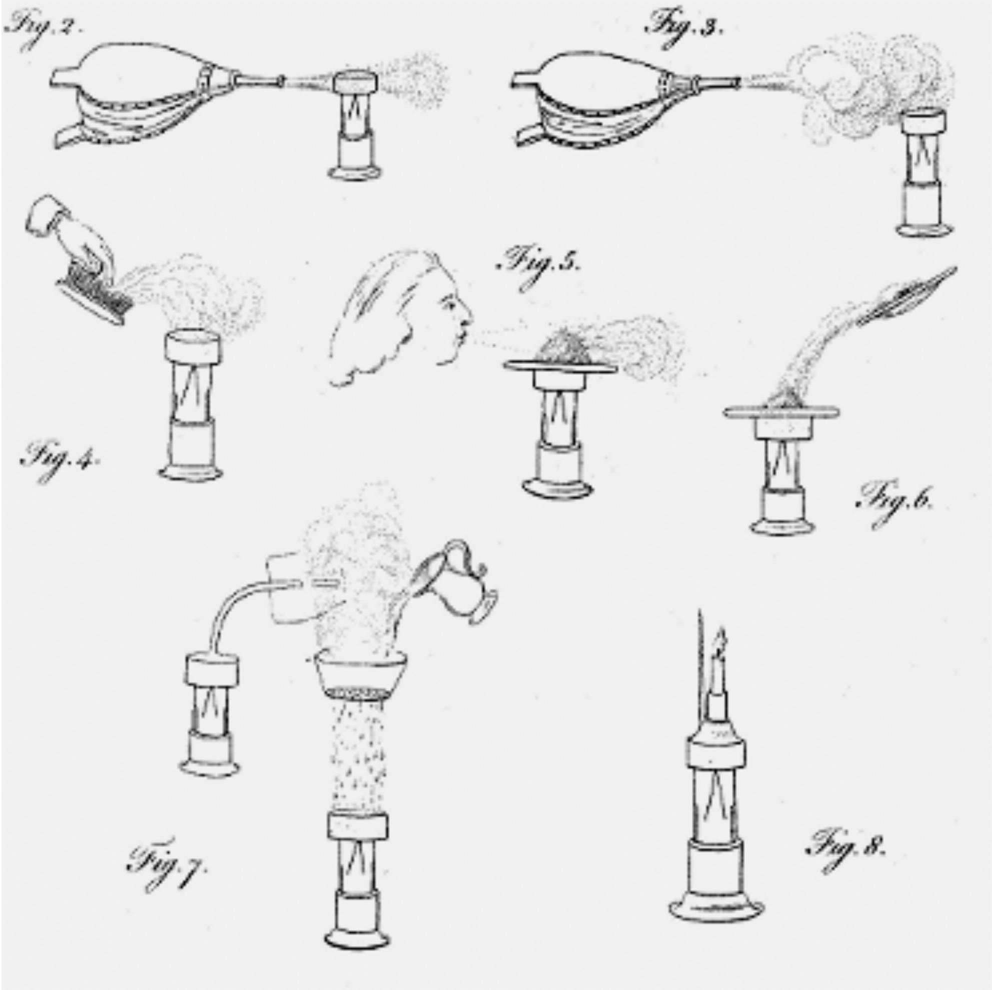

Figure 2.9: **Sketches of Bennet's experiments** that accompanied his description of his new electrometer in 1787.[99]

"powdered chalk… into a pair of bellows" and pumping it over the electrometer showed that, in the process of being compressed and expelled, the powder had been "electrified".[100] He tried "other methods of producing electricity with chalk and other powders", such as "projecting chalk from a goose wing, chalking the edges of books and clapping the book suddenly together, also sifting the powder upon the cap". He

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[99] Ibid.

[100] Bennet, 1787a, 27.

discovered that all of these methods charged the dust.[101] Moreover, he noted that "sometimes the electricity of an approaching cloud has been sensible without a kite". (Franklin proposed this method, as a way to detect atmospheric electricity, the kite siphoning electrical fluid from clouds and conveying it to ground.) Bennet observed that when a "thunder cloud pass[ed] over… the leaf gold [struck] the sides of the glass very quick at each flash of lightning." "No sensible electricity", however, was "produced by blowing pure air, projecting water, by smoke, flame, or explosions of gunpowder."[102]

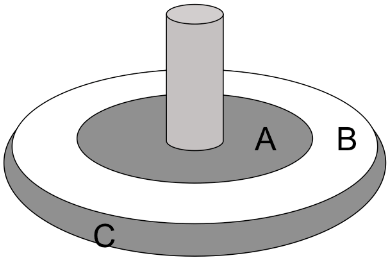

Figure 2.10: **Volta's Condenser.** A metal plate with a wooden handle, *A*, was brought to rest on an insulated conductor with a wax surface, *B*, and a metal underside, *C*.

In addition to constructing electrometers out of lighter, more responsive materials, instrument makers also devised "doublers" or "multipliers", which amplified or "intensified" weak electrical charges into a measurable amount of fluid. For example, Volta developed the condenser in 1778, depicted in Figure 2.10.[103] Its name reflected its believed function. A thin metal plate coated with resin or varnish was placed on a wooden table or insulating material. A metal plate was then placed on top, flush with the wax side of the disc. Attached to this metal plate was an insulating handle, usually made out of wood. A person then touched a weakly charged object to the metal plate while it

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[101] Ibid, 28.

[102] Ibid, 30.

[103] Volta, like Bennet, was interested in measuring atmospheric electricity and determining whether differences in electrical fluid accompanied chemical change. While on a tour of Europe in 1781-1782, he met with some of the leading figures in natural philosophy in France and England, such as Lavoisier, Laplace, Priestley, and Cavendish. While in London, Volta also presented and demonstrated the condenser to Bennet, Richard Kirwan, and Tiberius Cavallo. See, Pancaldi, 2003, chapter 5.

sat on top of the non-excited resin cake. A point conductor could also be connected to the metal disc and projected into the air, to collect or “condense” a sample of the electricity present in the atmosphere. Removing the electrified body and lifting the metal disc intensified the amount of electrical fluid on the metal until it was measurable by a standard electrometer.[104] (Cavendish also observed this effect in an unpublished manuscript, namely that separating charged plates magnified their electrical discharge.)

There were, however, difficulties with this device. Tiberius Cavallo was a well-respected experimental philosopher who consecutively gave the Royal Society’s Bakerian lectures on instruments used in the study of heat and electricity between 1780 and 1792.[105] Like many of his contemporaries, he was interested in diverse topics in medicine, chemistry, and physics. His treatise, *The Elements of Natural or Experimental Philosophy*, included, for example, a discussion of electricity and chemistry. He also wrote several popular textbooks on electrical phenomena, the medical applications of electricity, and electrical instruments, specifically comparing the accuracy of available detectors.[106] He noted that both Volta and Bennet’s devices were prone to error, often indicating the presence of an external electrical charge when there was none. This suggested that either the materials in the device contained or emitted electrical fluid. Volta admitted that extra precautions needed to be taken to ensure that his apparatus was not electrified before performing an experiment. He suggested that the thinly coated plate was especially susceptible to friction and, hence, to becoming charged. Before

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[104] Volta, 1782.

[105] For a list of Cavallo’s lectures, see http://royalsociety.org/Content.aspx?id=3436.

[106] See, for example, Cavallo, 1777a; Cavallo, 1788a; Cavallo, 1795; Cavallo, *The Elements of Natural or Experimental Philosophy*.

performing any experiments, it was necessary to remove any existing electricity within the device. Volta recommended connecting the lower disc to ground and baking it in the sun and/or bringing a candle's flame near, as Priestley had proposed. Although Cavallo acknowledged that Volta's instrument was useful, he urged caution. Even if one followed these directions, there was "frequent uncertainty" in the reliability of the results: "it [was still] difficult to say, whether in certain cases the electricity obtained comes from the instrument itself, or from the substance [being examined]".[107]

The development of "doublers" and lightweight electrometers brought to the fore two related problems that could not be ignored: why did these instruments give false readings and why did separating charged plates increase the strength of electrical fluid? It was well known that "insulating conductors", e.g. by suspending them in air (as in Bennet's electrometer) or coating them with an electric like varnish or wax (as in Volta's condenser), limited their ability to transfer electrical fluid, rendering them semi-electric. Franklin showed that electrics stored charge in proportion to their surface area, but did not permit the transfer of electrical fluid through their substance. He surmised that this property had something to do with the chemical composition of electrics. Unlike glass and wax, however, insulated conductors could hold more charge per unit surface area. Cavendish hypothesized that the material structure of metals allowed electrical fluid to settle not just along the surface of the insulated conductor, but several layers deep, interspersed amongst the particles of metal.[108] Cavallo's analysis of the exactness and

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[107] Cavallo, 1788a, 255; Cavallo, 1795, 98; Nicholson, 1788; Walker, 1936.

[108] For a discussion of the distribution of electrical matter within substances see, Cavendish, 1771, 585-595. Also, see Priestley, *HPSE 1775*, 451-457, 627-637.

distribution of measurements made by electrometers utilizing insulated conductors tentatively supported this view: the readings steadily became less reliable with prolonged use. He concluded, once an insulated conductor was electrified, it was difficult, if not impossible, to completely discharge, perhaps because of the location of remaining electrical particles within the body.[109]

To examine just "how much electric fluid was lost by [an insulated conductor] in a certain time [after having been initially exposed to a charged object]", Cavallo built a gold-leaf electrometer similar to Bennet's and electrified it, such that the angular displacement between the leaves was "16 equal parts". He then used a telescope "and by means of a micrometer measured the… angles of divergency, setting down the time elapsed between each pair of contiguous observations". Table 2.1 shows his results.

Angle	Time Between Measurements
16	0', 0"
8	1', 0"
4	3', 30"
2	17', 0"
1	75', 0"

Table 2.1: **Tiberius Cavallo's measurements of the diminution of electrical charge with respect to time in a gold-leaf electrometer.** The left hand column represents the angle of divergence, thought to be directly proportionate to electrical strength. The right hand column is the time elapsed between measured angles of divergence in units of minutes and seconds.[110]

Cavallo found that the amount or "density" of electricity within the device decreased as a non-linear function of increasing time. He noted that:

> …in repeating this experiment, the times elapsed between the corresponding observations did not follow strictly the same proportion of increase… which may be attributed in great measure to the inaccuracy in observing, and to the fluctuating [electrical] state of the air; but it could be safely inferred from all the experiments, that the times required for the dispersion of the electricity

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[109] Cavallo, 1788a, 17-18.

[110] Ibid, 19-20.

> were at least greater than the inverse duplicate proportion of the densities of the electricity remaining in the electrometer.

Assuming that the angle of leaf-displacement “continue[d] to diminish in [approximately] the same proportion of increasing time”, he calculated “that about two years after [initial electrification] the electrometer would still [conservatively] retain [at least] the hundredth part of the electricity communicated to it in the beginning of the experiment”. Given the propensity of insulated conductors (and electrics) to retain electrical fluid, how was one to distinguish between an object’s natural electricity and a body weakly electrified by an external process?[111]

As Cavallo noted, this problem was further compounded by the proximity and motion of charged objects, which affected the electrical fluid in bodies. For example, whether the source of weak electricity in the condenser was internal or external, the act of separating its plates magnified the intensity of its charge, making it detectable. Similarly, bodies with seemingly no charge suddenly became electrified when their physical position with respect to other charged objects changed. No contact was necessary. Experimenting with combinations of electrified, uncharged, electric and conducting plates, natural philosophers, like Beccaria and Volta, attempted to address this issue. Focusing on the phenomena produced by the condenser: why did separating charged plates increase the measured strength of electrical fluid?

Beccaria argued that unlike gravitational forces, which lacked a definitive material cause, electrical phenomena could be explained by the motion and action of its fluid. Like Franklin, Beccaria also thought charged particles were surrounded by an

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[111] Ibid, 20.

electrical atmosphere, capable of communicating electrical forces to other bodies through local spatial regions. He noted that electrified objects, especially electrics, had a tendency to adhere to oppositely charged bodies. More specifically, Beccaria recounted an observation made by Robert Symmer, a British physician, natural philosopher, and Fellow of the Royal Society, to illustrate this point:

> …when he put on a white silk stocking, and upon this another of black silk: he [Symmer] observed that as long as these were upon his leg, they gave, though rubbed ever so strongly, but very weak signs of electricity; when they were drawn off together, they gave hardly any; but when he afterwards drew the white stocking from the black one, most vivid signs of electricity arose…[112]

Symmer's experiments were well known to electricians and easily repeated.[113] Beccaria further experimented not only with "flexible" electrics, like socks, but also rigid electrics, such as glass and hardened wax, and metallic plate conductors. Like Symmer and, later Volta, he found that when charged plates were separated, sparks ensued. Franklin had argued that in the process of electrifying one side of an electric, its opposing surface took on the opposite charge. Building on Franklin's theory, Beccaria postulated that when two plates (or materials) of equal and opposite charge were brought together, the fluids (plus and minus) located along their adjoining surfaces were neutralized (returned to a natural state) while the charges located along their outside surfaces remained unaffected. Upon separation, the charged exterior influenced the state of the interior surface, effectively re-charging or restoring its original electrification. Beccaria referred to the charge induced

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[112] Beccaria, *Artificial Electricity*, 394-403, 395.

[113] Symmer published an account of his experiments in the *Philosophical Transactions*. See Robert Symmer, "New Experiments and Observations Concerning Electricity " *Phil. Trans.* 51 (1759): 340-393.

by a “surplus” or “deficiency” of electrical fluid in a substance no longer neutralized by contact as *vindicating* electricity.

Furthermore, he noted that the power of “adhesion” between two charged plates could be increased by manipulating the amount of electricity located on the exterior surfaces of the plates. He experimented with two different colored silk ribbons:

> Let the white ribbon be more strongly electrified by excess [plus electricity] than the black one by deficiency [minus electricity]; the ribbons in this case will indeed run to each other, but then mutually adhere with less force than if the deficiency in the black ribbon had been equal to the excess in the white one; a redundant electricity will prevail in the two united ribbons; and if the point of a needle be moved along the black ribbon, the two ribbons will after this cease to give any farther signs of electricity, the overplus of the electricity diffusing itself into this needle; and the adhesion of the ribbons will moreover encrease.”[114]

Touching one of the electrics with a conductor influenced the amount of electricity located on its outer surface. More specifically, in the above example, Beccaria argued that the electrical atmosphere of the excess fluid in the white ribbon repelled any remaining fluid in the black ribbon to its exterior. A needle (or point conductor) siphoned this electrical fluid away from the black ribbon, making it more negatively charged. This in turn strengthened the interaction between the two ribbons and, upon separation, increased the amount of vindicating electricity, evidenced by the production of (often measurable) sparks at the point of separation.[115]

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[114] Beccaria, *Artificial Electricity*, 393-403, 401-402.

[115] Beccaria also examined how electrified ribbons behaved towards plates with different charge. See Ibid, 400-403.

Volta developed a more sophisticated theory of the phenomena produced by separating electrified plates, which significantly differed from Beccaria's approach.[116] In contrast to many of his contemporaries, who believed there existed a relationship between the chemistry of a substance and the electrical effects it exhibited, Volta asserted: "mechanical forces… could explain why friction, percussion, and 'chemical motion' affected the electrical properties of a body."[117] He used the theory of Roger Boscovich, an influential Jesuit mathematician and natural philosopher, as a starting point for re-considering electricity's material dependencies.[118]

Boscovich combined Newton's concept of force with a modified version of the mechanical philosophy, advocating that matter was made of "geometrical points surrounded by… spheres of attraction and repulsion" whose motions and interactions gave rise to observable phenomena. (Mechanical philosophers promoted the idea that natural phenomena could be best accounted for by matter in motion.) He asserted that this view was compatible with Franklin's one-fluid model of electricity, since it was the "relative saturation" of a body with these particles that gave rise to electrical effects.[119]

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[116] Volta, early in his career, tried to establish a rapport with Beccaria, but their correspondence highlighted their differences in personality and scientific approach. Subsequently, Beccaria asked Volta to stop writing him letters about electricity. See Pancaldi, 2003, 89-91, 96.

[117] Ibid, 88.

[118] Ibid, 86-90. Boscovich's theories influenced many natural philosophers, including Joseph Priestley and Michael Faraday. See, for example, Frank James, "Reality or Rhetoric? Boscovichianism in Britain: The Cases of Davy, Herschel, and Faraday," in *R. J. Boscovich: Vita E Attività Scientifica - His Life and Work* (Rome: Istituto della Enciclopedia Italiana, 1993); Robert Schofield, *The Enlightenment of Joseph Priestley: A Study of His Life and Work from 1733-1773* (University Park, PA: Pennsylvania State University Press, 1997), 56-57; Schofield, 2004, 69-73.

[119] Schofield, 1997, quote on 247; Schofield, 2004, 72.

(In Franklin’s theory, electrical fluid was self-repulsive, while the corpuscles of substances were mutually attracting.)[120]

Taking this notion of “relative saturation” further, Volta argued that repulsion could be explained in terms of attractive forces alone: “…any two bodies, which are not in equilibrium [with] respect [to] their electrical status, attract each other.”[121] In an idealized form, if two small nearby bodies possessed only a tiny amount of electrical fluid, each body would experience an attractive force in the direction of the nearest charged object. They would, most likely, move away from each other, e.g. towards the walls of the container in which they were enclosed, mimicking repulsion. Furthermore, Volta postulated that: “the amount of electric fluid present in a body did not depend exclusively on properties intrinsic to each substance. It depended, more generally, on ‘mechanical forces’ determined by the internal, corpuscular texture of the body as well by its relations with surrounding bodies.” Unlike Beccaria, who asserted that the electricity located on the adjoining surfaces of two oppositely charged plates was nullified by contact, Volta argued that the charge difference was locally preserved; only to the observer did its electrification appear to disappear. Thus, within this framework, positive and negative electricity were less important than the amount and distribution of electrical particles. [122]

Returning then to the original question: why did separating two charged plates increase the strength of the emitted electrical discharge? Volta introduced the term

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[120] Pancaldi, 2003, 88-89.

[121] Ibid, 126.

[122] Ibid, 88.

capacity to refer to the amount of electricity a substance was capable of absorbing. Through the systematic study of combinations of electrified plates, he determined that capacity depended upon material composition, shape, the distance between charged objects, and their available surface area, meaning “surfaces which are free, or uninfluenced by an homologous [electrical] atmosphere”.[123] Furthermore, he was able to show that capacity was inversely proportional to electrical strength or intensity, which he defined as “the endeavour by which the electricity of an electrified body tends to escape from all the parts of it, to which tendency… especially the degree of elevation of an electrometer correspond[s]”.[124] Thus, in contrast to Beccaria, Volta made a clear distinction between the quantity of electricity and its intensity.[125]

In his 1782 letter to the Royal Society in which he formally introduced the condenser to its readership (Volta had been in England earlier that year and had personally demonstrated his device to a handful of well-known British electricians, including Bennet and Cavallo), Volta wrote:

> Take two metal rods of equal diameter, but one of them a foot, and the other five feet long; and let the first be electrified so high as that the index of [Henly’s] electrometer annexed to it may be elevated to 60°; then let this electrified rod touch the other rod, and in that case it is evident, that the intensity of the electricity, by being parted between the two rods, will be diminished in proportion as the capacity is increased so that the index of the electrometer, which before was elevated to 60°, will now fall to 10°, viz. to one-sixth of the former intensity, because now the capacity is six times greater than when the same quantity of electricity was confined to the first rod alone.[126]

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[123] Volta, 1782, xxi.

[124] Ibid, xiv-xx.

[125] Pancaldi, 2003, 112-121.

[126] Volta, 1782, xx.

Using a graduated electrometer, similar to Henly's design, Volta was able to measure changes in the intensity of electrical fluid as additional conducting surfaces were brought together. He found that if he effectively lengthened an existing charged conductor by attaching a materially identical rod, the intensity of the charge decreased in proportion to the increase in length.

Keeping the physical parameters the same, such as the type and size of material, Volta discovered that he could also affect the electrical intensity of two plates by varying the distance between them. He found that if he brought a charged plate, attached to a graduated electrometer, towards an insulated surface, such as a wooden table or a disc of resin, the angle of displacement steadily decreased. He noted, "[n]otwithstanding this appearance ['that the index of the electrometer falls gradually' as the distance between the conductor and insulator becomes smaller], the quantity of electricity in the plate remains the same". He argued: "[t]he decrease, therefore, of intensity is owing to the increased capacity of the plate." He further noted that, as he moved the plate farther away from the insulated surface, the strength of its electricity measurably increased. Similarly, Volta argued that as the charged plate was moved farther away from the insulated surface, its capacity decreased and a corresponding increase in electrical intensity was measured.[127]

How did proximity to other bodies affect capacity and, hence, the intensity of electricity? Volta asserted that "the reason of this phenomenon" was owing to "the action of electric atmospheres", which altered the capacity of the system, affecting the

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[127] Ibid, xxi-xxii.

absorption and distribution of electricity without contact. He suggested that "the parts [of the table or disc] immersed into the sphere of action of the electrified metal plate, contract[ed] a contrary electricity", which he referred to as *accidental* electricity, "so that the electric fluid of the table, agreeably to known laws, retir[ed] to the remoter parts of it, becom[ing] rare in those parts which are exposed to the metal plate, and this rarefaction becomes greater the nearer the electrified metal plate is brought to the table." This *accidental* electricity "compensat[ed] for the *real* electricity of the metal plate, [and] diminish[ed] its intensity, as is shewn by the depression of the electrometer."[128]

To further clarify and distinguish his theory from others, Volta adopted the terms *tension* and *actuation* to help explain the action of electrical atmospheres, both real and accidental.[129] Actuation referred to the ability of electrical fluid to project a "sphere of activity" or influence over neighboring charged bodies. The amount of electricity present in an object was defined as "the sum of all the electricities contained in all the points making up the surface of the electrified body." Tension referred to "the force exercised by each one of these points, in order to get itself rid of the electricity it enjoys, and to reestablish its equilibrium". Thus, tension was directly related to intensity and dependent upon both capacity and actuation.[130]

As Guiliano Pancaldi notes in his masterful biography of Volta: "[h]e [Volta] summarized it by saying that any electrified conductor brought close to another [non-

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[128] Alessandro Volta, "Del Modo Di Render Sensibilissima La Piu Debole Elettricita Sia Naturale, Sia Artificiale," *Philosophical Transactions* 72 (1782): 237-xxxiii, xxii.

[129] Beccaria was the first to use this terminology, but as Pancaldi notes, he referred to the material propagation of electric forces through electrical atmospheres whereas Volta was moving away from a strictly materialist interpretation.

[130] Pancaldi, 2003, 128-129.

electrified] conductor ‘actuates’ the latter, that is, it increases its tension [as the external force emanating from the electrified body affected the natural electrical balance of the conductor] and [produced] ‘accidental’… electricity [redistributing the electrical fluid within the conductor], limiting [the conductor’s] ability to acquire additional tension and reducing its capacity.”[131] Volta represented this relationship mathematically: $Q = C\ T$; or in other words, the amount of electricity present on the surface of an object, denoted Q, was limited by its ability to absorb electricity (its capacity, C), and the cumulative forces, both internal and external, acting on its electrical particles (tension or intensity, T).[132] If the surface of a conductor was already saturated with electricity, whether real or accidental (e.g. induced by the presence of another charged body), it could not take on additional charge. If the amount of electricity was fixed within a substance, a decrease in its capacity (whether real or accidental), therefore, caused a measurable increase in the tension or intensity in its electrical fluid, manifest by the degree of the fluid’s ability to repel, attract, or produce discharges.

Returning then to the condenser: a metal plate was placed on an insulated conductor, charged, and then lifted. Within this framework, the metal plate had more capacity for electrical fluid because of the insulated conductor. The insulated conductor allowed electrical fluid to gather along its surface and that of the metal plate, enlarging the area available for collecting charge. Electrifying the metal plate and then lifting it away from the insulated surface reduced its capacity. Subsequently, the charge it retained upon separation experienced a measurable increase in tension or intensity.

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[131] Ibid, 118.

[132] Ibid, 128.

Electricians readily used Volta's experimental findings, such as the effect of capacity on measured electrical strength, but did not adopt his theory in full. Many scientists, such as Cavendish, Aepinus, and Beccaria, subscribed to the view that electricity was a fluid, "the particles of which repel each other and attract the particles of all other matter".[133] Those who adopted a two-fluid model also promoted the idea that electricity possessed both the properties of repulsion and attraction: they were equally real effects. Volta, by adopting the position that attractive forces alone could account for repulsion, took an unorthodox stance.[134]

Volta's theory also had a level of abstraction that many of his contemporaries found difficult to follow. Volta himself struggled to communicate his ideas, for many of his concepts, like tension, had no simple analog within the existing terminology.[135] Many eighteenth-century electricians believed that what an electrometer like Henly's measured was the density of electrical fluid present on the surface a charged object: the more charged particles per unit area, the more spectacular the observed electrical effects. Although electricians, like Beccaria and Cavallo, discussed electrical "strength" and "intensity", it was assumed to correlate to quantity.[136] In contrast, Volta's theory implied that an identical number of charged particles could have markedly different "strengths".

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[133] Beccaria, *Artificial Electricity*; Cavendish, 1771, 585; Roderick Home, "Aepinus and the British Electricians: The Dissemination of a Scientific Theory," *Isis* 63 (1972): 190-204.

[134] Two fluid theorists included: Galvani, Nollet, and Coulomb. See. Galvani, 1953, Introduction; Heilbron, 1979, 431-448; Home, 1979.

[135] Pancaldi, 2003, 108-109.

[136] See, for example, Beccaria, *Artificial Electricity*, 232-233; Cavallo, 1795, vol. 1, 242-243. Beccaria argued that the cross-sectional area of a spark reflected the number of charged particles, while the length of the discharge correlated to its density or strength.

What one measured then was not necessarily the amount of electricity, but rather the result of a network of electrical forces.[137]

Whether electrometers measured electrical density or tension, scientists were most concerned with the properties they had discovered by studying the electrical effects of combining materials. The development and analysis of instruments renewed interest in understanding how substances affected the distribution and behavior of electricity. Cavallo's research into the reliability of electrometers showed that charged insulated conductors and electrics retained electrical fluid for significantly long periods. This affected the consistency and precision of electrical detectors. Volta's experiments demonstrated that physical parameters, such as surface area and distance to other charged bodies, also affected an object's measured electricity. As research into electrometers and their material make-up became more sophisticated, new instruments were developed, which generated electricity without friction. These devices helped to frame the discourse on animal electricity and forced electricians to reconsider electricity's origins.

2.3.2: From Detectors to Generators, the Growth of Material Science

> We know, for instance, that a piece of glass, or other electric, when rubbed will produce that power which we call electricity, that the glass will communicate the acquired electricity to a piece of metal, that the piece of metal will retain that power in certain circumstances, and so on; but no person has shewn how that power is generated by the friction, or what prevents its passage through the substance of some particular bodies. It has been ascertained, that the air of most countries, and probably the whole world, as well as the clouds, fogs, rain, &c. are almost always electrified; but we are ignorant of the office which this electricity can have in the great laboratory of nature; for surely so general and so active a power can hardly

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[137] Priestley adopted a similar view in 1769, suggesting that there was a difference between the amount of electricity and "how high a phial is charged, or the exact force of the charge while it is contained in the glass." See Priestley, HPSE 1769, 129.

> be intended by nature, merely to intimidate mankind now and then with the thunder and the lightning. It appears, therefore, that [we] ought to examine the electrical power not so much in its accumulated, as in its incipient state. Its first origin, or very beginning, ought to be investigated…[138]
>
> Tiberius Cavallo (1788)

As discussed in section 2.2, the torpedo ray's abilities left natural philosophers, chemists, and physicians in a quandary. Did the fish emit electricity? If so, how? Was animal electricity, or galvanism, identical to friction-based electricity? These issues of identity and origin took on additional significance in the late eighteenth and early nineteenth centuries as other types of non-frictional electricity were discovered.

Research into the behavior of various combinations of metal plates and electrics indicated that friction was not the only means of generating electricity. In addition to constructing electrometers and multipliers, electricians found that they could generate electricity using insulated conductors. I will briefly discuss two of these instruments: the electrophorus, conceived of in 1762 by Johan Carl Wilcke, a Swedish experimental philosopher, and popularized by Volta in 1775, and the revolving doubler, created by William Nicholson in 1788. The electrical behavior of these two devices suggested a different model for the torpedo's electrical organ, one grounded in the physics of (insulated) conductors.[139]

Priestley reported on Wilcke's electrical experiments in *History and Present State of Electricity* in 1767. Wilcke was a member and later secretary of the Royal Swedish

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[138] Cavallo, 1788a, 3.

[139] William Henly, "Experiments and Observations on a New Apparatus Called a Machine for Exhibiting Perpetual Electricity," *Phil. Trans.* 66 (1776): 513-522; Nicholson, 1788. For a discussion of Volta's intellectual debt and subsequent priority dispute with Wilcke over the electrophorus, see Pancaldi, 2003, chapter 4, especially 75-112.

Academy of Sciences, an institution that supported research and education initiatives in all branches of natural philosophy, including chemistry, and promoted international discourse through active correspondence with members of other scientific organizations, such as the Royal Society and the Academy of Sciences in France.[140] In this tradition, Wilcke and Priestley exchanged many letters about Wilcke's experiments examining the behavior of "contrary electricities".

In 1762, Wilcke postulated that electrified resin and metal could be used in conjunction to generate electricity, after observing that a conductor coated with molten wax emitted sparks.[141] In 1775, Volta published his own account of a device called the electrophorus, which demonstrated this remarkable phenomenon. The resulting priority dispute, over the originality of the instrument, was one of many throughout Volta's career. Regardless of its novelty, Volta's widely read account of the electrophorus earned him widespread recognition.[142]

Like the condenser, the electrophorus (or "perpetual electricity" machine) consisted of an insulated conductor, mounted wax-side up on a table, and a moveable metal plate. Volta first rubbed the resin with fur or a brush. The metal disc was then placed on top of the waxed surface, becoming charged. Lifting the metal disc by its insulating handle and bringing it near a pointed conductor produced a visible spark, as electrical fluid traveled from the metal plate to the uncharged body. Merely retouching the metal to the insulated conductor, however, restored its charge. It was not clear why

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[140] http://www.kva.se/en/About-the-academy/History/

[141] Priestley, HPSE 1775, 218-221.

[142] Henly, 1776; Pancaldi, 2003, 73-109.

this simple device consistently produced electricity with only minimal applications of friction to the resin. Where did the excess electrical fluid come from?[143]

The electrophorus was not theoretically well understood until the mid-nineteenth century.[144] In the late eighteenth century, it was known that friction machines utilizing an electric and a conductor produced more electricity than other designs, e.g. by rubbing a wax cylinder with a metal brush. Franklin argued that this contributed to Nature's efficient generation of lighting: water vapor (a conductor) interacted with salt and air (an electric) to produce electricity.[145] In the 1780s, research into electrometers further demonstrated that insulated conductors retained electrical fluid for significant periods of time, that the proximity and capacity of charged bodies affected the measured electricity, and that small amounts of electrical fluid were exchanged between bodies, e.g. between the metallic layer in an insulated conductor and the atmosphere. These observations suggested to Volta that metals might play a more dynamic role in electrical generation than previously thought. An instrument created by William Nicholson gave further credence to this idea.

Let me take a moment to properly introduce Nicholson, one of the least discussed yet remarkably influential British natural philosophers and chemists in this period. Unlike Cavendish, who had a substantial legacy, or Volta, who participated in a well-established

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[143] William Henly, "Observations and Experiments Tending to Confirm Dr. Ingenhousz's Theory of the Electrophorus, and to Shew the Impermeability of Glass to Electric Fluid," *Phil. Trans.* 68 (1778): 1049-1055; John Ingenhousz, "Electrical Experiments, to Explain How Far the Phenomena of the Electrophorus may be Accounted for by Dr. Franklin's Theory of Positive and Negative Electricity," *Phil. Trans.* 68 (1778): 1027-1048; Walker, 1936, 81-84.

[144] For a discussion of induction, see Michael Faraday, *Experimental Researches in Electricity* (2009).

[145] Franklin, 1751, 36-49.

patronage system, Nicholson was a self-made man and entrepreneur. Jane Austen, in *Persuasion*, described the social and financial mobility afforded by British expansion and conflict. Nicholson was very much a product of this era.

He began his career overseas in the employ of the East India Company and later worked in Holland for Josiah Wedgwood, the prominent English potter and philanthropist. When Nicholson returned to England, he used his savings to publish and conduct electrical and chemical research. He translated several French works on chemistry, including *Elements of Natural History and Chemistry* by Antoine Francois Fourcroy, an important French chemist who assisted Lavoisier in the development of a new chemical nomenclature. Nicholson also edited and published benchmark British texts, such as Richard Kirwan's *An Essay on Phlogiston* in 1787, along with a translation of Lavoisier's annotated rebuttal of Kirwan's theory in 1789. This latter publication was significant as it marked a turning point in the debate between phlogistonists and oxygen-theorists. Kirwan, persuaded by the anti-phlogistic argument, publicly recanted his defense of phlogiston and accepted the existence of oxygen and caloric.[146]

Nicholson also financed, edited, and contributed to the monthly *Journal of Natural Philosophy, Chemistry and the Arts* from 1797 to 1813. Nicholson's journal, as it was commonly called, was the first popular science periodical of its kind. Nicholson, who was never inducted into the Royal Society, allowed anyone willing and able to pay the monthly fee of "two shillings and sixpence" to subscribe to the journal. It served as a

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[146] Akeroyd, 2003; Boantza, 2008; Antoine-François Fourcroy, *Elements of Natural History and Chemistry*, trans. William Nicholson (Edinburgh: printed for C. Elliot and T. Kay 1790); Holmes, 2000; Kirwan, *Essay on Phlogiston*; Thomas Thomson, *The History of Chemistry* (London: Henry Colburn and Richard Bentley, 1830), 138-139.

clearinghouse for scientific knowledge, making many previously inaccessible articles available in Britain to a diverse readership.

As a practicing and knowledgeable natural philosopher and chemist, Nicholson guided the content of the journal. It contained papers by amateur and professional, British and foreign chemists, electricians, and natural philosophers as well as re-prints of essays read at the Royal Society and the French Academy of Sciences on themes of contemporary importance. It covered an assortment of topics, including, but not limited to: electricity, the discovery of chemical elements, meteorological instruments and experiments, research on light (optics) and magnetism, and essays on natural history (especially geology and mineralogy). Of particular relevance to this dissertation, the first papers on the chemical effects of the pile also appeared in his journal.

Through his publication initiatives, Nicholson helped shape the intellectual landscape of British science. Unfortunately, by the early nineteenth century, these initiatives were also at the root of his social decline and deteriorating health. Nicholson could not make his journal profitable. To increase circulation, he had to either modify the content, making it less technical and more appealing to a broader audience, or make it more expensive. He was unwilling to compromise on either price or content.

To support his growing number of scientific publications, Nicholson over-extended his resources in a series of unfortunate and unsuccessful ventures, e.g. by financing water works projects just as railways were gaining currency in Britain, buying patents for promising inventions that turned out not to be commercially viable, and producing other expensive publications with small readership, such as the six-volume

British Cyclopaedia of Natural History. In short, he had poor business sense. He lacked the financial management skills needed to keep his businesses in good stead. In 1813, he was forced to declare bankruptcy and spend time in debtor's prison, his reputation sullied. Overcome by poverty and illness, he sold his journal to rival editor and entrepreneur, Alexander Tilloch of the *Philosophical Magazine* and, following Nicholson's death in 1815, the two periodicals were merged into the *Philosophical Magazine and Journal*.[147]

Although Nicholson died in obscurity, his contributions to science were numerous and noteworthy. While his editorial and publishing responsibilities occupied more and more of his time in later years, his early forays into natural philosophy included novel observations and research in electricity and chemistry.[148]

Like many of his contemporaries, Nicholson was particularly concerned with the relationship between thermal and electrical phenomena, and substance. For example, in 1787, he suggested a more nuanced definition of conductivity, noting the effects temperature had on the transfer of electricity. In 1770, Priestley had demonstrated that charcoal, generally thought to be an electric, became a conductor after heating. In 1782, Volta showed that "the escape of vapor or elastic fluid from bodies in a state of combustion, from water thrown on hot coals, or from chemical menstrua in a state of effervescence, leaves the residue negatively electrified." These experiments suggested

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[147] Henry Carrington Bolton, *A Catalogue of Scientific and Technical Periodicals (1662 to 1882)* (Washington, DC: Smithsonian Institution, 1885), 445; Lilley, "Nicholson's Journal (1797-1813)."

[148] See, for example, Golinski, *Science as Public Culture: Chemistry and Enlightenment in Britain, 1760-1820*, 129-152, 141-144; Sudduth, 1980.

that electricity and heat were intimately connected.[149] Extending Priestley's original experiments, Nicholson systematically studied how the electrical properties of materials changed with temperature.[150] He found that:

> …whatever the conducting power may depend on, it seems to be governed by the heat of the body: glass, resin, baked wood, air, and many other non-conductors, are conductors when made very hot; and, on the contrary, ice cooled to 13° below 0, on Fahrenheit's scale, becomes a non-conductor, or electric body. There is therefore some ground to conjecture that the disposition to conduct electricity is produced in metals by a very low degree of heat, in water by a greater, and in resins and glass by degrees still greater; or generally that there is a certain degree of heat at which a given body may be at the medium between perfect conducting, and non-conducting, above which degree it becomes a conductor, and beneath, a non-conductor. If this be true, it will follow, that conductors are bodies whose electric or non-conducting state is placed at a temperature far below that which is usual in the atmosphere, and that non-conductors are those whose conducting state is placed at a degree of heat far above the mean temperature.

Nicholson's research demonstrated that a substance's ability to conduct electricity depended, in part, upon the temperature of the material. Metals were conductors at room temperature, while traditional electrics, such as glass and wax, became conductive near their melting point. This suggested that all substances possessed the ability to be a conductor in a specific temperature range and an electric in another.[151]

Nicholson, like many of his colleagues, found his experiments hampered by his inability to detect and measure weak electricity. In order to determine the efficacy of

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[149] Nicholson noted that "[t]he [heat] capacities not only differ in various bodies, but also in the same body, accordingly as it is either a solid, fluid, or vaporous state. All the experiments hitherto made conspire to shew, that the capacity, and consequently the specific heat, is greatest in the vaporous, less, in the fluid, and least in the solid state." Similarly, the amount of electricity in a body also varied with temperature. He suggested that "these important facts seem to point at a general law of electricity, that may tend in future to explain the phenomena in which heat is latent, and to which it bears a striking analogy. It appears to be a fair deduction from these facts, that as bodies take up electricity when they assume an elastic form, so they must deposit it when they are again condensed." See Nicholson, 1787, Vol. 2, 117, 345-346.

[150] Ibid, Vol. 2, 301-306; Priestley, 1770.

[151] Nicholson, 1787, Vol.2, 301-316, quote on 303-304.

conductors at different temperatures, it was necessary to be able to measure minute differences in the amount of conducted charge. Having read Cavallo's analysis of available electrometers and his concerns about their accuracy, Nicholson devised a new multiplier.[153]

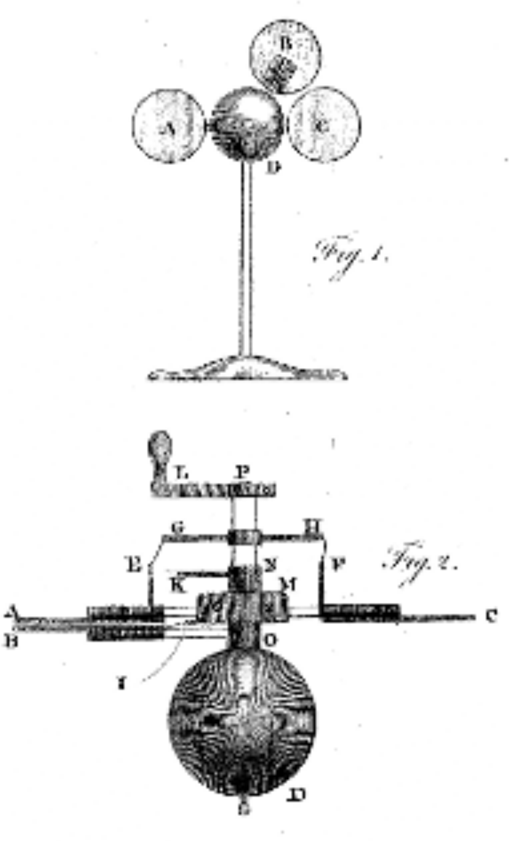

Figure 2.11: **Nicholson's Doubler**[152]

In 1788, he wrote to Joseph Banks, President of the Royal Society, announcing his invention of the "revolving doubler", depicted in Figure 2.11. Unlike Volta and Bennet's instruments, which relied on the contact and separation of plates, Nicholson's device "produce[d] the two states of electricity without friction or communication with the Earth" by rotating conductors. It consisted of three brass plates, mounted about a central axis above a concentric brass sphere. Two plates, *A* and *C*, were fixed opposite each other in the same plane. The third plate, located slightly below the fixed plane and labeled *B*, could be rotated about the central axis by a hand crank. As it rotated, it passed beneath discs *A* and *C* producing a spark or, if either *A* or *C* were already charged, magnified the existing charge.[154]

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[152] Ibid, 406.

[153] Nicholson, 1788.

[154] Nicholson, 1788, 403.

Cavallo and Volta were not surprised that changing the distance between charged conductors in the instrument affected its measured electricity. This was a well-known phenomenon. It was, however, more difficult to explain why the motion of uncharged plates produced sparks. Volta was personally delighted with Nicholson's device because it demonstrated a principle he had long postulated: metals contained electricity.[155]

Franklin defined conductors as transmitters of charge, materials capable of instantaneously communicating electrical fluid from areas of high concentration to low. Cavallo's research demonstrated that insulated conductors retained electrical fluid for long periods of time. Subsequent study showed that insulated conductors lost electricity faster than electrics. It was thought that this difference was due to the presence of metal in the insulated conductor: metals easily transferred electrical fluid to other bodies, including air. Although air was an electric, it was not a perfect insulator. It was well known that if a body possessed electrical fluid of sufficient strength, its charge could jump through the gas to a neighboring, lesser-charged object. Thus, air possessed the ability to both store and, under certain conditions, to transfer charge. This transfer was often accompanied by chemical change. Volta's analysis further indicated that metals were able to reciprocally collect charge from neighboring electrics, like air, if the conductor was not in direct contact with the earth. If the metal was connected to ground, either directly or via other conducting bodies, it immediately transferred its charge to the earth, which acted as a large electrical sink. This suggested two possible sources of electrical fluid within Nicholson's apparatus: either the metals themselves intrinsically

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[155] Pancaldi, 2003, 179-186.

contained electrical fluid or the metal plates collected and condensed electrical fluid from the atmosphere.

Regardless of how electrical fluid came to reside in the disks, natural philosophers agreed there had to be weak electricity present in the device. This was a key point for both Cavallo and Volta. It suggested that all bodies not in contact with the earth, including conductors, were electrified to some degree.

Cavallo asserted that his experiments, supported by "a great number of instances… related in books on the subject of electricity, and in the *Philosophical Transactions*, of pieces of glass, of sulphur, of sealing-wax, &c. having remained electrified so far as to affect an electrometer for months after they had been excited, or even touched", demonstrated the importance and persistence of weak electricity. He noted, "what is called [a] small difference of the proportionate distribution [of electrical fluid], insomuch as it does not affect our instruments, may be sufficient for several operations of nature". In other words, undetectable disparities in the distribution of electrical fluid could be responsible for measurable effects, the most plausible explanation for the behavior of Nicholson's doubler. Changing the distances between its plates would enhance the presence of even a small amount of electrical fluid.[156]

Cavallo argued it was paramount that natural philosophers develop a better understanding of the origins of weak electricity. He suggested that the slightest friction likely caused these tiny charge differences, not normally detectable by standard instrumentation. He wrote:

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[156] Cavallo, 1788a, 18; Cavallo, 1795, 83-85, 98.

> If it be asked, what power communicates the electricity, or originally disturbs the equilibrium of the natural quantity of electric fluid in the various bodies of the universe; we may answer, that the fluctuating electric state of the air, the passage of electrified clouds, the evaporation and condensation of fluids, and the friction arising from diverse causes, are perpetually acting upon the electric fluid of all bodies, so as either to increase or diminish it, and that to a more considerable degree than is generally imagined.

Cavallo contended that if friction could cause large-scale electrical effects such as lightning, it was plausibly also responsible for weak electrical effects.[157]

Volta, on the other hand, developed a broader theoretical account, spurred on by Galvani's claims to have discovered a new form of electrical fluid: animal electricity or, as it became more commonly called, galvanism. Volta, like many of his contemporaries, supported a Franklinist interpretation of electricity. There existed one fluid, whose presence, motion, and associated electrical forces were responsible for all observed electrical effects. It was difficult, however, to reconcile this position with animal electricity. Galvani's experiments reaffirmed the well-known fact that friction-based electricity caused muscle spasms, but also showed that living organisms possessed their own intrinsic charge. Volta did not deny that electricity affected the muscular motion of animals. He did, however, object to Galvani's proposed source of electricity and used Nicholson's doubler to help demonstrate his theory.

Volta's experience with insulated conductors and weak electrical phenomena suggested that friction was not the only means of affecting electricity. Volta agreed with Cavallo that friction was an important motive force, affecting the flow and distribution of electrical fluid, but argued that other types of forces needed to be taken into consideration

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[157] Friction, the enemy of all electrical instrument makers, required special handling. Cavallo, 1788a, 21.

as well. For example, he considered the effects of percussion and, as discussed in the previous section, actuation and tension. Nicholson's device demonstrated that metals were (weakly) electrified. Volta asserted that it should be possible to set their fluid in motion in a variety of ways, e.g. by varying the distance between plates, as evidenced by Nicholson's doubler, or tapping the two metals together. To give an analogy, imagine that two buckets filled with water were traveling at a constant speed towards each other. When the buckets collided, the water within them would spill. Similarly, Volta postulated that the force of contact between two metals containing electrical fluid might set their charge in motion, emitting a detectable discharge. Furthermore, as experiments on the behavior of insulated conducting plates demonstrated, the presence of small amounts of electrical fluid could cause macroscopic effects, perhaps even Galvani's purported animal electricity.

Volta was particularly concerned with Galvani's apparatus: animal electricity was most pronounced if the tissue was mounted between two different kinds of metals. Volta asserted that this could not be a coincidence. He began to examine the electromotive capacities of materials, ranking substances according to their ability to produce sparks via contact and to conduct electrical fluid. Although he could not explain why conductors affected the movement of electrical fluid to different degrees, this did not invalidate the phenomenon. As with his other studies, Volta analyzed how the combination and proximity of different materials, including wet conductors, affected the measured electricity. He found that electrical discharges were most easily detected when two different metals, far apart on his scale, were struck together, i.e. a perfect with an imperfect conductor.[158]

It is interesting to note that Cavendish had started a similar line of inquiry in the 1770s, only to abandon it to pursue the study of other weak forces, such as gravity, and the chemistry of atmospheric gases.[159] Like Volta, he recognized that the categories – conductor and electric – did not allow for variations in the ability of substances to collect and transmit charge. Cavendish, because of his interest in the torpedo ray and, more generally, chemistry, was especially concerned with the conductive properties of liquids, such as salt water and oil of vitriol (sulphuric acid).[160] Using what Pancaldi has referred to as a "midrange concept", a measurable property whose cause was not yet understood,[161] Cavendish attempted to quantify "resistance", defined as "the whole force which resists [the flow of electricity]". Unlike many of his contemporaries, who associated electrical strength with density, Cavendish correlated it to velocity. Electrical strength was, thus, a measure of the change in velocity experienced by electrical fluid as it traveled through different media.[162]

Volta, who was familiar with Cavendish's research, appropriated this idea of resistance to further his developing theory of metallic electricity.[163] He argued that the "[c]ontact of different metals could set electric fluid in motion inside them because

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[158] Pancaldi, 2003, 178-210.

[159] Cavendish, 1771; Cavendish, 1784a; Cavendish, 1785; Cavendish, 1798.

[160] Cavendish, 1967, 359-361.

[161] Although Pancaldi developed this idea to help explain Volta's process of experimentation, I think it also applies to Cavendish in this context. See, Pancaldi, 2003, 112-121.

[162] Cavendish, 1967, lix-lxii.

[163] Heilbron, 1999, 478; Pancaldi, 2003, 120-121.

conductors opposed very little 'resistance' to its motion." Furthermore, once electrical fluid began to flow, it was subject to known physics and, more specifically, Newton's first law – an object in motion tends to stay in motion.[164]

Armed with these three key points: that metals were electrified, that the contact of two dissimilar metals produced sparks, and that Galvani's experiments relied on the use of two different metals, Volta publicly challenged Galvani's theory of animal electricity. He contended that Galvani had erred. He had misinterpreted the effects of his apparatus for that of the animal.[165]

2.3.3: The Invention of the Pile

> …we know nothing more of the nature of *substance*, than that it is something which supports *properties*, which properties may be whatever we please, provided they be not inconsistent with each other...[166]
>
> Joseph Priestley (1772)

Volta, over the course of three decades, came to view the production of electricity as a process related to the force of contact between two dissimilar metals. He noted that Galvani's experiments utilized one metal contact, attached to a nerve, and a second, different metal, attached to its muscle. These two metals were then made to touch, closing the circuit. Although Galvani experimented with different conductors to connect the nerve and muscle, he did not attach any particular significance to the metals. While he argued that the different conductors facilitated the transmission of the animal's electrical

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[164] Pancaldi, 2003, 185.

[165] Kipnis, 1987 provides an overview of the debate between Volta and Galvani, and the reception of Galvani's experiments in the medical community more generally.

[166] Joseph Priestley, *History and Present State of Discoveries Relating to Vision, Light, and Colours* (London: J. Johnson, 1772b), 393.

fluid, Volta argued that the metals played a greater role in Galvani's results than Galvani recognized. Volta asserted that his research showed that bringing two different metals together created tension between their charged particles, and at the moment of contact actively imparted a percussive force to the electrical fluid in the metal containing the most electricity. This effectively pushed the fluid out, setting the charge in motion. Furthermore, he contended that this movement was observable, as light, sound, and/or muscle contraction were produced.[167]

There were, however, both practical and conceptual problems with Volta's theory. I will discuss the experimental difficulties first and then briefly address some of the theoretical issues. Electricians struggled to detect sparks from percussion. Experiments investigating the contact of two metals and their associated electricity were equivocal. In 1795, "after many fruitless attempts", Cavallo reported that he had finally detected an electrical discharge, but the origins of the measured electricity were in question as "the air seems to be in a great measure concerned in those experiments, and perhaps the whole effects may be produced by that surrounding medium." Cavallo elaborated on his experiments with significant results.[168]

He "fastened" a tin plate, eight inches in diameter, "to a small piece of wood about three inches in length." He then attached the wood to "two glass sticks covered with sealing-wax". These were then "cemented into a larger piece of wood, which forms the stand or basis of this instrument." Standing next to the platform, he dropped the same

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[167] The most comprehensive overview of the debate between Galvani and Volta remains Pera, 1992. See also, Bresadola, 2008; Kipnis, 1987.

[168] Cavallo, 1795, 111.

metal ten times in succession onto the tin plate from a height of approximately three inches. Lifting the plate by its wooden supports, he touched the edge of the tin to a multiplier of his own design. He then recorded the number of multiplications, described below, and measured, where possible, the strength of the electricity with a cork-ball electrometer.[169]

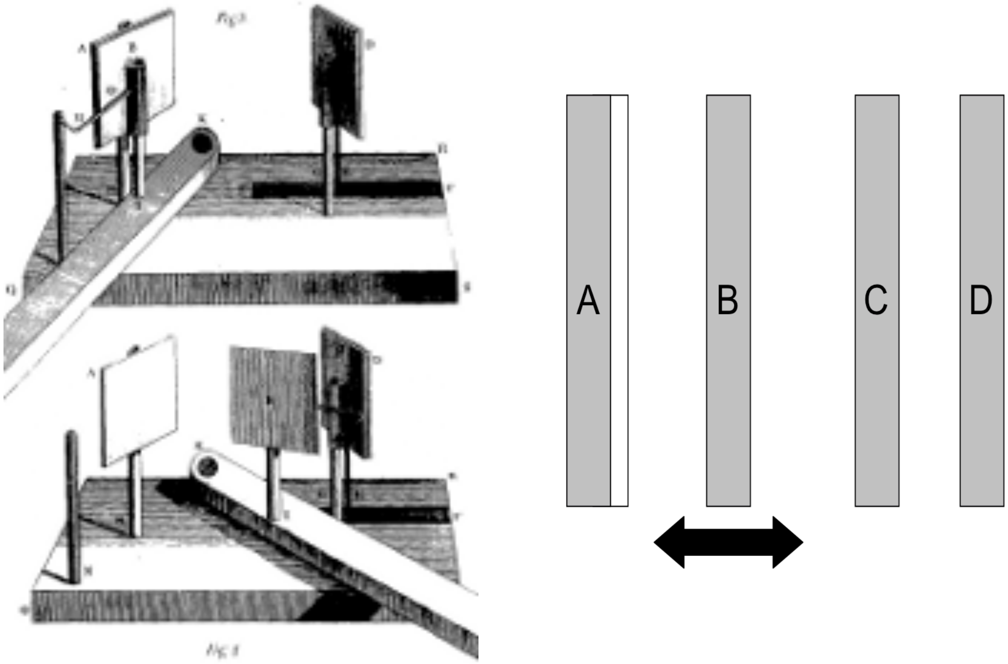

Figure 2.12: **Cavallo's multiplier (1795).** The right hand image shows a simplified schematic of his device.[170]

As discussed in section 2.2.1, multipliers were used to magnify existing electrical fluid into measurable charge. Cavallo's analysis of the reliability of electrometers had shown that most doublers were suspect, often indicating the presence of electricity when there was no external source. Cavallo attempted to circumvent this problem by designing an instrument seeded with a fixed amount of charge. This device is depicted in Figure

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[169] Ibid, 113-114.

[170] Cavallo, 1795, 305.

2.12. Using the schematic as guide, it consisted of: an insulated conductor, *A*; a moveable metal plate, *B*; a second fixed, metal disc, *C*, behind which was mounted a parallel, moveable plate, *D*. *A* and *B* behaved together like an electrophorus. Touching a charged body to *A* electrified the insulated conductor. By means of a lever, *B* was brought into direct contact with *A* and received a small amount of the insulated conductor's electrical fluid. Plate *B* was then moved, again by lever, to *C*. Plate *C* had a large capacity for electrical fluid because of the proximity of *D*. Consequently, *C* acted like "a kind of reservoir, into which the successive charges of the plate *B* [could be] collected." *B* could, thus, be moved back and forth, transferring charge from *A* to *C*. After several "additions" or "multiplications" of electrical fluid, Cavallo would then remove plate *D*. As he noted, this reduced the capacity of plate *C*, increasing the strength of its electrical fluid to a (hopefully) measurable state.[171]

Cavallo argued this was a more stable configuration than Nicholson's doubler. In the doubler, changing the capacity of the metal plates by altering the distance between them magnified charge. Insulated metals, however, were notorious for collecting unwanted electricity. The amount (or tension) of electrical fluid at any given time on the plates was in flux. Small fluctuations in charge were amplified, sometimes masking the original source of weak electricity. Cavallo contended that it made more sense to fix a sample of the electrical fluid under investigation on the insulated conductor, and use that electricity as the source of charge. He also advocated minimizing the motion of any

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[171] Ibid, 98-104.

conducting surfaces, as friction between metal and air could weakly electrify the detector. This would limit other potential sources of error.[172]

Returning then to the experiment: Cavallo took “a piece of zinc, which weighed little more than half an ounce” and “dropped” it “ten times successively upon an insulated tin plate.” He then touched the tin plate to the multiplier. He found that after “ten additions of electricity, the plate *C* communicated to the electrometer a sufficiently sensible quantity of positive electricity, which shews that the tin plate had been electrified negatively by the contact of the zinc.” The zinc, therefore, had been charged positively. He repeated this experiment “four times within the space of half an hour” and got the same result. “[O]n the following day”, however, using the same apparatus, “the effect was found to be less conspicuous, for three times twenty additions just enabled plate *C* to communicate a sensible degree of positive electricity to the electrometer.” As Cavallo noted, this suggested that the electrical state of the atmosphere had some influence on the measured electricity.[173]

In order to clarify the source of electricity, whether it came from the contact of metals or the atmosphere, Cavallo repeated this experiment many times, on different days, and with a variety of substances. His results are summarized in Table 2.2. He made three important observations on the electricity emitted by the contact of metals.[174]

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[172] Ibid, 105-107.

[173] Ibid, 113.

[174] Table 2.2 was based on the trials Cavallo described and documented in Ibid, 111-139.

Resting Plate	Striking Material	Trial	Weight	Temp.	# of Additions	Electricity	
						Type	Strength
Tin	Zinc	1	0.5	R	10	+	
		2	0.5	R	10	+	
		3	0.5	R	10	+	
		4	0.5	R	10	+	
		5	0.5	R	10	+	
		6	0.5	R	60	+	
		7	6	R	10	+	
		8	6	110	20	+	More
	Shilling	9		R	10	+	Little
		10		R	NA	NA	NA
	Half-crown	11		R	50	+	Little
		12		>100	50	+	Little
	New guinea	13		R	20	+	More
		14		130	20	+	Little
	Copper	15	a half penny	R	20	+	0.12
		16		130	20	+	Little
	Platina	17	3	R	30	NA	NA
		18	3	130	20	-	
		19	3	130	20	-	
	Lead	20	16	R	20	+	0.25
		21	16	130	60	-	0.1
		22	16	>130	40	-	0.5
		23	16	>>130	60	-	Little
	Grain tin	24	4	R	40	+	0.25
		25	4	130	NA	-	Little
	Bismuth	26	1	R	20	-	More
		27	1	>R	NA	-	Little
		28	1	>>R	NA	+	Little
Silver spoon	Zinc	29	0.5	R	20	+	0.5
		30	0.5	R	20	+	
		31	0.5	R	20	+	
		32	0.5	R	20	+	
		33	0.5	110	20	+	More
		34	0.5	>110	20	+	1.0
	Bismuth		1	R	NA	-	Little

Table 2.2: **Summary of Cavallo's analysis of how the contact of two metals affected their electrical state.** The columns from left to right indicate: the fixed plate material, the striking substance, the trials conducted with those materials, the weight of the striking material measured in ounces, the temperature of the striking material (R denotes room temperature in degrees Fahrenheit, > refers to a temperature somewhat higher and >> refers to a temperature significantly greater than the specified quantity), the number of multiplier additions, the type of electricity (+ indicates positive electricity, and – refers to negative electricity), and the strength of electricity, measured by the amount of divergence between cork balls and recorded in inches. If an exact measurement could not be made, Cavallo took note of the relative positions of the cork and reported whether he observed more or less divergence from a standard trial.

First, Cavallo noted that different metals produced different types of electricity. Also, the type of electricity emitted by some metals, such as lead and bismuth, appeared to be temperature dependent. At room temperature, lead emitted positive electricity, but at temperatures greater than 130° F it became negatively charged. In contrast, zinc always generated positive electricity, while platina produced a negative charge independent of temperature. Although temperature affected the type of electrical fluid, it too seemed to affect metals distinctively, i.e. no two metals behaved exactly the same when heated.[175] He argued, "whether the electricity be derived from the air, from the hand, or merely from the contact of the two metals, its different [electrical] quality cannot depend upon any other circumstance than the particular nature of the metal employed, that being the only thing varied in the experiment." Thus, "the production of different electricities [must be] owing to the different natures of the metallic substances."[176]

Second, Cavallo noted that the strength of the electricity emitted upon contact was extremely weak and highly variable. Volta theorized that the electrical fluid produced by conductors caused muscle spasms. Cavallo asked: if the contact of metals was responsible for the observed animal electricity as Volta alleged, why did contractions not vary more in terms of strength and duration? Furthermore, "[a]fter a careful review of the foregoing experiments", he reasoned that metals with the greatest amount of opposite electricity should produce more substantial effects on the organism, yet there was no discernible difference in connecting tissues with zinc (positive with silver) and bismuth

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[175] Cavallo wrote: "I am inclined to suspect, that different bodies have different capacities for holding the electric fluid, as they have for holding the elementary heat…" Ibid, 139.

[176] Ibid, 132-133.

(negative with silver) than with zinc (positive with silver) and silver (uncharged). In both cases, the resulting contractions appeared identical. He wrote,

> Had the action of the same metals upon the prepared animal bodies produced effects as fluctuating as those of the preceding experiments, we might without hesitation have admitted the proposition; but when we find that in different states of the atmosphere, the action of metallic bodies produces the contractions of prepared animal limbs, with hardly any observable difference; and when we consider that zinc and bismuth, which though in the above-mentioned experiments do more generally produce different states of electricity, yet they are not more powerful exciters of Animal Electricity, than zinc and silver, or zinc and gold; we can then hardly conclude with saying that the effects observed in Animal Electricity are to be entirely attributed to the electricity produced by the contact of the metallic bodies.[177]

Cavallo did not doubt that metals produced an electrical discharge on contact, but rather questioned whether their electricity was sufficient to account for galvanism.

Thirdly, Cavallo argued there had to be an additional source of electrical fluid to produce animal electricity. It was generally agreed that "animal limbs" behaved like highly sensitive electrometers. "When a Leyden phial is used in experiments on prepared animals, the quantity of electricity employed cannot be properly estimated" by standard instruments, yet muscles contracted, indicating the passage of weak electrical fluid.[178] Walsh and Cavendish had observed that although the torpedo ray could produce (a type of) electricity sensible to humans, it was also not measurable by electrometers. Cavallo asked: what "quantity of electricity… is sufficient to contract the prepared animals" and how does that amount compare to the electrical fluid produced by the interaction of two dissimilar metals?

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[177] Cavallo, 1795, 135.

[178] Ibid, 136.

Cavallo began by charging "a [cork-ball] electrometer until its pendulums diverged to about a twentieth of an inch". He viewed electrical strength as a measure of fluid density. He then "touched the electrometer with an insulated piece of metal, the surface of which was about 200 times greater than that of the conducting parts of the electrometer". Within this framework, this meant "that the electrometer was left with about the 200th part of that electricity, which had been at first communicated to it." He noted that "on touching the prepared legs of a frog with this electrometer, possessed of that small quantity of electricity, no contractions ensued." Given the number of multiplications needed to make the electricity produced by the contact of two metals manifest, Cavallo argued that "the electricity produced [by percussion] is very frequently much less than that which was possessed by the electrometer [in this experiment]." Yet, contact between two dissimilar metals and muscle tissue always produced visible contractions. Cavallo concluded,

> Are we then not authorized to say, that either the quantity of electricity which is produced in the act of touching animals with metallic substances, is greater than that which is produced by the contact of one metal with another metal; or that the contractions excited in animal bodies by the application of metals, must be attributed to some other property of metallic substances, independent of electricity?[179]

If metallic electricity was not sufficient in quantity to cause muscle spasms, there were only two ways to account for galvanism: either living organisms contained electrical fluid, as Galvani had postulated, or contractions were caused by a yet unknown property of metals.

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[179] Ibid, 137-138.

Cavallo’s research supported Volta’s claim that the contact of two different metals emitted electricity. His experiments, however, raised substantial problems with Volta’s attribution of metallic electricity to galvanism. Although the percussion of dissimilar metals produced electrical fluid, its weakness and variability made it unlikely that it was the sole source of electricity and cause of muscle spasms.

In addition to practical problems with Volta’s theory, natural philosophers and physicians also pointed out several conceptual issues. The first is well known. In 1797, Galvani rebutted Volta’s argument that he, Galvani, had mistaken the effects of the apparatus for that of the frog. Galvani argued that, even if metallic electricity explained his frog experiments, it could not adequately account for the torpedo’s emission of electricity because the fish contained no metals.[180]

Cavallo raised a second objection. Volta had concentrated on metals, but there were other types of conductors. It was well known, for instance, that the human body contained conducting materials like salt water. Animals also contained electrics, such as fat and oil. Although living things were imperfect conductors, they were potentially subject to the same electrical actions as metals. He used an example to further illustrate his point. Paper was easily electrified just by gently rubbing one’s hand across its surface. Holding the paper by one corner with his right hand and the other with his left hand, he had an assistant probe the strength of the charge at various points on the paper’s surface. They found that the electricity varied in a non-homogeneous fashion over the surface of

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[180] Galvani reported these results in his 1797 discussion of contact theory and its weaknesses. Bresadola suggests that Cavallo was eventually convinced by Volta’s argument. See Bresadola, 2008, 26-31; Pera, 1992, 146-149.

the paper. For instance, Cavallo noted that the measured electrical fluid was weakest in the region of the paper nearest his hands and strongest towards its center. This unequal distribution of charge suggested that, even though the paper appeared to be uniform, parts of it more readily conducted electrical fluid away from its surface while other parts acted more like an electric and retained charge. He argued that organic tissue, like paper, could have complex electrical properties, which did not preclude the production of electricity.[181]

Nicholson raised a third objection. He noted that neither account, whether the electricity came from the contact of two dissimilar metals or muscle tissue, adequately explained the dynamic abilities of the torpedo. Nicholson's own research into weak electricity had convinced him of the conceptual difficulties with likening the torpedo's electrical organ to the Leyden jar. Although Franklin squares, metal-glass-metal units, could be stacked in such a way as to mimic the regularity of the fish's partitions, Nicholson argued that the source of electrical fluid for the phial was an insurmountable obstacle. The Leyden jar would always be an inadequate model of the torpedo's organ because its electricity originated with a friction machine, an instrument that the fish did not, even in a metaphorical sense, possess. Contact theory accounted well for a single electrical discharge. Galvani's theory described the motion of electrical fluid within animals, but both theories were ill equipped to deal with the continuous emission of electrical fluid from the fish into its local environment.[182]

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[181] Cavallo, 1795, 16-19.

[182] William Nicholson, "Observations on the Electrophore, Tending to Explain the Means by Which the Torpedo and Other Fish Communicate the Electric Shock," *Nicholson's Journal* (1797): 355-359.

Building on the work of Cavendish, Cavallo, and Volta, Nicholson suggested that it might be possible to construct a machine that perpetually released electrical fluid in a manner more analogous to the actual organ of the torpedo ray. Like Volta, Nicholson made a distinction between the quantity and intensity of electricity.[183] In the 1780s, he had conducted a series of experiments comparing the properties of electrics and on what he called compensation (induction). He discovered that talc (magnesium hydroxyl silicate) had three interesting characteristics. First, it tended to be naturally electrified. Talc emitted sparks upon being “split in two” and its surfaces “were found to be in opposite states”. Second, it stored significantly more electrical fluid than electrics with identical surface area and thickness. Third, using Lane’s electrometer, he found that “the intensity of the very dense charge on the talc was so low as to afford an explosion of no more than about one-tenth of an inch, while that of the glass jar it was compared with exploded through about five inches.”[184] In 1797, he saw an application for this high yield, low intensity electric. He wrote,

> Respecting the manner of operation [by which the torpedo acts], there are no facts which shew how [its] charge is actually produced, maintained, and communicated. Whether electricity be actually collected, composed, or decomposed in the organs of the fish or whether it simply exists in those organs, as perhaps it may in all bodies, in the state of what is called compensation, are questions [about] which we in fact know nothing. It has appeared to me, from the observation of the high electric state which talc naturally possesses, and from the innumerable shocks the electrophore is capable of giving by mere change of arrangement, that a machine might be constructed also capable of giving numberless shocks at pleasure, and of retaining its power for months, years… I will not here describe the mechanical combinations which have occurred to me in meditating on this subject, but… the dimensions of [its] organs… possible motions and the

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[183] See for example, Nicholson, 1787, Vol. 2, 325-330.

[184] Nicholson, 1789, 285-287.

> allowable supposition of conducting and non-conducting powers, may produce the effects we observe. How far it may be probable must undoubtedly be left to future experimental research.[185]

He noted that Volta's electrophorus generated electricity with minimal applications of friction. Rather than charging the apparatus by this artificial means, Nicholson suggested using talc as the insulator. It naturally contained large amounts of weak electricity and could act as the source of electrical fluid. Extending Volta's theory, the metals in the apparatus would then provide additional motion to the fluid as the electrophori slowly discharged through compensation (induction) in a cascading sequence. Thus, Nicholson postulated that by layering insulated conductors in metal-talc-metal arrangements, one might more effectively mimic the torpedo's electrical abilities.

Pancaldi has demonstrated that Nicholson's paper was groundbreaking. Volta had seriously started to consider the effects of wet, imperfect conductors (tissue) on metals. Volta thought that imperfect conductors augmented the flow of electrical fluid from dissimilar metals, although he did not know why. He was already experimenting with different combinations of substances to examine this effect in more detail, when he read Nicholson's paper in 1799. (It was originally published in 1797, but communications across Europe were hampered by the French revolutionary wars, Napoleon having invaded the Italian states and conquering Austria that year.) It suggested to Volta a new line of investigation, one in which materials were layered in multiple units of three. Volta incorporated this idea into his own research: the contact of different metals produced sparks and the interaction of different metals and organic tissues generated even more

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[185] Nicholson, 1797, 358.

electricity than two metals alone. Experimenting with groupings of metals and fluids, he finally hit upon it. A column of alternating layers of pairs of silver and zinc, separated by cardboard soaked with salt water, produced a continuous and powerful stream of electricity.[186]

2.4: Conclusion - One, Two, or Three Forms of Electricity?

> Common electricity is excited upon non-conductors, and is readily carried off by conductors and imperfect conductors. Voltaic electricity is excited upon combinations of perfect and imperfect conductors… The animal electricity resides only in the imperfect conductors forming the organs of living animals, and its object in the œconomy of nature is to act on living animals. Distinctions might be established in pursuing the various modifications or properties of electricity in these different forms…[187]
>
> Humphry Davy (1829)

Volta's study of metals and their electrical properties led him to conclude that conductors not only transmitted electricity, but were an important source of electrical fluid. Originally christened the "artificial electrical organ" to reinforce its analogy with the torpedo ray, the pile was made by alternating layers of silver and zinc with an imperfect conductor, such as wet paper.[188] (Figure 2.13) Volta argued that bringing the zinc near the silver created tension between the electrical fluids in the metals. Allowing the metals to touch 'pushed' out the electrical fluid in the metal containing the most (in this case zinc). The act of percussion imparted a motive force to electrical fluid in metals because conductors were readily able to transmit charge. Placing a wet conductor

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[186] Giuliano Pancaldi, "Electricity and Life: Volta's Path to the Battery," *Historical Studies in the Physical and Biological Sciences* 21 (1990): 123-160; Pancaldi, 2003, 196-207. See also, Sudduth, 1980 and John Heilbron, "Analogy in Volta's Exact Natural Philosophy." *Nuova Voltiana* 1 (2000): 1-24.

[187] Humphry Davy, "An Account of Some Experiments on the Torpedo," *Phil. Trans.* 119 (1829): 15-18, 17.

[188] Volta, 1964, 112.

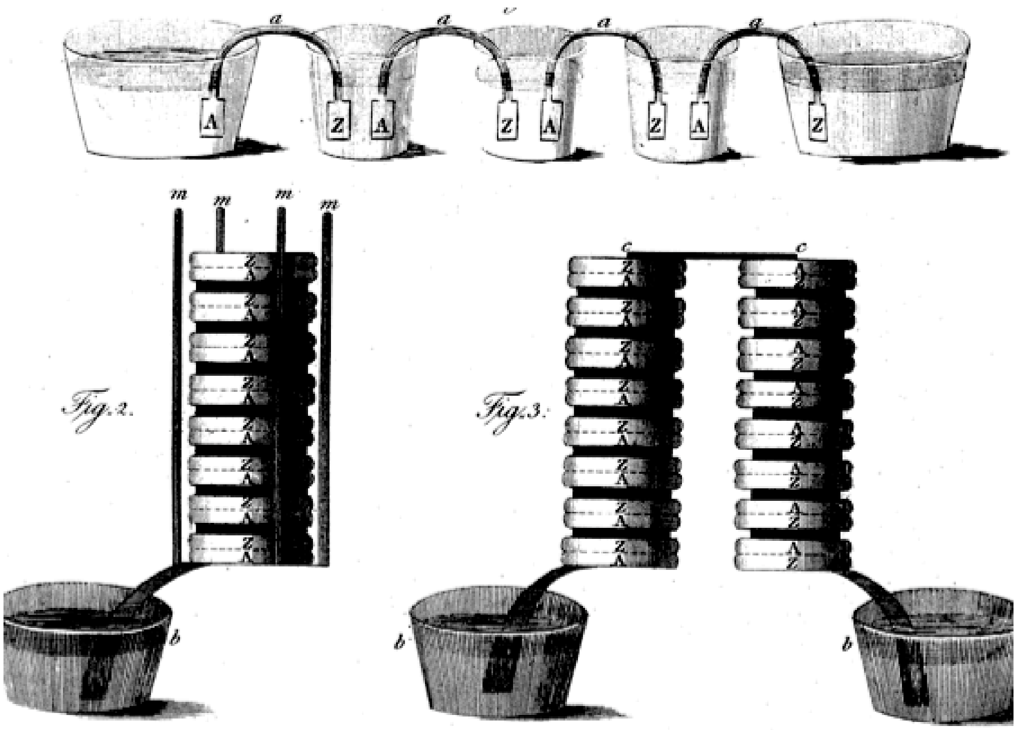

Figure 2.13: **Various Configurations of Volta's Pile (1800).**[189]

between the zinc and the next pair of silver/zinc plates enhanced this effect. Since electricity traveled from regions of high tension (or density) to low, connecting the lower surface of the bottom silver plate to the upper surface of the top-most zinc plate (with a wire) kept the electrical fluid in motion. Once the electrical fluid flowed, it tended to stay in motion, as it was alternately pushed out of regions of high tension (or density) and pulled into areas of low tension (or density) through the different layers. This cyclic process was observed as a 'continuous' current.

Volta's explanation for the pile's electricity assigned an active role to metals. By studying how metals behaved under a variety of conditions and with different substances,

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[189] Alexander Volta, "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds," *Phil. Trans.* 90 (1800): 403-431.

electricians developed a more nuanced and sophisticated understanding of conductivity. In the early eighteenth century, ‘conductor’ was a class of material. In the late eighteenth century, Priestley tried to show that conductivity was correlated to the presence of phlogiston. By the end of the eighteenth century, it was a property, which all substances possessed with varying efficacy, e.g. even electrics, like glass, became conductive at high temperatures. Electricians found that conductivity depended upon the material, temperature, and the amount and strength of electricity. Furthermore, Volta, Nicholson, and Cavallo’s experiments demonstrated that metals also contained electrical fluid. For Volta, an exciting by-product of the property, conductivity, was that certain materials also had the ability to move charge. He argued this facilitated the distribution of electrical fluid. External forces, such as friction and contact, could therefore set the electrical fluid in metals in motion. He asserted that together: external forces, motion, and attraction, a force intrinsic to electrical charge, accounted for all electrical phenomena.

Many natural philosophers and chemists, including Franklin, Aepinus, Cavendish, Beccaria, Nicholson, and Cavallo, also subscribed to the view that a single fluid produced electrical effects. Most one-fluid theorists thought there existed two states of electricity, positive (plus) and negative (minus), which corresponded to the distribution of electrical fluid within bodies. In contrast to Volta, however, many one-fluid electricians believed repulsion was also a real and independent phenomenon from attraction. Some, like Franklin and Cavendish, even argued that repulsion was the only force intrinsic to charge and it was the common matter of bodies that possessed an attraction or affinity for electricity. Yet another group of natural philosophers thought that there were two distinct electrical fluids, positive and negative, including Dufay, Nollet and Charles-Augustin Coulomb who demonstrated that the force between two electrified bodies was proportional to the inverse square of distance between them. Whether there was one fluid or two, however, natural philosophers adopted the generic terms positive and negative to refer to friction-based electricity.

With the invention of the voltaic pile, a source of constant current, and the alleged discovery of animal electricity, electricians were left in a quandary. Were frictional, animal, and voltaic electricity three different forms of (positive and negative) electricity or were they simply different expressions of it? Cavendish and Walsh had tried by similarity of effect to show that animal and friction-based electricity were different manifestations of the same fluid. A series of Leyden jars produced phenomena analogous to the torpedo ray. Galvani argued that because animal electricity had a different cause, it was a unique fluid. Volta contended that the contact of metals produced electricity in a comparable way to frictional electricity. In both cases, an external force set electrical fluid in motion, producing sparks and other effects. Furthermore, Volta argued that the pile, whose similarity of effect and similarity of form made it a compelling analogical model for the torpedo's electrical organ, demonstrated that contact theory accounted for galvanism as well. Percussion, frictional, and animal electricity were different expressions of the physics of one fluid.

Contrary to many histories of the invention of the pile, the debate over the cause of its electrical effects did not end here. Galvanism was not subsumed into contact theory.[190] Experiments conducted by Davy and other British chemists suggested a different mechanism of electrical generation. For example, Davy demonstrated that a pile constructed of silver, zinc, and pure water (distilled) did not produce electricity (at least not in detectable amounts).[191] He tried systematically altering the third conducting substance, and found that if it contained salt, or some other oxidizing agent, electricity flowed. Moreover, the amount of electricity produced by the pile appeared to be proportional to the oxidizing power of the third material. For example, a pile constructed of eighteen two-inch square plates of zinc, silver, and muriatic acid (hydrochloric acid) produced an equivalent shock to a common pile (zinc, silver and salt water) with seventy plates.[192] Natural philosophers and chemists asked “why”?

Three distinct theories were proposed to account for these phenomena: one physical and two chemical. As already discussed, many natural philosophers, like Volta, argued that mechanical and electrical forces alone could account for observed electrical phenomena, including voltaic and animal electricity. Within this framework, differences in the amount of electricity generated by the pile were attributed to differences in the electromotive abilities of materials. Davy and Giovanni Fabbroni, an Italian naturalist and chemist, suggested a radical reinterpretation of electricity: electrical effects were not caused by the existence and motion of a unique substance, but rather were the result of complex chemical changes. Other chemical theorists like William Wollaston modified

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[190] See for example, Pera, 1992; Piccolino, 2003; Mertens, 1998.

[191] Humphry Davy, "Notice of Some Observations on the Causes of the Galvanic Phaenomena, and on Certain Modes of Increasing the Powers of the Galvanic Pile of Volta," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839d), 155-163, 156.

[192] Ibid, 162.

the late eighteenth century chemical view: electricity was a substance capable of chemically combining with and being separated from other materials. Chemical changes taking place within the pile released this substance.

The next chapter focuses on early nineteenth century chemical accounts of non-frictional electricity in Britain. This dissertation then concludes with a discussion of the debate between natural philosophers and chemists over their theoretical conclusions drawn from experiment. It demonstrates that contact theory appealed to natural philosophers, especially those in France, because it was perceived as quantifiable. Why were chemical experiments and theories deemed less quantifiable? I ask what was "quantification" in this context and what did it entail?

Chapter 3: Electricity, Fluid or Product of Chemical Change?
British Electrochemistry in the Early Nineteenth Century

> The identity of the general causes of electrical and of galvanic effects is now doubted by few; and in this country [Britain] the principal phenomena of galvanism are universally considered as depending on chemical changes; perhaps, also, time may show, that electricity is very materially concerned in the essential properties, which distinguish the different kinds of natural bodies, as well as in those minute mechanical actions and affections which are probably the foundation of all chemical operations; but at present it is scarcely safe to hazard a conjecture on a subject so obscure, although Mr. Davy's experiments have already in some measure justified the boldness of the suggestion.[1]
>
> Thomas Young (1807)

Introduction

The previous chapter demonstrated that the development of electrometers and multipliers in the late eighteenth century played a formative role in electrical theory and practice. Detectors often behaved in surprising and unintentional ways, for example, by registering the presence of electricity when there were no extant charged bodies. With each instrument modification, electricians learned more about the properties and behavior of electrical fluid.

As natural philosophers investigated how the quantity and quality of electricity varied with substance, including organic tissue, the study of electricity became more sophisticated and tangled. In the early eighteenth century, one electrical fluid accounted for all electrical phenomena. By the end of the century, there were possibly three different forms of two states of electricity responsible for observed effects. Central to this quagmire was weak electricity, electrical fluid of either insufficient strength or substance to be detected by ordinary means. In order to resolve the relationship between weak

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[1] Young, *A Course on Natural Philosophy*, 684.

forms of electricity, i.e. whether friction, the contact of metals, or living organisms produced the same fluid, natural philosophers developed new instruments, measuring the strength, amount, and distribution of electrical fluid, to determine the identity and origins of electricity. Table 3.1 summarizes the state of electrical knowledge at the turn of the nineteenth-century. The resulting discourse affected the construction of an innovative electrical generator in 1799: the voltaic pile or battery.

Source	**Effects**					
	Heat	Light	Attraction Repulsion	Detection Method		Chemical
				Physiological	Electrometer	
Friction	X	X	X	X	X	X
Animal		X		X	??	?
Contact		X		X	X (with multiplier)	
Voltaic*	X	X	X	X	??	X

Table 3.1: **The four sources of electricity and their associated effects, marked with an X.**[2]

* - Voltaic electricity was a special case, as it was not caused by friction or physiology. Volta argued it was produced by contact, whereas chemists asserted it was caused by chemical changes occurring between the substances in the pile. This debate forms the basis for this chapter.

? – Natural philosophers, such as Volta and Ritter, found that if they touched two different metals to opposite sides of the tongue, one side tasted sharp or acidic, while the other tasted chalk-like or basic. This suggested to Ritter that the electricity in animals also caused chemical changes.

?? – Although animal and voltaic electricity were perceptible by the senses and produced chemical changes, standard instruments did not easily measure them, e.g. there was debate as to whether electrometers responded to either form of electricity. For instance, Nicholson and William Cruickshank claimed to have detected the pile's electricity with Bennet's gold-leaf electrometer, whereas Henry Haldane reported a null result with similar apparatus.

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[2] This is a modified version of a table presented by Michael Faraday on the different sources of electricity and its associated phenomena. See Faraday, 1833, 48.

Far from definitively answering the question of how electrical fluid was produced, the pile suggested novel experiments and interpretations of its electricity. As discussed in the last chapter, Volta thought the pile validated contact theory, his explanation for electrical generation. Volta argued that fluid mechanics and electrical forces could explain the motion of electrical fluid and hence its effects. The pile, however, produced a form of electricity unparalleled in kind and duration. Unlike friction machines, which relied on the contact and motion of a solid electric and conductor, the pile had no moving parts, and its electrical action depended on the arrangement and type of conductors used in its construction. Furthermore, not all material combinations worked and those that did generated different degrees of electrical fluid. Natural philosophers and chemists debated how these substances interacted to produce current.[3]

More specifically, three different theories were proposed to account for the pile's electricity. First, Volta extended contact theory. In the late 1790s, he and other electricians, such as Christoph Pfaff, a well-connected natural philosopher who actively promoted Volta's theory in Germany, attempted to construct "electrical tension series" based on experiment. These lists ranked materials according to conductivity. Within this framework, differences in the pile's electricity were caused by variations in the electromotive abilities of substances. Thus, by improving their understanding of the

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[3] There is a small, but growing literature on this topic. See, for example, Kipnis, 2001; Kragh, 2000a; Pancaldi, 2003, chapter 7: "The Reception of the Voltaic Pile in Europe".

electrical properties of conductors, they hoped to better account for the pile's electrical output.[4]

Second, Giovanni Fabbroni, an Italian chemist and naturalist who participated in the development of the metric system, and Humphry Davy, at least early in his career, suggested a radical new interpretation. Electricity was not a material per se, but rather an effect of chemical changes taking place between the constituents of common matter. For example, Fabbroni, in the early 1790s, observed that the rate of oxidation (oxygen absorption) in metal increased if it was placed in contact with a dissimilar metal.[5] In 1800, Nicholson and Davy also noticed that in a pile constructed of silver, zinc, and salt water, the zinc was "rapidly" oxidized. Systematically studying the chemical effects of layering different conductors, Davy noted that the amount of electricity produced by the pile correlated to the type and degree of chemical change occurring between its components. These experiments suggested that electricity might be a chemical effect and not a substance.[6]

Third, William Cruickshank, professor of chemistry at the Royal Military Academy in London, and William Hyde Wollaston, a British metallurgist and chemist who became famous and wealthy for his platinum research and isolation of two new elements, rhodium and palladium, also adopted a chemical theory of electricity, but with

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[4] Kragh, "Volta's Apostle: Christoph Heinrich Pfaff, Champion of the Contact Theory"; Helge Kragh and Malene M. Bak, "Christoph H. Pfaff and the Controversy over Voltaic Electricity," *Bulletin for the History of Chemistry* 25, no. 2 (2000b): 83-90.

[5] Fabbroni, 1799; Giovanni Fabbroni, "On the Chemical Action of the Different Metals Upon Each Other at the Common Temperature of the Atmosphere, and Upon the Explanation of Certain Galvanic Phenomena," *Nicholson's Journal* 4, no. June (1800): 120-127.

[6] Davy, "Early Miscellaneous Papers"; Nicholson and Carlisle, 1800.

significant differences. In 1800, Cruickshank argued that electrical fluid was a chemically active substance. Through a series of complex chemical changes, in which electricity decomposed and recombined with other materials, it was pushed and pulled through the pile. In contrast, in 1801, Wollaston proposed that the process of oxidation, observed to occur between the pile's metals and wet conductor, released electrical fluid that had been chemically bound to the metal.[7] Although Cruickshank and Wollaston used different chemical reactions to explain the motion of electrical fluid, they both advocated that electricity was a substance with unique chemical properties and affinities.

This chapter examines chemical theories of the pile. Although chemists conducted innovative experiments with the battery, reinforcing a chemical interpretation of its electrical action, many natural philosophers continued to support contact theory, such as Jean-Baptiste Biot, the French natural philosopher and mathematician, and Georg Simon Ohm, the German physicist. Why were natural philosophers not persuaded by chemists' arguments?[8]

I argue there were two important reasons. First, there was widespread disagreement amongst chemists as to the chemical nature of electricity. This weakened their position. For example, Davy argued that electricity was an effect of complex chemical changes (later he suggested it was a form of energy) while Wollaston

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[7] Wollaston, 1801.

[8] See for example, Biot, 1803; Wilhelm Ostwald, *Electrochemistry: History and Theory [1896]* (New Delhi: Amerind Pub. Co. (for the Smithsonian Institution and the National Science Foundation), 1980), 370-413; Pancaldi, 2003, 224-245; Jürgen Teichmann, "Volta and the Quantitative Conceptualization of Electricity," *Nuova Voltiana* 3 (2002): 53-80. For a brief biography of Biot and Ohm, see Eugene Frankel, "Career-Making in Post Revolutionary France: The Case of Jean-Baptiste Biot," *British Journal for the History of Science* 11, (1978): 36-48; Jürgen Teichmann et al., "Physicists and Physics in Munich," *Physics in Perspective* 4 (2002): 333-358, 339-341.

maintained that it was a fluid not unlike caloric.[9] Some chemists also recognized a significant and seemingly insurmountable problem: did the motion of electrical fluid cause chemical change or did chemical change produce current? Although both Wollaston and William Henry, a well-known pneumatic chemist and collaborator of John Dalton, supported a chemical theory of the pile, they noted that it was difficult "[t]o decide which [was] to be considered as the cause, and which as the effect" because the "two events", current and chemical change, were "invariably connected, [and] not distinguished by an appreciable interval of time."

Second, as discussed in chapter two, contact theory had a long history. In the early nineteenth century, it began to appeal more to natural philosophers, especially those in France, because it was perceived as quantifiable.[10] Why was contact theory considered quantifiable in this context while chemical theories were not? Natural philosophers, in part, argued that Volta's experiments, measuring the electrical fluid produced by the contact of two dissimilar metals and the pile, were more reliable than chemists' qualitative findings. This dissertation concludes with a discussion of the methodological differences emerging in the study of electricity at the turn of the nineteenth century.

This chapter analyzes the history of electricity as a chemical phenomenon in Britain and, more specifically, Davy's contribution to the debate over how the pile produced electricity. Although Volta argued that differences in the electromotive abilities of conductors generated current, there was also historical precedent for considering

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[9] Davy, 1807; Wollaston, 1801. See also Faraday's criticism of their respective positions, Faraday, 1833, 24-25, 34-38.

[10] See for example, Biot, "Recherches Physiques Sur Cette Question: Quelle Est L'influence De L'oxidation Sur L'électricite Dévelopée Par La Colonne De Volta," *Annales de Chimie* 14 (1803): 4-45.

electricity as a chemical substance capable of combining with other materials. Unlike Volta, whose methods focused on the development of new instrumentation with which to measure the intensity and distribution of electrical fluid, electrochemists studied the relationship between sparks, current, and chemical change by appropriating chemical methods to the study of electricity. For example, as discussed in chapter one, chemical practitioners redesigned the pneumatic trough to create eudiometers to measure how the sparking of airs affected gas volume and composition. This chapter demonstrates that early nineteenth-century British electrochemists built on this experimental tradition by using their knowledge of chemical reactions to manipulate the conditions under which current formed and acted, to learn how electricity affected and was affected by chemical phenomena. It concludes with an analysis of the conceptual problems posed by the pile's chemical effects.

3.1 – The Pile and the Rebirth of British Electrochemistry

> Following extensive [re]views, he [the natural philosopher] will combine together mechanical, chemical, and physiological knowledge, whenever this combination may be essential; in consequence his facts will be connected together by simple and obvious analogies, and in studying one class of phænomena more particularly, he will not neglect its relations to other classes [of phenomena].[11]
>
> Humphry Davy (1802)

In 1781, Volta embarked on a scientific tour of France and England. It was a formative year. He spent several months in each location, conducting experiments and discussing contemporary issues in natural philosophy with local scientists. Subsequently

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[11] Davy, "Early Miscellaneous Papers," 315.

in 1782, he published the results of his research: experiments investigating the electricity of gases and a new invention, the condenser.[12]

In Paris, he met Franklin, Lavoisier, and Laplace, but over all found "the experience… a mixed one".[13] Franklin had abandoned his electrical research for political pursuits and few French natural philosophers were actively engaged in the study of electricity at that time. Many were also occupied with the development of sophisticated mathematical accounts of natural phenomena.[14] While epitomizing the eighteenth century "quantifying spirit",[15] Volta had "limited mathematical training, that did not go beyond arithmetic".[16] French natural philosophers were interested in some aspects of Volta's experimental work. For example, after witnessing a demonstration of his multiplier, Lavoisier "ordered a large condenser with a marble plane to be made" to examine whether chemical changes produced electricity.[17] They were, however, less receptive to Volta's burgeoning theory of electrical action with its "midrange concepts" and lack of mathematical analysis.[18]

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[12] Pancaldi, 2003, 112-121; Volta, 1782.

[13] Pancaldi, 2003, 158.

[14] See for example, Crosland, "A Science Empire in Napoleonic France"; Frankel, 1977; Charles Coulston Gillispie, *Science and Polity in France at the End of the Old Regime* (Princeton: Princeton University Press, 1980); Gillispie, *Science and Polity in France: The Revolutionary and Napoleonic Years* (Princeton: Princeton University Press, 2004).

[15] Historiography on the "quantifying spirit" includes: Bandinelli, 2007; Buchwald, 2006; Heilbron, 1990; Holmes et al., *Reworking the Bench: Research Notebooks in the History of Science*; Wise, ed., 1995.

[16] Pancaldi, 2003, 137.

[17] Together with Lavoisier and Laplace, Volta "obtained unequivocal signs of electricity from the evaporation of water, from the simple combustion of coals, and from the effervescence of iron filings in diluted vitriolic acid." Volta, 1782, xxix.

[18] Pancaldi, 2003, 156-160.

His visit to England was a study in contrasts. Although Volta struggled with the English language, he found himself steadily engaged by a number of avid, practicing electricians and instrument makers, who were interested in both his ideas and experiments. Volta met with Priestley, Bennet, and Cavallo, and spent a great deal of time with the Coffee House Philosophical Society in London, a ragtag group of natural philosophers, chemists, and industrialists who met at local coffee shops to discuss informally contemporary problems in science and politics, and "banned [from their meetings] the esoteric language of mathematical demonstrations in favour of the common coin of readily accessible facts". Nicholson was at that time secretary. Like Volta, these men were predominantly experimentalists. Not surprisingly, given their common interests, Volta found it to be a place of vibrant and open intellectual exchange. [19] After his cool reception in France and overwhelmingly positive experience in England, Volta became a self-professed anglophile.[20]

After nearly two decades of fruitful correspondence with British electricians, Volta chose to write the Royal Society to announce his invention of the pile. Before his letter had been read, however, news of the battery was leaked by Joseph Banks, then President, to his friend, a respected physician named Anthony Carlisle, and Nicholson. Together, Nicholson and Carlisle constructed a pile and began experiments.[21]

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[19] Geoffroy Cantor, "Discussing Chemistry and Steam: The Minutes of a Coffee House Philosophical Society 1780-1787 (Book Review)," *Annals of Science* 62 (2005): 270-271, 271.

[20] Unlike many of the other European countries he had visited, Volta wrote to friends that England seemed undaunted by a century of war. It was a place of growth with opportunities for social, economic, and intellectual mobility. See, Pancaldi, 2003, 160-164.

[21] Knight, *Ideas in Chemistry*, 70-71; Sudduth, 1980.

Their device consisted of “17 half crowns, with a like number of pieces of zinc, and of pasteboard, soaked in salt water” stacked in a column “in the order of silver, zinc, card, etc”. As Nicholson noted, there were striking parallels between this instrument and the organ of the torpedo ray. He readily accepted the pile as demonstrative proof that galvanism and contact electricity were identical because of the many “happy points of resemblance between their structure and effects”. It was, however, with more “surprise” that he and Carlisle observed “the chemical phenomena of galvanism”.[22]

First, by attaching wires to either end of the pile and placing the leads into different liquids, such as water and muriatic (hydrochloric) acid, they discovered substances were profoundly altered by the pile’s electricity. Water was decomposed. Hydrogen gas was produced in the region connected to the negative end of the pile, while oxygen gas was emitted from the positive end.[23] As the gas was evolving, Nicholson also noted that the wire connected to the positive end of the pile began to disintegrate in the water. This suggested that an acid had formed near the wire in the solution. As discussed in chapter one, acids were a set of highly reactive compounds, which typically tasted sour, caused corrosion, and, according to Lavoisier’s theory, contained oxygen. They were also capable of dissolving some metals. Alkalis or bases, on the other hand, were reactive, caustic, and interacted with acids to form salts. The presence of an acid or a base could be detected by an assortment of plant extracts, which changed a unique color when exposed to an acid or a base. For example, litmus, derived from lichen, turned red in an

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[22] Nicholson and Carlisle, 1800, 180-181, 181.

[23] Ibid, 181-183. Using his revolving doubler, Nicholson measured the electricity present at each end of the pile.

acid and blue in an alkali solution, whereas a "tincture of Brazil wood" turned purple only in the presence of a base. It could not be used to detect an acid. Repeating the experiment with a mixture of water and litmus, Nicholson and Carlisle found that the area around the positive wire turned red, while the region near the negative lead turned blue.[24] In the case of muriatic acid, when copper wires were used, the wire attached to the positive end of the pile began to corrode, while the wire attached to the negative side became coated with a copper precipitate and produced hydrogen gas.[25]

Second, they observed that the plates used in the pile's construction were also chemically changed with prolonged use. For example, the zinc plates were "oxidized on the wet face [developing a thick, white film], and hydrogen given out". After "about two days", the corrosion was so extensive that it was "necessary to renew them [the zinc plates] … by scraping or grinding." Furthermore, the salt-water solution was also altered as "the common salt [was] decomposed, and exhibit[ed] an efflorescence of soda round the edges of the pile". This affected the amount of electricity produced by the pile. Nicholson and Carlisle asked why?[26]

Eighteenth-century electricians had long studied the effects of electricity on substances. For example, sparking gases often chemically changed airs. Natural philosophers debated the role of electricity in this process. As discussed in chapter one, Priestley argued that electricity was a form of phlogiston and, therefore, participated in

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[24] Ibid, 183. In modern terms, when a standard pile is connected to water, the two half reactions may be expressed as: $2H^+ + 2e^- \rightarrow H_2$ (g) and $4\ OH^- \rightarrow O_2$ (g) + $2H_2O + 4e^-$. See Appendix IV, for a more detailed description of the electrical decomposition of water and the formation of acids and bases in electrolytic solutions.

[25] Ibid, 187.

[26] Ibid, 183-185, 183.

chemical change. Cavendish, in contrast, asserted that because of the rapidity of sparks, there was no time for electrical fluid to chemically interact with gas particles. He contended that electricity, like heating, imparted motion to gaseous bodies, fracturing existing compounds. This facilitated chemical change as the individual constituents of the airs recombined in more favorable ways. There was widespread dissatisfaction with both views.[27]

This question of whether electricity facilitated or participated as a substance in chemical change took on additional significance with the invention of the pile. As Nicholson and Carlisle observed with an electrometer, if the pile's wet conductor dried out, the battery produced no appreciable electricity. Furthermore, the amount of electricity decreased with the oxidation of zinc. The pile's current also affected the composition of external substances. In the case of water, oxygen and hydrogen gas evolved near the positive and negative leads respectively. Although Nicholson could not explain these results, he argued they were suggestive "and seem[ed] to point at some general law of the agency of electricity in chemical operations."[28]

3.1.2 - A Brief History of the Electrical Composition of Water

> It must be acknowledged that substances possessed of very different properties may be composed of the same elements, in different proportions, and different modes of combination. It cannot, therefore, be said to be absolutely impossible but that water may be composed of dephlogisticated [oxygen] and inflammable air [hydrogen], or of any other elements. But then the supposition should not be admitted without proof; and if a former theory will sufficiently account for all the *facts*, there is no occasion to have recourse to a new one, attended with no peculiar advantage… that phlogiston

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[27] See Chapter 1, Section 1.2. Also, Lavoisier, like Priestley, adopted a materialistic explanation of heat, but unlike Priestley's phlogiston, caloric had no obvious relation to electricity.

[28] Nicholson and Carlisle, 1800, 183.

> is an element in the composition of water is, as I have more than once observed, not improbable; since water conducts electricity like metals and charcoal, into which the same principle enters; and because, when fresh distilled, it attracts dephlogisticated air [oxygen] from the atmosphere, which is the property of other substances containing phlogiston.[29]
>
> Joseph Priestley (1800)

In 1751, Franklin argued that lightning was produced by nature's own friction machine: water particles (conductors) interacted with the air (an electric) to create sparks.[30] Electrics were known to be repositories of charge and so it was thought that water vapor collected electricity already present in the atmosphere and transmitted it to ground. Cavallo and Volta's research into the behavior of insulated conductors demonstrated that all bodies were electrified, including metals. Sandwiching animal tissue, which contained a large percentage of water, between two metals, enhanced the electrical power of contact electricity.[31] Furthermore, Cavendish's experiments on the sparking of airs demonstrated that electricity could be used to synthesize water out of dephlogisticated (oxygen) and inflammable (hydrogen) airs.[32] With the invention of the pile, electric current could also be used to decompose water. Thus, for over half a century, electrical studies suggested a connection between electricity and water.[33]

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[29] Priestley, 1800, 55-56.

[30] Franklin, 1751. Also see Chapter one, Section 1.1.

[31] See Chapter 2, Section 2.3.3.

[32] Cavendish, 1784a.

[33] Sudduth argues that Nicholson and Carlisle's electrical experiments with water demonstrated that water was indeed a compound of hydrogen and oxygen. Some scientists, however, contested this interpretation. For example, Ritter, like Priestley, continued to promote the view that water was an element: oxygen was a compound of water and negative electrical fluid, and hydrogen a mixture of water and positive electrical fluid. See, Sudduth, 1980; Andreas Kleinert, "Volta, the German Controversy on Physics and Naturphilosophie and His Relations with Johann Wilhelm Ritter," *Nuova Voltiana* 4 (2002): 29-39, 35; Walter D. Wetzels, "Johann Wilhelm Ritter: Romantic Physics in Germany," in *Romanticism and the*

Some scientists, like Wollaston and Cruickshank, suggested that the pile's electricity resided in the chemical interaction of the different conductors with water, ubiquitously used as the solvent in the pile's wet conductor. They asserted that water was not just a compound of hydrogen and oxygen, but like metals also contained and had a predilection for electrical fluid.[34] This interpretation of the pile's electricity is the focus of the following section. I will first briefly discuss the historical precedent for considering water to be a compound of hydrogen, oxygen, and an imponderable fluid, like electricity and/or heat.

A common explanation for both the chemical agency and electricity of the pile extended the late eighteenth-century discourse on the chemical effects of sparks. Priestley, in arguing that electricity was a form of phlogiston or heat, gave it the status of a chemical substance, meaning that it could be combined with other materials to form distinct compounds. Within this framework, a metal like 'zinc' was a conductor because it was an amalgam of zinc and phlogiston. Left outside, it would become brittle and white, losing its conductivity. Priestley argued that in the process of weathering the metal experienced dephlogistication: the air slowly absorbed its phlogiston, leaving behind a simple substance and insulator, a metal calx.[35] While Lavoisier could not speak to the property of conductivity, he asserted that the metal had undergone rusting, a form of gradual combustion. As it slowly "burned", it absorbed oxygen from the air, becoming a

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Sciences, ed. Andrew Cunningham and Nicholas Jardine (New York: Cambridge University Press, 1990), 199-212.

[34] William Cruickshank, "Some Experiments and Observations on Galvanic Electricity," *Nicholson's Journal* 3 (1800): 187-191, 254-264; Wollaston, 1801.

[35] See Chapter 1, Section 1.2.

metal oxide.[36] Although phlogiston eventually disappeared from the vernacular as the material cause of heat, the idea of electricity as a chemical substance persisted and was reinforced by experiments investigating the composition of water.

In 1784, Cavendish demonstrated by systematically sparking airs that water had at least two components. He noticed that when he passed an electrical discharge through a mixture of common and inflammable (hydrogen) airs that water (dew) formed along the sides of the eudiometer. He also noted that passing an electrical discharge through a homogenous gas produced a null result: a pure air was chemically unchanged by a spark. This was an important point. An electrical discharge could also be used to determine air quality and, hence, to minimize potential sources of error in chemical experiments. For example, Cavendish observed that dephlogisticated air (oxygen) derived from the heating of metal calxes contained unwanted amounts of phlogisticated air (nitrogen), whereas the respired air of plants had fewer impurities.[37] He then tried combining inflammable air with each of the known constituents of common air: phlogisticated air and dephlogisticated air. He found that when inflammable air and dephlogisticated air were mixed in a container and sparked, water was produced. He concluded that these results supported two different interpretations of the chemical composition of water. Either "dephlogisticated air [is] water deprived of phlogiston; or, in other words, that water consists of dephlogisticated air united to phlogiston; and that inflammable air is either

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[36] See Chapter 1, Section 1.3.

[37] Cavendish, 1784a, 145-148.

pure phlogiston, as Dr. Priestley and Mr. Kirwan suppose, or else water united to phlogiston."[38]

As David Miller, an historian examining the nineteenth-century dispute over the discovery of water's composition, remarked, "[Cavendish's] inferences seem to refer to phlogiston as elemental, and the airs as compounded, but the status of the water remains ambiguous."[39] Both explanations, however, suggested phlogiston was an attribute of water. For Priestley, this was an important experimental result. He advocated the identity of phlogiston with electricity. If water contained phlogiston, this accounted for its electrical properties and substantiated Franklin's theory of lightning by providing an explanation for why water, a substance fundamentally different from metals, behaved like a conductor at temperatures greater than 32°F.[40] (It was well known that ice behaved like an electric or insulator. Priestley postulated this was because at lower temperatures, ice contained less heat or phlogiston than water. In 1787, Nicholson's systematic study of the effects of temperature on conductivity tentatively supported Priestley's hypothesis. As Nicholson noted, "there [was] a certain degree of heat at which a given body may be at

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[38] Ibid, 137.

[39] Over the course of the nineteenth century, scientists became increasingly concerned with documenting the history of their disciplines. (See, for example, Thomson, *The History of Chemistry*.) There was a subsequent dispute amongst British chemists over who discovered the composition of water first: Cavendish, Lavoisier, or James Watt, the co-inventor of the steam engine. The issue was not one of experimental discovery: Watt and Cavendish synthesized water about the same time. Cavendish, however, published first. The more pressing issue was which should be privileged: Lavoisier's theoretical interpretation of Cavendish's experiments or Cavendish's experimental findings. See Jungnickel and McCormmach, 1999, 271-277; Miller, *Discovering Water: James Watt, Henry Cavendish, and the Nineteenth Century 'Water Controversy'*.

[40] Priestley maintained that phlogiston was a necessary component of water until his death in 1804. In 1800, he admitted that Trootswyk and Deiman's experiments on the electrical decomposition of water, discussed later in this section, and the research of Mrs. Elizabeth Fulhame on the chemical composition of water and the process of oxygenation in metals, were puzzling, but did not conclusively negate phlogiston theory. See for example, Elizabeth Fulhame, *An Essay on Combustion with a View to a New Art of Dying and Painting* (London: J. Cooper, Bow Street, Covent Garden, 1794), 161-180; Priestley, 1800, 54-60.

the medium between perfect conducting, and non-conducting, above which degree it becomes a conductor, and beneath, a non-conductor."[41])

While Cavendish's experiments relied on chemical synthesis, Lavoisier argued that he had verified by synthesis and analysis, i.e. by the decomposition of complex substances, that water was a compound of hydrogen and oxygen alone. First, to synthesize water, Lavoisier sparked a gaseous mixture of hydrogen and oxygen, as Cavendish had done, and obtained identical results.[42] Second, previous experiments had shown that "100 [grams] of carbonic acid gas consist[ed] of 72 [grams] of oxygen, combined with 18 [grams] of charcoal".[43] In a series of sophisticated experiments, Lavoisier used this knowledge to decompose distilled water by exposing steam to eighteen grams of very hot charcoal. He continued to add steam to the charcoal in small measured amounts until no charcoal remained. Examining the products, he found that only carbonic acid gas and hydrogen had formed in the vessel. He noted that the amount of water required to completely transform eighteen grams of charcoal into carbonic acid weighed 85.7 grams. He concluded, "[the charcoal] acquired 72 [grams] of oxygen from [the 85.7 grams of] water", to form carbonic acid. Therefore, "85.7 [grams] of water are composed of 72 [grams] of oxygen, combined with 13.7 [grams] of a gas susceptible of

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[41] Nicholson, 1787, 301-316, 303-304.

[42] Lavoisier, *Elements of Chemistry [1789]*, 93-94.

[43] Ibid, 86. The reaction was more complicated than Lavoisier realized, as carbon dioxide also combined with water to produce carbonic acid: $CO_2 + H_2O \rightarrow H_2CO_3$. The chemical formula of charcoal varies, but typically contains carbon, hydrogen, and any number of impurities, including small amounts of water and minerals. Although Cavendish and Lavoisier's independent chemical syntheses indicated that two volumes of hydrogen combined with one volume of oxygen, Lavoisier's experiments provided incorrect weight measurements of water's components. Out of 85.7 grams of water, there should have been 10.7 grams of hydrogen and 75 grams of oxygen.

combustion", i.e. hydrogen or inflammable air. Water, he asserted, was a compound of oxygen and hydrogen gases.[44]

As discussed in chapter one, Lavoisier thought that substances consisted of unique combinations of elements and caloric. Water, a compound of hydrogen and oxygen, existed in three different states, solid, liquid, and gas, because of variations in its caloric content. While this explanation accounted well for observed thermal phenomena such as water's distinct specific and latent heats, it did not explain why water behaved like a conductor nor why heating a mixture of hydrogen and oxygen did not produce water, whereas sparking did.

With only a few exceptions, natural philosophers accepted that water contained hydrogen (inflammable air) and oxygen (dephlogisticated air), but continued to ask what role heat and electricity played in the formation of compounds.[45] Most phlogistonists and calorists thought that heat actively participated as a chemical element in chemical reactions.[46] As phlogiston theory became increasingly untenable in the wake of the "new chemistry", the relationship between thermal and electrical phenomena became murky. If electricity was a material, a view supported by the majority of natural philosophers, and it was not phlogiston, what was it? Why did electricity promote the synthesis of water while caloric did not? Experiments conducted in the 1790s reinforced the idea that electricity was a chemical element and a component of water.

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[44] Ibid, 87.

[45] Priestley was the most prominent exception. See for example, Priestley, 1800; Schofield, 2004, 360-368.

[46] Cavendish was a notable exception. Although he described electricity as a fluid, he argued that both heat and electricity imparted motion to substances, facilitating chemical change. See for example, Cavendish, 1785, 380; Jungnickel and McCormmach, 1999, 282-295.

More specifically, in 1797 George Pearson published a set of experiments investigating the electrical decomposition of water in Nicholson’s newly minted journal.[47] Pearson was a respected English physician and chemist. In the early nineteenth century, however, he gained notoriety for his ill-founded, highly public, and mean-spirited priority dispute with Edward Jenner, the esteemed British physician who developed smallpox vaccine. Pearson’s biographer, Noel Coley, noted that “[h]is reputation was [irrevocably] damaged” by the affair.[48] Nevertheless, in 1801, Wollaston repeated Pearson’s experiments on the effects of passing multiple discharges through water. Wollaston argued that these investigations demonstrated that friction-based electricity produced the same kinds of chemical change as the voltaic pile: water was decomposed into hydrogen and oxygen.[49] This will be further discussed in section 3.2.[50]

Pearson modeled his research after experiments conducted in 1789 by the Dutch chemists, A. Paets van Troostwyk and J. R. Deiman, and the English instrument maker, John Cuthbertson.[51] Their apparatus has been schematically represented in Figure 3.1. A glass tube, *B*, was sealed at one end with a wire, *C*, and connected to an insulated brass ball, *A*. The brass ball was then placed a variable distance from the prime conductor of a

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[47] Pearson, 1797b; Pearson, 1797a.

[48] Norman Beale and Elaine Beale, "Evidence Based Medicine in the Eighteenth Century: The Ingenhousz-Jenner Correspondence Revisited," *Medical History* 49 (2005): 79-98; Noel G. Coley, "George Pearson, MD, FRS (1751-1828): The Greatest Chemist in England?" *Notes and Records of the Royal Society* 57 (2003): 161-175, 161.

[49] Wollaston, 1801.

[50] It is interesting to note that Faraday also repeated Pearson’s experiments in 1833. In contrast to Wollaston, Faraday argued that Pearson’s sparking apparatus did not in a strict sense cause “electro-chemical decomposition”. See, Faraday, 1833, 38-39.

[51] Snelders examines the reception of Trootswyk and Deiman’s research on the continent. See H. A. M. Snelders, "The Amsterdam Experiment on the Analysis and Synthesis of Water (1789)," *Ambix* 26, no. 2 (1979): 116-133.

friction machine, *P*. The tube was then placed in a trough filled with mercury, *D*, and filled with distilled water. A wire was inserted, through the mercury, into the bottom of the tube, *E*. This wire was then connected to one side of a Franklin square, *F*, while its opposing side was connected to the prime conductor of the friction machine.[52] By adjusting the distance between *A* and *P*, they controlled the intensity of sparks transmitted from the friction machine to the glass tube.[53]

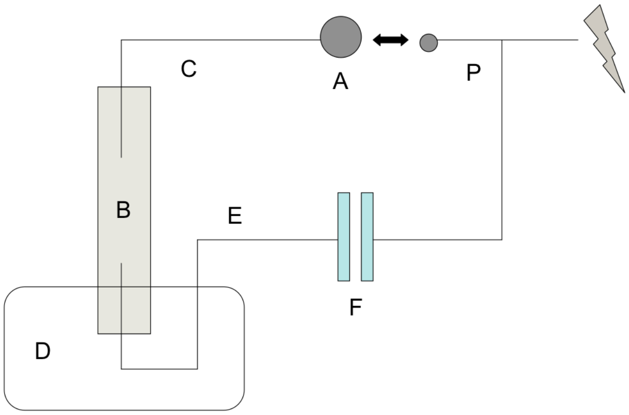

Figure 3.1: **A Schematic of Pearson's Experimental Apparatus for Sparking Water (1797).**

Troostwyk, Deiman, and Cuthbertson observed:

> When the brass ball and that of the prime conductor were in contact, no air or gaz was disengaged from the water by the electrical discharges; but on gradually increasing their distance from one another, the position was found in which gaz disengaged; and which ascended immediately to the top of the tube. By continuing the discharges, gaz [continued to form] till it reached to the lower extremity of [the tube], and then a discharge occasioned the whole of the gaz to disappear, a small portion excepted, and its place was consequently supplied by water [sic].[54]

They noted that as they increased the intensity of the electrical discharges the water was vaporized. Gas continued to form in the tube until very little of the original liquid remained. A visible spark then jumped through the vapor between the wires *E* and *C* in the tube and the gas immediately condensed, producing water.

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[52] For a description and discussion of a Franklin square, see chapter 2, 105-106.

[53] Pearson, 1797a, 142-143.

[54] Ibid, 143.

"Labouring with Mr. Cuthbertson, since he came to reside in London," Pearson extended these original experiments over a two-year period.[55] In particular, he was interested in chemically analyzing the gases produced by the alleged electrical decomposition of water, something Troostwyk and Deiman had not done, but there were two experimental difficulties to overcome. First, to collect any appreciable gas from water required the application of thousands of high intensity sparks over a prolonged period of time. For instance, Pearson and Cuthbertson found they obtained "15 sparks" on average for every twenty-five revolutions of "a thirty-four inch single plate electrical machine". Applying 1600 sparks to the water over the course of "three hours" only produced "a column of gaz [sic] two-thirds of an inch in length and one-ninth of an inch wide". Second, the high intensity discharges often shattered the glass tubing, ruining the experiment.[56]

To make the process more efficient and safe, they devised "a new method of disengaging gaz [sic] from water… by means of *uninterrupted* or *complete discharges*". First, they noted that water in large quantities behaved like a perfect conductor, whereas small amounts poorly transmitted charge. For example, fixing the distance between *A* and *P*, they found that if the tube was filled with air instead of water, twice as much electricity was passed through the tube and collected on the Leyden jar. While large amounts of air acted like an insulator, small quantities more readily allowed the transmission of electrical fluid. Thus, they tried incorporating small, measured amounts of air into tube with the water to minimize the number and intensity of sparks needed to

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[55] Ibid, 144.

[56] Pearson, 1797b, 144-145.

vaporize it. There were, however, drawbacks to this approach. As Pearson acknowledged, this made the chemical analysis of the trapped gases more challenging.[57]

Second, Pearson and Cuthbertson customized the sparking apparatus to produce more gas. Using trial and error, they modified each component in the apparatus, noting its effect. They observed that “the distance between the insulated ball, and the prime conductor, must always be less than the distance between the extremities of the wires”. If the distance between *A* and *P* was smaller than the spark gap in the tube, the discharge would not be of sufficient intensity to vaporize the water. If the distance between *A* and *P* was larger, the tube might break.[58] Furthermore, the wires “must be of a proper length and thickness” and “the tubes… of a [correspondingly] proper length and diameter”. Cuthbertson found that thin wires contributed to the apparatus’s fragility. He made a shorter tube, hermetically sealing a thicker wire in one end. He then changed the orientation of the tube, such that the closed, wired end was pointed downwards. In the open end, he inserted a brass funnel, added distilled water to the tube, and then attached a fitted “brass dish” over the funnel. This served as the other point of electrical contact. Pearson and Cuthbertson found, by varying the distance between the wire and brass funnel, that at “about one-twentieth of an inch… gaz [sic] will be produced at each discharge.”[59] Even with these modifications, Pearson advocated that interested

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[57] Ibid, 244-245.

[58] Ibid, 244.

[59] Ibid, 247-248; Pearson, 1797a, 145-146.

electricians procure “the power of a horse, to turn the electrical machines; the expense of labourers being considerable.”[60]

Using this machine and a mock-up of the Troostwyk-Deiman apparatus, they collected gas and conducted dozens of experiments on it. For example, Pearson sparked a sample of the gas. Not all of the gas was converted back into water. He then measured the diminution in gas volume and the amount of liquid produced by the “explosion”, and compared these results to the original known quantities of water and air used in the experiment. Although he expected there to be a small percentage of oxygen left over from the air, which Cavendish had shown consisted of approximately eighty percent nitrogen and twenty percent oxygen, the residual gas exceeded the original volume of air.[61] He then added a fixed quantity of nitrogen to the remaining gas and using the nitrous air test determined how much oxygen remained in aerial form. If less nitrous acid was produced than nitrogen added, he continued to add oxygen to the mixture until all of the nitrogen had been converted into nitrous acid. If there was still residual gas, Pearson added more oxygen and then sparked the remaining airs one more time. He found that, even in this late stage of the experiment, water was often produced.[62]

This suggested that hydrogen and oxygen gas were emitted separately from the water, but that not all of the gas was converted back into water after sparking. Upon the addition of nitrogen, nitrous acid, a compound of nitrogen and oxygen, was produced. This indicated that the residual oxygen was free to form new compounds. This was an

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[60] Pearson, 1797b, 244-248. Pearson, 1797a, 147.

[61] Cavendish, 1784a.

[62] Pearson, 1797b, 302-304.

important point. Ordinary forms of heating, like boiling water over a candle's flame, produced water vapor or steam not discrete gases. Electricity, in contrast, could be used to decompose complex liquids or encourage different chemical combinations of elements to form.[63] (It is interesting to note that Pearson did not comment on the order of chemical combinations, i.e. why sparking a mixture of nitrogen, oxygen, and hydrogen gases formed nitrous acid first and then water.)

Pearson contended that these experiments showed that electricity had combined with the elements of water, producing two unique compounds: hydrogen and oxygen gas.[64] Franklin had proposed that electricity, like heat, was self-repulsive. It acted in concert with other substances to produce the various states of matter, e.g. a gas was a material with a high density of electrical fluid (or heat).[65] Although Lavoisier did not discuss electricity, he assigned caloric the same basic qualities. It was a self-repulsive material attracted to the particles of ordinary matter. The amount of caloric within a substance determined both its temperature and state.[66] Pearson, an early supporter of Lavoisier's theory of heat in Britain, was uninhibited by earlier theories likening electricity to phlogiston. For Pearson, electricity was just as Franklin had described, i.e. it was similar to Lavoisier's caloric. Thus, he argued that these experiments demonstrated

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[63] Ibid, 353.

[64] Coley, 2003, 165-166.

[65] Franklin, 1751, 39.

[66] Beretta, 2001; Lavoisier, *Elements of Chemistry [1789]*, 78; Lavoisier and LaPlace, *Heat*.

that electricity acted like a form of concentrated heat, so high in temperature that standard thermometers could not measure it.[67] He asserted:

> The fire of the electric discharge, in a very condensed state […] interposes betwixt the constituent elements of the ultimate and invisible particles of water, that is, betwixt the hydrogen and oxygen, of which water is compounded, so as to place them beyond the sphere of their chemical attraction for one another; and each ultimate particle of hydrogen and of oxygen uniting with a determinate quantity of [this electric] fire [form] new compound… particles, consisting of hydrogen and caloric, and of oxygen and caloric, that is, hydrogen gaz and oxygen gaz [sic]…[68]

Therefore, electricity chemically interacted with the components of water, first fracturing the compound, its force of self-repulsion being greater than the "cohesive attraction" between hydrogen and oxygen. It then re-combined with each element to form hydrogen gas and oxygen gas respectively.[69]

To further support his theory, Pearson concluded with a discussion of what happened when a mixture of hydrogen and oxygen gas was sparked. He noted, that during the process of synthesis, an extremely bright light was emitted. He speculated "[that] the ultimate particles of these gazes [sic] nearest to the flame are drivers from it in all directions, as from a centre, by the interposition of fire, or of caloric and light; so that they are brought within the sphere of their chemical attraction". In other words, with the addition of more concentrated heat or electricity, the caloric united to the gas was pushed farther away from the gas. If hydrogen and oxygen were near each other when this occurred, they would "unite, and the caloric and light, [now being fully] disengaged by that union, [would move outwards,] act[ing] in a similar manner… producing union

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[67] Pearson, 1797b, 304-305, 349-350.

[68] Ibid, 349.

[69] Ibid, 350.

among the next set [of gas particles] in order of proximity". If the spark did not contain an adequate density of electrical or caloric particles, this collection of cascading reactions would end prematurely and only some of the gas mixture would be converted back into water.[70]

Pearson questioned whether he had presented sufficient evidence to support his claims. He recognized that there was a second possible explanation as put forth by Cavendish, namely that the "two gazes [sic] consist of water and [some other] imponderable matter; and that during combustion the water is precipitated". He thought this view to be less likely, given the numerous arguments in favor of caloric.[71] He noted, however, the inadequacy of chemical research in deciding between the two theories: "chemistry, in its present state, ought not to pretend to vie with mathematical philosophy in its demonstrations". Most of the changes taking place within sparked matter were occurring between "hydrogen and oxygen, which are ponderable" and "caloric, and perhaps light [or some other material], which are imponderable." He remarked: "I cannot perceive, by the senses, the existence of the composition of gazes [sic] just stated, nor of their decomposition", but through "the art of observation, and the invention of artifices for rendering the properties of matter evident to the senses", one can "advance" in understanding and "knowledge of facts" about the natural world.[72] He argued, until more was known about electrical decomposition, "opinion must be adopted on the side of

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[70] Ibid, 350-351.

[71] Ibid, 352.

[72] Ibid, 355.

which the evidence preponderates according to the laws of reasoning in physical science." In short, Pearson asserted: electricity was a form of caloric.[73]

Cavendish and Priestley both argued that dephlogisticated air (oxygen) was water deprived of its phlogiston and that inflammable air (hydrogen) was either phlogiston or water with phlogiston. When the two gases entered into chemical combination, the inflammable air compensated for the dephlogisticated air's diminished phlogiston, and water was produced. In contrast, Pearson asserted, like Lavoisier, that water was a compound of oxygen and hydrogen. Electricity converted it into two discrete gases by separating and chemically combining with water's components. Both explanations, however, stressed the existence a form of "imponderable" matter in water and its different states.

3.1.3 - Water, A Source of Oxygen and Electricity

> [I]t seems extremely mysterious how the oxygen should pass silently from the extremity of the silver wire [connected to the silver or negative end of the pile] to that of the zinc wire [connected to the zinc or positive end of the pile], and there make its appearance in the form of a gas. It is to be observed likewise, that this effects takes place which ever way the wires are placed, and whatever bends may be interposed between their extremities, provided the distance be not too great.[74]
>
> William Cruickshank (1800)

Whether electricity existed as caloric, phlogiston, or a material onto itself, the idea that it chemically combined with other elements gained additional currency with the invention of the pile. In 1800, news of the pile, its electricity, and its chemical agency

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[73] Ibid, 352.

[74] Cruickshank, 1800, 257.

rapidly spread.[75] In 1789, Lavoisier had listed thirty-three chemical elements, including light and caloric. It is noteworthy that by 1815, eighteen new elements had been discovered, seven by electrical decomposition.[76] Unlike Pearson's apparatus, the pile was easy to reconstruct and its effects so pronounced that many chemists immediately began to experiment with it. Nicholson's journal quickly became a central distribution node for articles written by interested British electrochemists. In the first six months alone, he published eleven essays on the chemical agency of voltaic electricity.

Like many of his British colleagues, William Cruickshank, a friend of Nicholson's and professor of chemistry at the Royal Military Academy in London, began experiments with the pile in 1800.[77] His investigations represented the first systematic study of the pile's chemical effects in Britain. Davy and William Henry often cited Cruickshank's research. Their experiments will be discussed in the following two sections.[78]

Cruickshank first replicated Nicholson and Carlisle's experiments using a battery composed of pairs of silver and zinc, separated by cardboard soaked with muriate of ammonia (ammonium chloride). He attached silver wires to each end of the pile. Using Cruickshank's convention, I will refer to the wire connected to the positive end of the pile as the "zinc wire", and the lead attached to the negative end as the "silver wire".

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[75] Pancaldi, 2003, chapter 7, "Appropriating Invention: The Reception of the Voltaic Battery in Europe", 213.

[76] Lavoisier, *Elements of Chemistry [1789]*; Eric Scerri, *Periodic Table: Its Story and Its Significance* (Oxford: Oxford University Press, 2007), 5-10.

[77] Cruickshank, 1800, 187.

[78] See for example, Davy, "Early Miscellaneous Papers," 175, 190, 203, 211, etc; William Henry, "Experiments on the Chemical Effects of Galvanic Electricity," *Nicholson's Journal* 4, no. August (1800b): 223-226, 224.

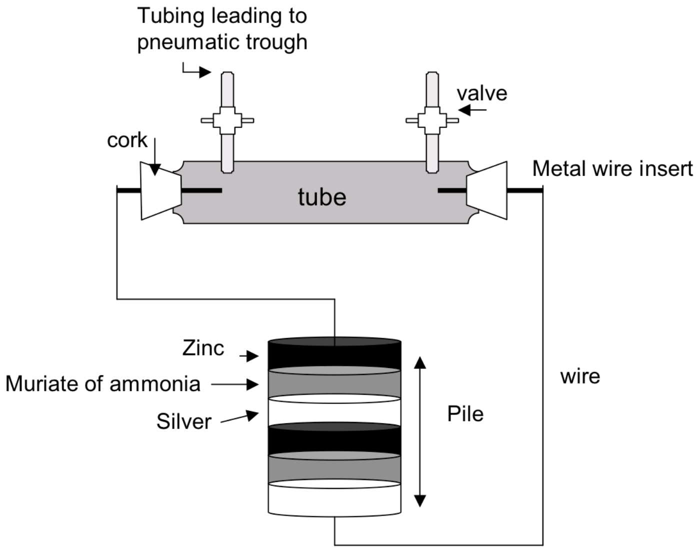

Figure 3.2: **A Schematic of Cruickshank's Primary Apparatus (1800).**

Cruickshank then inserted one wire through each end of a tube filled with distilled water. (Figure 3.2) Like Nicholson and Carlisle, he found that hydrogen and oxygen gas were emitted separately: hydrogen in the region nearest the silver wire and oxygen in the area closest to the zinc wire.[79]

Repeating the experiment with water mixed with a "tincture of Brazil wood", a vegetable dye, which changed color in the presence of a base, he observed that:

> …the fluid surrounding the silver wire, particularly towards its extremity, became purple, and this tinge increased so fast, that the whole fluid surrounding this wire, and occupying the upper part of the tube, soon assumed as deep a colour, as could be produced by ammonia [a strong base]. The portion of the fluid in contact with the zinc wire became very pale, and almost colourless, nor could the purple tinge extend below its upper extremity.

In addition to documenting the location and spread of the color change, he observed that the zinc wire slowly dissolved into the liquid, corroborating Nicholson and Carlisle's observations. As Cruickshank noted, these results strongly suggested that "an acid […]

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[79] Cruickshank, 1800, 187-189.

[was] produced at the wire proceeding from the zinc [end of the pile], and an alkali" near the silver wire.[80]

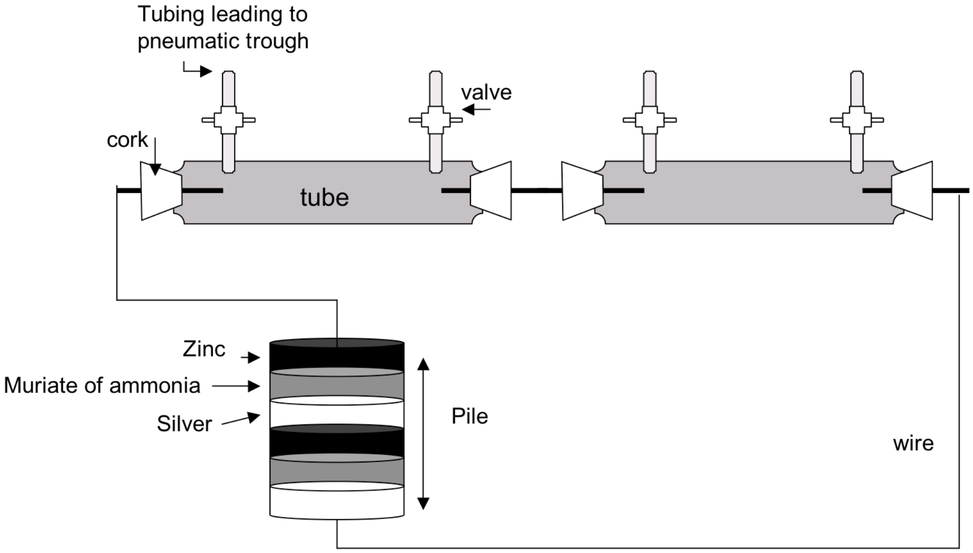

Figure 3.3: **A Schematic of Cruickshank's Secondary Apparatus (1800).**

"In order to ascertain how far [the galvanic] influence might be carried", Cruickshank modified the existing apparatus. (Figure 3.3) He filled two tubes with distilled water and connected them to each other by a single metallic wire inserted through adjacent cork stoppers. As in the original experiment, each end of each tube was then connected in a similar manner to the pile. He found that "[a] quantity of [hydrogen] gas as usual was disengaged at the extremity of the silver wire […], and [that a] portion of the connecting wire in the same tube was partly dissolved". In the second tube, the zinc wire "corroded", while oxygen gas evolved near its connecting wire.[81] This showed that effects of voltaic electricity could be carried by conductors from one vessel to the

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[80] Ibid, 189.

[81] Ibid, 190.

next and further reinforced Nicholson and Carlisle's interpretation that electrical decomposition occurred primarily at or near the wires in solution.

Cruickshank then began a series of tests to determine what controlled the amount and kind of gas production. He noted: "It is a well known fact, that hydrogene gas when heated, or in its nascent state, reduces the calces of the metals." In other words, placing a metal oxide in a hydrogen rich environment and applying heat caused combustion, producing a metal, oxygen gas, and water. He hypothesized that if he used a "metallic solution", i.e. a metal oxide dissolved in water, the hydrogen gas produced near the silver wire, having been heated by pile's electricity, would interact with the metal oxide to produce metal, oxygen gas, and water. This would effectively increase the amount of oxygen gas produced by electrical decomposition.

Using the apparatus described in Figure 3.2, he "fill[ed] the glass tube with… acetite of lead" (lead acetate) and repeated the experiment. He was surprised by the results:

> When the communication was made in the usual way, no gas could be perceived, but after a minute or two, some fine metallic needles were perceived at the extremity of the wire connected with the silver. These soon increased, and assumed the form of a feather, or rather, that of the crystals of the muriate of ammonia. The lead thus precipitated was perfectly in its metallic state… a little gas escaped from the [zinc] wire… and it was considerably corroded as usual.[82]

With the electrical decomposition of aqueous lead acetate, Cruickshank had expected an increase in the production of oxygen gas. Instead, he found that lead was pulled out of the solution, forming a crystallized structure on the silver wire, and that no gas was produced

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[82] Ibid, 189.

near the silver wire. The zinc wire continued to rapidly corrode, emitting only small amounts of oxygen gas. He repeated this experiment with a variety of different metallic solutions, such as “sulfate of copper” (copper sulfate) and “silver in nitrous acid”, which formed “the most beautiful precipitate… as in the Arbor Dianæ”, a crystal resembling a conifer. In each case, a precipitate formed on the silver wire, no hydrogen gas evolved, and little oxygen gas was produced.[83]

He repeated these experiments several times with different metallic wires, filling the tube with distilled water, tap water or a metallic solution. He found that the results varied with the conducting material used to connect the pile to the external solution. Table 3.2 summarizes his most salient observations.

For example, filling the tube with distilled water, he found that “when the gases obtained by [connecting the tube to the pile via] gold or platina [platinum] wires, [were] collected together and exploded over mercury, the whole nearly disappear[ed] and form[ed] water, with probably a little nitrous acid.” When silver, zinc or tin wires were placed in distilled water and attached to the pile, “a small portion of oxygenous gas [was] likewise given out, but the wire itself [was] either oxydated or dissolved, or partly oxydated and partly dissolved”. Filling the tube with tap water and using silver wires, he found that other gases were also produced. Chemical analysis of these vapors yielded hydrogen gas, oxygen gas, and muriate of silver (silver chloride). (There was likely a little salt in the solution.)[84] When “metallic solutions [were] employed instead of water, the same wire which separates the hydrogen revives the metallic calx, and deposits it at

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[83] Ibid, 190.

[84] Ibid, 188.

the extremity of the wire in its pure metallic state; in this case no hydrogen gas [was] disengaged." The type of wire used did not affect these results.[85]

Conducting Material		Intermediary Solution	Chemical Changes Observed	
Negative Wire	Positive Wire		Negative Wire	Positive Wire
Gold	Gold	Distilled Water	Hydrogen gas	Oxygen gas; (Nitrogen gas; Nitrous Acid)
		Water	Hydrogen gas; Ammonia*	Oxygen gas; Nitrous acid
		Lead Acetate	Lead precipitate	Oxygen gas
Platina	Platina	Distilled Water	Hydrogen gas	Oxygen gas; (Nitrogen gas; Nitrous Acid)
Silver	Zinc	Distilled Water	Hydrogen gas	Oxygen gas; Zinc oxide
Silver	Silver	Distilled Water	Hydrogen gas	Oxygen gas; Silver oxide
Silver	Silver	Water	Hydrogen gas; Ammonia*	Oxygen gas; Muriate of Silver gas; Silver oxide
Silver	Silver	Lead Acetate	Lead precipitate	Oxygen gas; Silver oxide
Silver	Gold	Distilled Water	Hydrogen gas	Oxygen gas
Gold	Silver	Distilled Water	Hydrogen gas	Oxygen gas; Silver oxide

Table 3.2: **Summary of Cruickshank's experiments.** Cruickshank investigated the relationship between the conducting material connecting the pile to the external solution and the chemical changes observed at each lead.

*Although a second gas smelling similar to ammonia was detected, there was not enough gas to chemically analyze.

Cruickshank's explanation for these phenomena focused on the interaction of oxygen in aqueous solution and electricity. More specifically, he drew on Lavoisier's generally accepted account of combustion, that metals possessed a stronger affinity for oxygen than caloric, as a model for considering the movement of electric fluid and its chemical effects. He wrote:

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[85] Ibid, 257.

> …it appeared to me, that the easiest and simplest mode of explanation [for these phenomena], would be, to suppose that the galvanic influence (whatever that may be) is capable of existing in two states, that is in an oxygenated and deoxygenated state. That when it passes from metals to fluids containing oxygen, it seizes their oxygen, and becomes oxygenated; but when it passes from the fluid to the metal again, it assumes its former state, and becomes deoxygenated. […] the [galvanic] influence enters [the fluid] from the silver side deoxygenated… it seizes the oxygen of the water [or from the metal oxide], and disengages the hydrogen [or metal], which accordingly appears in the form of gas [or crystal]; but when the influence enters the zinc wire, it parts with the oxygen, with which it had formerly united, and this either escapes in the form of gas, unites with the metal [wire] to form an oxyde, or, combined with a certain portion of water, &c. may… form nitrous acid.[86]

Cruickshank hypothesized that electrical fluid was capable of existing in both an elemental or pure state and in combination with oxygen. His experiments suggested that electricity possessed a strong affinity for oxygen in water (or metallic solutions) while metals, not in solution, had a stronger affinity for oxygen than electricity. From the silver end of the pile, electrical fluid entered the water (or metallic solution). There it separated the water (or metallic solution) into its components: hydrogen (or metal) and oxygen. It chemically combined with the oxygen and hydrogen gas evolved (or a metal precipitate formed). It then traveled through the solution to the zinc wire. There it disposed of its oxygen, which was either released as a gas or if the wire was an oxidizable substance it combined with the material of the wire to form a metal oxide or if there were other free elements present in the solution, like nitrogen, an acid formed. Having deposited its oxygen, the electrical fluid then flowed unimpeded in its elemental state back to the pile.

Cruickshank's study emphasized water's susceptibility to electrical decomposition, the production of hydrogen (or metal precipitate) and oxygen, and the

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[86] Ibid, 257-258.

apparent predilection of electricity to combine with aqueous oxygen particles. He extended his theory to the pile. Nicholson and Carlisle also observed chemical changes taking place along the layered surfaces of the battery.[87] Cruickshank witnessed similar alterations in his own pile. For example, the zinc plates became oxidized along their wet face and bubbles formed. He hypothesized that the changes observed by applying electricity to external solutions might also be occurring inside the pile. Perhaps electricity was also pushed and pulled through the pile by differences between its affinity for oxygen and that of other materials. He noted that solutions not rich in oxygen, such as alcohol and oil, were unaffected by voltaic electricity, lending credence to his suppositions.[88]

Cruickshank's account of the pile's chemical effects combined the late eighteenth-century British electrical discourse with Lavoisier's chemistry. Priestley and Pearson's experiments suggested that electricity, a form of heat, could chemically combine with elements to produce new compounds. In particular, Pearson's research indicated that electricity could be used to decompose water into its components. The electrical fluid then recombined with its elements to form hydrogen and oxygen gas. Lavoisier's research on heat further suggested that subtle fluids, like caloric, behaved similarly to ordinary matter: caloric was an element, which entered into unique chemical combinations with substances as evidenced by the different amounts of heat required to produce temperature and state changes. Cruickshank drew on these two traditions to propose that electricity traveled through solutions via a series of chemical changes. He

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[87] Nicholson and Carlisle, 1800, 183-185.

[88] Cruickshank, 1800, 258.

reasoned that the oxygen responsible for the corrosion and calcination of the zinc wire originated with the electrical decomposition reaction occurring at the silver wire. According to its affinity, electrical particles then combined with free oxygen particles and (somehow) passed through the solution to the zinc wire. He admitted that this transference of oxygen from the silver wire to the zinc wire was somewhat “mysterious”. At the zinc wire, the electrical fluid released its oxygen to substances more favorably disposed to absorb it, resulting in the formation of a gas, an acid and/or an oxide. In contrast to Franklinist theories, however, he postulated that electricity flowed from the silver or negative wire to the zinc or positive lead. Cruickshank freely admitted that he was “not… intirely satisfied” with this “hypothesis”, but hoped that such speculations would “incite” others “to make experiments” and “reason upon the subject”.[89]

3.2 - Humphry Davy’s Early Experiments with the Pile

> Considering these Essays dispassionately after a lapse of forty years, the chief fault of them was, decidedly, that which their Author [my brother, Humphry Davy] almost immediately perceived, namely hastiness of generalization, - and the apparent presumption indicated by it. As regards the speculations themselves in which they abound, though some of them were ingenious and may be true, many of them it must be allowed, were wild, and probably visionary; but, on that account, they are not uninstructive; they strongly shadow forth the infant mind of the Philosopher…[90]
>
> John Davy (1839)

Humphry Davy led a tumultuous and energetic life.[91] In 1795, he was indentured to an apothecary in Penzance in Cornwall, England, a popular seaside resort for people

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[89] Ibid, 258-260, 258.

[90] Davy, 1839a, 3.

[91] The literature on Davy is large. For an overview of his life and science, see, for example, June Fullmer, *Young Humphry Davy: The Making of an Experimental Chemist* (Philadelphia: American Philosophical

afflicted with tuberculosis. There he met Thomas Wedgwood and Gregory Watt, the sons of Josiah Wedgwood and James Watt, influential members of the Lunar Society. Both young men suffered from consumption. Like Davy, they were also broadly interested in natural philosophy and the three quickly became friends. In addition to these important connections, Davy also met Dr. Thomas Beddoes, a physician and pneumatic chemist who, impressed with Davy's scientific acumen, hired him to work as an assistant at the Medical Pneumatic Institute in Bristol in 1798.[92] Under Beddoes' tutelage, Davy conducted experiments on the composition and physiological effects of various gases, such as nitrous oxide (laughing gas) and carbon monoxide, often testing these airs on himself to the detriment of his long-term health. While in Bristol, he also became friends with Samuel Coleridge and Robert Southey, and began seriously to write poetry.[93] He simultaneously began to conduct research on heat and electricity.

In 1799, he formally entered the natural philosophic community with his controversial *Essay on Heat, Light, and the Combinations of Light*. Extending Count Rumford's experiments on the physicality of heat, Davy argued that caloric was not a material per se, but rather an effect of corpuscular motion.[94] With Priestley's

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Society, 2000); Ronald King, *Humphry Davy* (London: Royal Institution, 1978); David Knight, *Humphry Davy: Science and Power* (Oxford: Blackwell, 1992a).

[92] Pancaldi examines Beddoes influence on Davy's early experiments with the battery. See Pancaldi, 2009.

[93] See, for example, Richard Holmes, "The Coleridge Experiment," *Proceedings of the Royal Institution of Great Britain* 69 (1998): 307-323; Trevor H. Levere, "The Lovely Shapes and Sounds Intelligible: Samuel Taylor Coleridge, Humphry Davy, Science and Poetry," in *Nature Transfigured: Science and Literature, 1700-1900*, ed. John Christie and Sally Shuttleworth (Manchester, 1989), 85-101.

[94] Davy was convinced of the truth of Rumford's theory by a simple experiment. He brought two pieces of ice into contact in a cold environment using insulated metal clamps, and through friction alone melted the surface of the ice. Because there was no external source of caloric, there was no transfer of material heat. Therefore, the heat, which caused the ice to melt, must have come from the motion/friction of the ice cubes. See, Davy, 1839a, 10-12.

endorsement and encouragement, Davy also continued to investigate respiration, focusing on how light and different gases affected the growth and health of plants.[95] He also started a sophisticated research program analyzing the chemical effects of the voltaic pile. It was to become a life-long interest and pursuit.

As David Knight, one of Davy's biographers, remarked: "one of the ways in which sciences came to rival the churches in the nineteenth century was as vehicles for social mobility."[96] This was especially true for Davy. Through his electrochemical research, he earned independence and fame. In 1801, at the age of twenty-two, he was elected a member of the Royal Society and promoted to professor of chemistry by Rumford at the newly established Royal Institution, an organization founded to foster scientific research and education. In 1805, he won the Royal Society's Copley Medal and in 1807, the Napoleon Prize from the French Academy of Sciences, amongst other accolades. In 1812, he was knighted. In 1819, he received a baronetcy for his invention of the miner's safety lamp and, after the death of Joseph Banks in 1820, Davy was elected President of the Royal Society.[97]

At the pinnacle of his profession, however, Davy's health deteriorated and he became an increasingly difficult personality. In 1813, after a chemical accident damaged his eyesight and he dismissed his aide, he hired Michael Faraday as a research assistant. Davy's illness and administrative duties left him with little time for original research. As

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[95] Knight, 1992a, 23-25.

[96] Ibid, 2.

[97] Fullmer, *Young Humphry Davy: The Making of an Experimental Chemist*, 347-355; Knight, 1992a, 139-153; David Knight, "Humphry Davy: Science and Social Mobility," *Endeavour* 24 (2000): 165-169; Julianne Tuttle, "The Battery as a Tool of Genius in the Work of Humphry Davy," *Nuova Voltiana* 5 (2003): 105-116.

Faraday's career advanced, Davy grew more cantankerous and they became personally and professional estranged. Priority disputes with Faraday and other members of the Royal Society further contributed to his turbulent presidency.[98] In 1829, he died "one of the most respected and most disliked men of science".[99]

Historians have characterized Davy (like Priestley) as a brilliant experimentalist whose research was over shadowed by the theoretical contributions of his colleague, Michael Faraday (or in Priestley's case, Lavoisier). As with comparisons of Priestley and Lavoisier's work, Davy and Faraday's scientific practice appears incommensurable: Davy was a chemist while Faraday was a physicist.[100] Such anachronistic stereotyping, however, skews our understanding of the study of electricity, an area of research, which spanned both fields of inquiry in the early nineteenth century.[101]

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[98] Knight, 1992a, 121-138; David Phillip Miller, "Between Hostile Camps: Sir Humphry Davy's Presidency of the Royal Society of London, 1820-1827," *British Journal for the History of Science* 16 (1983): 1-47. Alan Hirshfeld, *The Electric Life of Michael Faraday* (New York: Walker & Company, 2006), 82-88.

[99] Knight, 1992a, 1.

[100] See, for example, Joseph Agassi, *Faraday as a Natural Philosopher* (Chicago: University of Chicago Press, 1971); Geoffroy Cantor, *Michael Faraday: Sandemanian and Scientist: A Study of Science and Religion in the Nineteenth Century* (New York: St. Martin's Press, 1991); Darrigol, *Electrodynamics from Ampere to Einstein*, 16-23. As Gooding, James, and Knight have observed, the idea that Faraday is best described as a physicist rather than as a chemist developed in the late nineteenth century and persists today, in part, because Faraday's electrical studies profoundly affected physics, e.g. through the conceptual development of electromagnetic fields, and engineering, e.g. motors and generators. See, for example, David Gooding and Frank James, "Introduction," in *Faraday Rediscovered: Essays on the Life and Work of Michael Faraday, 1791-1867* (New York: Stockton Press, 1985), 1-13; David Knight, "Davy and Faraday: Fathers and Sons," in *Faraday Rediscovered: Essays on the Life and Work of Michael Faraday, 1791-1867*, ed. David Gooding and Frank James (New York: Stockton Press, 1985), 33-50, 33-39.

[101] Steinle and Gooding, for example, discuss the different influences on Faraday's work and his experimental methods, both physical and chemical, documented in manuscript and laboratory notebooks. See, David Gooding, ""In Nature's School": Faraday as an Experimentalist," in *Faraday Rediscovered: Essays on the Life and Work of Michael Faraday, 1791-1867*, ed. David Gooding and Frank James (New York: Stockton Press, 1985), 105-135; Steinle, "The Practice of Studying Practice: Analyzing Research Records of Ampere and Faraday."

Davy, for example, considered himself to be not only a practicing chemist, but also a natural philosopher.[102] Unlike Priestley, whose dogged adherence to phlogiston theory garnered criticism, Davy has been charged with inconstancy in his attempts to develop an overarching theory of electrochemistry. For instance, Helge Kragh contends that Davy vacillated between a chemical interpretation of the pile's electricity and contact theory.[103] Although Davy modified his ideas in light of natural philosophic considerations, I argue that he maintained a chemical theory of electricity throughout his career.[104] His so-called conversion to contact theory was neither a simple nor complete endorsement of Volta's fluid dynamics.[105] Taking Davy's assertions about his practice seriously, that physics and chemistry should work in tandem to account for electrical phenomena, the following sections examine his more radical interpretation of experiments conducted early in his career between 1800 and 1802.[106]

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[102] See, for example, Davy, 1807, 44-48; Davy, "Early Miscellaneous Papers," 312, 315; David Knight, "Romanticism and the Sciences," in *Romanticism and the Sciences* (London: Cambridge University Press, 1990), 13-24, 15-22.

[103] Kragh, 2000a.

[104] Davy, in his later years, became increasingly religious and, like Priestley, looked for unifying principles that would simplify the relationships between complex phenomena. Although highly critical of *naturphilosophie* and German romanticism, Davy nonetheless increasingly appealed to a more holistic model of nature. More and more often, he also alluded to a spiritual essence in matter, saying only God knew the cause of cohesion and electrochemical effects. See, for example, Knight, "Humphry Davy: Science and Social Mobility"; Trevor H. Levere, "Humphry Davy: Romantic and Dynamical Chemistry: Electrical Ideas About Affinity," in *Affinity and Matter : Elements of Chemical Philosophy, 1800-1865* (Yverdon, Switzerland ; Langhorne, Pa.: Gordon and Breach Science Publishers, 1993), 23-67.

[105] See, for example, Davy, 1807, 44-48.

[106] This chapter significantly differs from Fullmer's analysis of Davy's early experiments in two ways. First, my intention is to place Davy within the broader context of the history of electricity. Second, I am interested in analyzing the methods chemists employed to learn more about the inner workings and effects of the pile, and how Davy's research compared with those studies. Fullmer's account is by design biographical and, although she discusses Davy's electrochemical experiments in some detail, her motivation for doing so is different. She is interested in analyzing how an ill-educated, young man came to be a respected experimental chemist and professor at the Royal Institution. Her narrative provides insight into Davy's career and scientific practice. Fullmer, *Young Humphry Davy: The Making of an Experimental*

In 1800, Davy acquainted himself with Volta's essay, announcing the invention of the pile and a brief description of contact theory, and the existing electrochemical literature. Cavendish, Priestley, and Pearson advocated that water was composed of two elements – hydrogen (inflammable air) and oxygen (dephlogisticated air) – and a form of imponderable matter. More specifically, Priestley argued that water was a conductor because it contained phlogiston, a form of electricity, while Pearson asserted that electricity was concentrated caloric, capable of fracturing water into two discrete gases. While Volta emphasized differences in the conducting powers of metals in the pile, Nicholson, Carlisle, and Cruickshank's experiments reinforced the relationship between voltaic electricity, water, and water's components. Cruickshank's investigations, in particular, suggested that electrical fluid had an affinity for oxygen in aqueous solution. Interested in further analyzing the pile's chemistry, Davy began his study by replicating and extending Cruickshank's experiments examining the materials formed at the silver and zinc wires respectively. Because Davy used Cruickshank's convention of referring to the wire connected to the negative end of the pile as "silver" and the wire connected to the positive end of the battery as "zinc", I will also continue to use this terminology.

Cruickshank hypothesized that the electrical decomposition reaction occurring at the silver wire in water was the source of oxygen observed at the zinc lead. To test the validity of Cruickshank's supposition, Davy's "first researches were directed towards ascertaining if oxygen and hydrogen could be separately produced from quantities of

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Chemist, 3-8, 284-320; Iwan Rhys Morus, "Review: The Making of an Experimental Chemist," *Isis* 93 (2002): 306-307.

water not immediately in contact with each other."[107] He constructed a pile consisting of "110 pairs metallic plates" of silver and zinc "with pieces of cloth" dampened "with [a] solution of green sulphate of iron" (iron II sulphate).[108] Like Cruickshank, he experimented with the effects of connecting the pile to external solutions with different conducting materials. In addition to using metallic wires made of gold, silver, and zinc, he also tried "muscular fibre, living vegetable fibre, or a moistened thread". He also used his own body, e.g. touching the pile with one hand while placing the other hand in solution, and recorded the sensations he experienced. He found there were advantages to using non-metallic, organic conductors: they were relatively inexpensive compared to some of the more inert metals, like gold, and less likely to react with the solution than zinc or silver.[109]

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[107] Humphry Davy, "An Account of Some Experiments Made with the Galvanic Apparatus of Signor Volta," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839b), 139-149, 140.

[108] Ibid, 139-140.

[109] As Fullmer notes, it was very common for scientists of this period to consider themselves as viable and useful pieces of laboratory equipment, and to participate physically in experiments. For example, in his letter announcing the invention of the pile, Volta discussed the experiments he had conducted on his own body with the apparatus. Nicholson reported that Volta had attached metal wires to each end of the pile and placed one lead in each ear: "A peculiar sound, like crackling or boiling, was heard; but the author did not think it prudent to make this experiment repeatedly." Fullmer, *Young Humphry Davy: The Making of an Experimental Chemist*, 6. See also, Davy, 1839b, 140-143; Nicholson and Carlisle, 1800, 181; Volta, 1800.

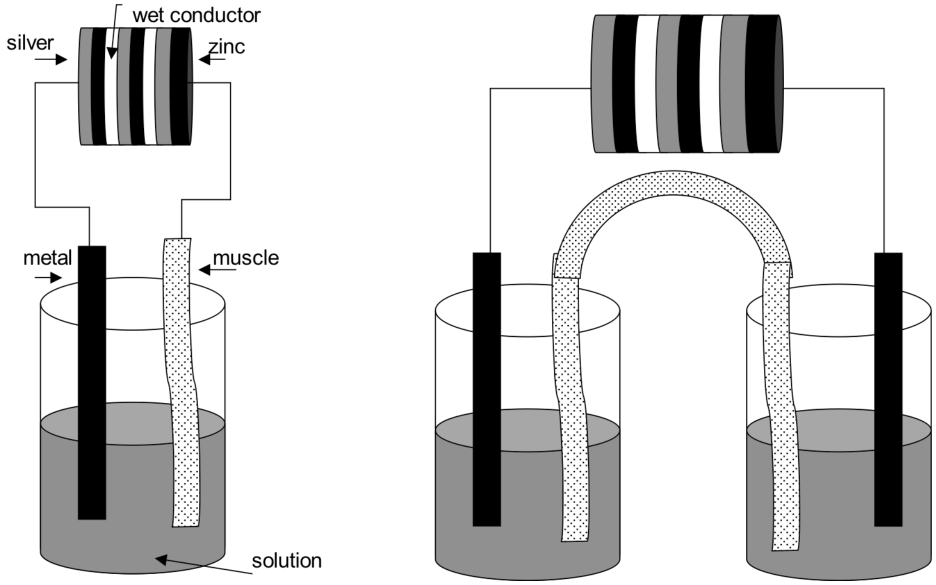

Figure 3.4: A schematic of two of Davy's experiments involving the pile. In the left hand image, using wire, a metal plate was attached to the silver side of the battery and a strip of muscle tissue to its zinc end. In the right hand diagram, a strip of animal fiber connected two glasses, filled with water. A metal plate was placed in the leftmost dish and attached to the silver side of the battery with wire. A metal bar was then placed in the rightmost glass and attached to the zinc end with wire, closing the circuit.

More specifically, Davy tried a series of different experimental set-ups, depicted in Figure 3.4. For example, he procured two glass dishes filled with distilled water and two silver wires. He attached one wire to the silver end of the pile and placed its free end in the first container of water, denoted the "silver dish". He then attached the second wire to the pile's zinc extremity and placed its free end in the second dish of distilled water, designated the "zinc glass". He then completed the circuit with his own body by placing one hand in the silver dish and the other in the zinc glass. Although he experienced pain and discomfort, Davy noted that no permanent damage was done to his hands. He also observed that no gas was emitted on or near his hand in either liquid, whereas at the silver wire, copious quantities of gas evolved, and the zinc wire "calcine[d] very fast [and] white clouds diffus[ed] themselves from it through the water."[110]

He repeated the experiment with frog sinew, in lieu of his own body, and captured and analyzed the gases evolved. He found that, at the silver wire, hydrogen gas was produced and, at the zinc wire, a mixture of oxygen and nitrogen gas evolved. He also found that the zinc glass contained nitrous acid. He suggested that the presence of nitrogen and nitrous acid came from the absorption of common air into the water during the experiment. (William Henry demonstrated in 1803 that the amount of gas dissolved in water was proportional to the gas pressure at the surface of the liquid.[111]) Davy repeated the experiment after boiling the distilled water, to remove any extraneous, dissolved gas, and placing it under a glass shield to limit its exposure to air. He found by applying current to the solution for seven hours that "the water connected with the zinc had given out twenty seven grain measures of oxygen apparently pure; from the water connected with the silver, fifty-seven measures of hydrogen had been extricated."[112] (Cavendish and Lavoisier independently showed and it was generally accepted that two volumes of hydrogen combined with one volume of oxygen to form water.)

"Having thus ascertained that oxygen and hydrogen, nearly in proportions required to form water, could be separately produced from quantities of water, having no communication with each other, except by means of the dry metallic conductors and muscular fibre", Davy "next endeavoured to ascertain, if the contact of the metallic wires,

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[110] Davy, 1839b, 140-143, 140.

[111] William Henry, "Experiments on the Quantity of Gases Absorbed by Water, at Different Temperatures, and under Different Pressures," *Phil. Trans.* 93 (1803): 29-42 and 274-276.

[112] Davy, 1839b, 140-143, 143.

with the metallic plates of the apparatus were essential to the effect."[113] He attached a silver wire to the silver end of the pile and placed its opposite end in a dish of distilled water. With one hand, he touched the pile's outermost zinc plate and placed his opposite hand in solution. Although no gas was produced on or near his hand, abundant quantities of gas evolved from the silver wire. He then reversed the points of contact, connecting the zinc end of the pile to the solution with a silver wire and placing one hand in solution while touching the negative or silver end of the pile with his other hand. Again no gas evolved in the region near his hand. At the positive wire, however, the metal immediately calcined and gas evolved. Repeating these experiments with frog sinew, in lieu of his own body, and capturing and analyzing the gases evolved, he found that a silver wire and zinc tendon produced only hydrogen gas at the silver wire. When a silver sinew and a zinc wire were employed, the zinc wire calcined and corroded, and oxygen gas evolved. No gas was produced at the silver fiber. He then tried connecting the pile to the distilled water using only sinew. He attached one fiber to the silver end of the pile and a second tendon to the zinc end of the battery. He then lowered each free end of muscular fiber into a glass of distilled water. No gas was produced.[114]

Davy concluded three things from these experiments. First, like Cruickshank, he found that the conducting material used to connect the pile to external solutions affected the outcome of the experiment, especially metals. When silver wires were attached to either end of the pile and placed in distilled water, hydrogen gas evolved from the negative wire while the zinc wire calcined, corroded, and emitted oxygen gas. Silver not

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[113] Ibid, 143-144.

[114] Ibid, 144-145.

only aided in the decomposition of water, but also participated in the electrochemical reaction occurring at the zinc wire. In contrast, inert metals, like gold, and conductive fibers were seemingly unaltered by the passage of electricity, and yet different chemical changes occurred at the interface between each conductor and the solution. For example, when he used gold wires to connect each end of the pile to distilled water, the silver wire emitted hydrogen gas, and near the zinc wire, oxygen gas evolved. Gold wires facilitated the decomposition of water, whereas animal fibers did not. Replacing the metallic wires with sinew, no gas was produced. These differences in chemical effects were consistent, but puzzling.

Second, Davy argued that these experiments demonstrated that the electrical decomposition reaction occurring at the silver wire was not the source of oxygen observed at the zinc wire. Cruickshank speculated that electrical fluid entered the solution at the silver wire, fracturing water into hydrogen and oxygen particles. Having an affinity for oxygen, electrical particles combined with the free oxygen, releasing hydrogen gas. This oxy-electric compound then traveled through the remaining liquid to the zinc wire, where it deposited its oxygen, as evidenced by the formation of oxygen gas, metal oxide, and/or acid. In contrast to this view, Davy asserted that his investigations showed that two “separate” and “distinct” sets of chemical changes occurred at the silver and zinc wires. When a silver wire and a zinc sinew were used to connect distilled water to the pile, only hydrogen gas was produced in the region surrounding the silver wire. Reversing the connectors, he found that no gas evolved near the silver sinew and that the zinc wire oxidized and oxygen gas emitted. He noted the most compelling example occurred when he placed a wire from each end of the pile into two separate glass dishes filled with distilled water and connected the vials with his body. Although his body conducted electricity, as indicated by the sensations he experienced while in the circuit, such as pain and tingling, no other materials were transmitted by his body from one dish to the other. Cruickshank speculated that the oxygen manifest at the zinc wire was carried through the solution to the lead by the electric current. Davy argued this was impossible. He observed no chemical changes on or near his hands. Therefore, the reactions producing hydrogen gas at the silver wire and oxygen gas at the zinc wire were discrete and independent.[115]

This was an important result. It suggested to Davy that substances could be analyzed by the types of chemical changes that occurred at each wire in solution. More specifically, he recognized the possible utility of using water as a solvent with different solutes in further experiments with the pile. “If the ratio between the quantities of the oxygen and hydrogen produced from the different wires be always the same, whatever substances are held in solution by the wire connected with them, this nascent hydrogen will become a powerful and accurate instrument of analysis.”[116] In other words, if the electrical decomposition of distilled water alone produced a fixed ratio of hydrogen to oxygen gas then it should be possible to isolate the materials present in a solution of water and solute. Materials other than hydrogen, oxygen, or any additional hydrogen (or oxygen), above and beyond that expected for water, must belong to the solute. Thus,

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[115] Ibid, 145.

[116] Humphry Davy, "Additional Experiments on Galvanic Electricity, in a Letter to Mr. Nicholson," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839c), 150-154, 150.

complex substances, soluble in water, could be decomposed, their constituents separated and studied.[117]

Third, from these investigations, Davy realized that his experiments could be re-tooled to examine the inner workings of the voltaic pile. Nicholson, Carlisle, and Cruickshank witnessed changes in a columnar pile, such as the calcination of zinc plates and the formation of gas bubbles along the points of intersection between the metals and wet conductor, similar to the effects produced by applying current to a solution via metallic wires. Davy wrote:

> Whenever the galvanic circuit, passing through the pile with wires, is broken by means of water, oxygen is uniformly produced at the zinc metallic point. This is shown from many experiments in Mr. Nicholson's Philosophical Journal. Considering analogies, an interesting question occurs. Do not the same phænomena take place in every part of the series [in the pile]? i.e. is not oxygen fixed in every plate of zinc, and hydrogen produced on every plate of silver, at the points of their contact with the water of the cloths?[118]

He asked whether the chemical changes observed to occur externally to the pile in solution where identical to those happening within the battery. Nicholson and Carlisle's research also indicated that the pile's electrical action was limited by chemical changes taking place between its constituents, e.g. if the wet conductor dried out or when the zinc plates became completely oxidized, electricity ceased to flow. Davy questioned: to what extent did chemistry affect the production of current? Volta's first pile consisted of a

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[117] Davy built on this research in his award-winning paper, *On Some Chemical Agencies of Electricity*, published in 1807. See Davy, 1807.

[118] Humphry Davy, "An Account of Some Additional Experiments and Observations on the Galvanic Phaenomena," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839f), 166-180, 170.

series of glass jars filled with water, connected to each other by alternating metals, such as silver and zinc. (Figure 3.5) Davy realized that his experimental set-up, in its simplest form, was structurally identical to one “galvanic circle” or unit of Volta’s pile. In other words, the standard pile, a column of layers of silver, zinc, and water, could be re-expressed as units of zinc, water, and silver. Thus, Davy proposed expanding the pile, effectively creating a series of electrochemical experiments, so that the changes occurring at the interface of each metal with the wet conductor and their associated electricity could be more minutely examined. He hoped, by studying the pile itself, to gain a better understanding of the source of electricity and the chemical changes taking place between the materials in solution. Davy turned his attention to the chemical phenomena of the battery.[119]

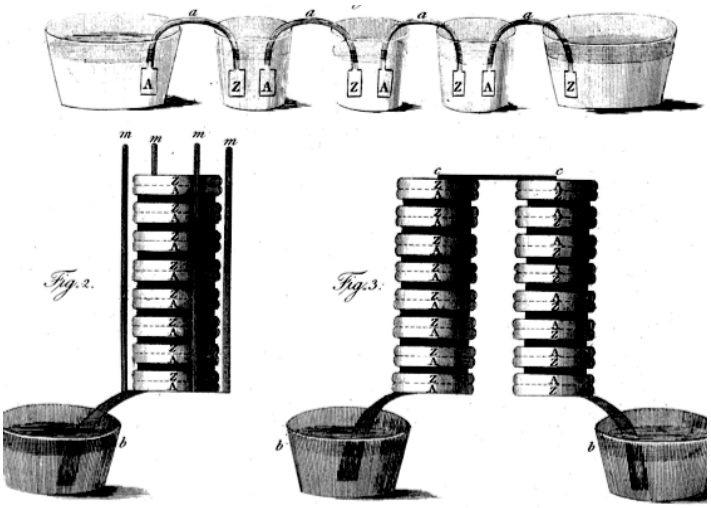

Figure 3.5: **Volta’s pile.** The bottom two images illustrate Volta’s columnar pile. The upper figure shows Volta’s original experimental set-up, which reminded Davy of his own electrochemical apparatus.

3.2.2: Influences on Davy’s Research: the Work of Fabbroni, Haldane, and Henry

> The voltaic battery was an alarm bell to experimenters in every part of Europe; and it served no less for demonstrating new properties in electricity, and for establishing the laws of this science, than as an instrument of discovery in other branches of knowledge, exhibiting relations between

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[119] Many of Davy’s early papers dealt with this issue. See Davy, "Early Miscellaneous Papers," 139-232.

> subjects before apparently without connection, and serving as a bond of unity between chemical and physical philosophy.[120]
>
> Humphry Davy (1810)

Davy, like Lavoisier, was not only an inspired experimenter, but also a synthesizer of information. He was able to mine the existing literature, to devise analogies between known "facts", and use those details to develop fruitful lines of scientific inquiry.[121] More specifically, Davy's research on the pile was influenced by three sets of papers published in Nicholson's journal by Giovanni Fabbroni, Lieutenant Colonel Henry Haldane, and William Henry. I will first briefly outline these three essays before discussing their significance to Davy's research program and his experiments on the inner workings of the pile.

I. Giovanni Fabbroni and the Oxidation of Metals

Davy credited Giovanni Fabbroni with being "the first who systematically attempted to prove that they [galvanic phenomena] were chemical effects".[122] Fabbroni participated in a variety of projects around the turn of the nineteenth century, including the founding and administration of the Natural History Museum in Florence, Italy. He was also interested in animal electricity. His few experiments on galvanism were little known in Britain until Nicholson translated, annotated, and published Fabbroni's original

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[120] Quoted in, David Knight, *The Transcendental Part of Chemistry* (Chatham: Dawson, 1978), 40-41.

[121] Davy described his scientific method in *Elements of Chemical Philosophy*, originally published in 1812. It also included a lengthy introduction to the history of chemistry. He wrote: "The foundations of chemical philosophy are, observation, experiment, and analogy. By observation, facts are distinctly and minutely impressed on the mind. By analogy, similar facts are connected. By experiment, new facts are discovered; and, in the progression of knowledge, observation, guided by analogy, leads to experiment, and analogy confirmed by experiment, becomes scientific truth."Davy, *Elements of Chemical Philosophy*, 2, 1-61.

[122] Davy, 1839d, 155.

1792 essay in two installments in 1799 and 1800, which Nicholson dubbed "On the Chemical Cause of Galvanism".[123]

Galvani's research on the source of muscle contractions, discussed in chapter two, indicated that a combination of metal-muscle-metal produced a unique form of electricity, which Galvani argued emanated from the animal. Volta, in contrast, asserted that the observed electrical fluid was made manifest by the contact of two dissimilar conductors, not the organism.[124] Fabbroni asked whether or not both were mistaken: perhaps "the effects produced on the bodies of animals, by the application of metallic coatings to the nerves and the muscles, may be attributed to a chemical operation".[125]

To explore this possibility, he conducted two related lines of experiments. In comparing exhibits of Etruscan shields and swords, he noted that certain metal alloys were more prone to rusting than others. Lavoisier's research demonstrated that calcination was a slow form of combustion in which oxygen was absorbed and heat (caloric) released. Using this as a starting point, Fabbroni examined how different metals chemically interacted when in contact with each other and in the presence of a third, wet conductor, like muscle or water. He postulated that the oxidation of metal, observed to occur in metal-muscle-metal combinations, might play a crucial role in the production of galvanic effects.

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[123] Valeria Mosini briefly discusses the reception of Fabbroni's work on the continent. See Fabbroni, 1799; Fabbroni, 1800; Daniel M. Klang, "Reviewed Works: Cultura, Intellettuali E Circolazione Delle Idee Nel 700 by Renato Pasta, Scienza Politica E Rivoluzione: L'opera Di Giovanni Fabbroni by Renato Pasta," *Journal of Modern History* 64, no. 4 (1992): 825-827; Mosini, "When Chemistry Entered the Pile."

[124] See Chapter 2, Sections 2.2 and 2.3.

[125] Fabbroni, 1800, 121.

First, he conducted three trials examining the relationship between metal, water, and oxidation. First, he "placed in different goblets filled with water", individual "pieces of metal" such as gold, silver, and copper. In a second set of dishes, he positioned "two pieces of [metal] one of which… was more, and the other less oxidable". "They were separated from contact by a small slip of glass." In the third and final set of containers, he placed two metals with different degrees of oxidation in direct contact with each other into the water. He found that the first two sets of goblets "exhibited no perceptible change". In contrast, in the third group of dishes, "the most oxidable metal was visibly loaded with oxide, a few moments after having been in contact with a different metal" in water. [126] Leaving the experiments for a month, he found there continued to be little change to the metals in the first two sets of containers. In the third group of dishes, however, the metal "oxide [had] gradually increased, so as to hang beyond the lower metal, uniting with it in a mass, and flowing in a cascade along the whole of the sides." Additionally, a "saline crystal" had formed in some of the solutions, and in each case, the two metals had developed a "considerable… adhesion, that in order to detach [for example] a piece of brass about two centimeters broad from a plate of tin, a force of no less than two kilogrammes was necessary." He argued that these experiments showed that profound chemical changes took place between two layered metals in water.[127]

Second, he examined the physiological effects of placing two different metals on exposed parts of the body, such as the tongue and eye. Lacking Galvani's sophisticated knowledge of anatomy and anatomical preparations, Fabbroni used his own body as a

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[126] Ibid, 122.

[127] Ibid, 122-123.

detector, documenting his personal experience. More specifically, he investigated the effects of placing one metal on his eye and a second, different metal in his mouth. He then connected the two metals with a third conductor and recorded any sensations. For example, he found that "if silver be placed on the eye, gold on the tongue, and they are united by means of copper, the sensation [he experienced was] very slight; but, on the contrary, it [was] very evident, if iron touches the eye, silver the tongue, and copper be used to form the communication."[128] With this latter combination of materials, he immediately noticed "a faint, but very distinct light" inside his eye. He also experienced "an unexpected taste [and, in some instances,] a convulsive contraction" in his tongue.[129] He repeated these experiments with a variety of different materials. Table 3.3 summarizes his results.[130]

Materials: Eye, Tongue, and Connector	
No Change	**Observed Light and Taste**
Tin, tin, silver Gold, silver, iron Iron, tin, tin Gold, silver, silver Silver, silver, iron Copper, tin, iron Silver, gold, copper	Iron, silver, copper Iron, gold, copper Iron, gold, silver Iron, silver, silver Silver, iron, iron Gold, iron, iron

Table 3.3: **Overview of Fabbroni's physiological experiments, using metals, his tongue, and his eye.** He noted that some combinations of materials caused a distinct taste in his mouth and a "faint light" to appear in his eye. He recorded which materials produced this response and which did not.

Fabbroni asked: why did only certain combinations of different metals produce sensations? He noted, for example, that when he touched a piece of tin to his eye, placed

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[128] Fabbroni, 1799, 310.

[129] Fabbroni, 1800, 120.

[130] Ibid, 125-126.

a piece of silver in his mouth, and connected the two metals by tin, he experienced no physiological effects. Volta claimed that a difference in the conducting ability of metals produced electricity. Fabbroni argued his experiments showed that Volta's argument was insufficient. Tin and silver were different conductors and yet, their contact produced no sensation in his body. He further noted that the combinations of metals producing the greatest differences in his vision were those most affected by being placed in water. He asserted that this could not be a coincidence: "It [galvanism, must] manifestly [be the effect of] a combustion or oxidation of the metal [observed to take place upon contact in the presence of water]; the stimulating principle [causing muscle contractions] might therefore be either caloric, which is disengaged, or the oxygen, which passes to new combinations [forming metal oxide]; or lastly, the new metallic salt", observed to form when metals were placed in aqueous solution.[131] This "combustion", he argued, was controlled by "the disposition of the metals, and their chemical affinity" for oxygen and not their electrical properties.[132] Thus, Fabbroni contended that the arrangement of two metals and a wet conductor did not produce galvanic phenomena per se. He concluded that electricians had mistaken a complex set of chemical changes for electricity.[133]

II. Henry Haldane and the Pile's Atmospheric Dependence

Lieutenant Colonel Henry Haldane was a British naval officer and a "zealous" amateur natural philosopher. Like many of his contemporaries, upon reading Volta's account of the pile in a newspaper, the *Morning Chronicle*, he immediately constructed a

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[131] Ibid, 123.

[132] Ibid, 125.

[133] Ibid, 120.

battery and began to experiment with it. While many British chemists analyzed its chemical effects, Haldane more generally wanted to know what affected its electrical production. He subjected the pile to a series of tests and reported his findings to Nicholson. Nicholson, impressed by the novelty of Haldane's research, published an annotated account of his experiments in his journal.[134]

Haldane built a standard pile, consisting of "forty half-crowns [silver], with an equal number of pieces of zinc, and 39 cards, which were wetted with pure water." He first tried measuring the amount of electricity emitted by the apparatus, but found that it did not "affect the electrometer of Bennet, nor [Nicholson's] spinning instrument [the revolving doubler]." He also "did not receive a shock" by touching either end of the pile "with wetted hands". He then tried placing "a sewing needle… beneath the skin of a finger" on each hand, and touching "the extremities" of the pile experienced "a sharp irritation… at the wounded parts, with a convulsive sensation, extending to the shoulders, and even the neck." Attaching wires to either end of the pile and placing the leads in water, he also found that water was decomposed into hydrogen and oxygen gas.[135]

Having no easy means with which to gage the "power" of the pile, Haldane used its chemical effects as a measure of its electricity. He collected the gases evolved by passing the pile's electricity through gold wires into water: more gas equaled more current. This was to become a standard, albeit relative measure of the pile's current until

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[134] Henry Haldane, "Experiments and Observations Made with the Newly Discovered Metallic Pile of Sig. Volta. With Remarks by W.N [William Nicholson]," *Nicholson's Journal* 4, no. September (1800a): 241-245, 241.

[135] Ibid, 242.

the invention of the current balance (or ammeter) in 1820 by André-Marie Ampère, which measured the force between two current carrying wires.[136]

Haldane then experimented with the environment and the individual parts of the pile. For example, "[h]e found its [the pile's] power diminished by diminishing the number of pieces; that it would not act if either of the three plates were omitted; that tinfoil instead of silver acted tolerably well; and that leather was preferable to card." Upon placing the entire apparatus in a bath of water, he observed that "its action was intirely suspended, but upon taking it out and wiping the external surface, without separating the parts, it acted as well as before." He next tried putting the apparatus in an air pump, "which was then exhausted of air, till the mercury in the gage stood at half an inch. The decomposition of water in a tube [connected to the pile] with copper wires, did not proceed during this state, but was renewed when the air was let in."

He then experimented with the metals used in the pile's construction. He found that "zinc will act with gold, tin, lead, iron, and copper; that iron will act with the same metals, as will also lead, though feebly." He also observed, "no other combinations of these metals would answer, except that tin and gold afforded a very faint cloud in the water." More interestingly, he found that "when iron and silver were used, the oxidation took place at the wire connected with the iron, and the gas flowed from that connected with the silver; but the contrary happened when zinc and iron were used, which acted

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[136] Davy succinctly described this approach. He wrote: "A measure of the intensity of that agency in galvanic batteries, which produced chemical changes in water, may be derived from the quantity of gas it is capable of evolving in a given time; or from the length of the fluid chain through which it can be transmitted." Davy, 1839k, 408; Henry Haldane, "Experiments Made with the Metallic Pile of Sig. Volta, Principally Directed to Ascertain the Powers of the Different Metallic Bodies," *Nicholson's Journal* 4, no. Oct. (1800b): 313-319, 318-319.

very powerfully, as in this case the iron connection afforded the gas" and the zinc wire calcined.[137]

Haldane did not attempt to explain or account for his observations. He freely admitted, however, that he was not convinced that the pile produced electricity. There were many factors, which affected its action. Its electrical fluid was not measurable by electrometers. It only produced a "very minute exhibition of the attractive and repellent powers, while [in contrast] the causticity, the shock, and the oxidation [of metals, observed by Nicholson and Cruickshank, were] so very powerful". The pile's ability to produce galvanic phenomena was further influenced by its environment, such as the presence of air, and the materials used in its construction. Haldane was not, as Nicholson noted, "persuaded that electricity [was] the principal agent [at work in the battery], though some [electrical fluid] might be generated, or disengaged during the operation of the apparatus."[138]

III. William Henry and the Electrical Decomposition of Muriatic Acid

As "a manufacturer of soda-water", William Henry was particularly interested in the interactions between gases and liquids. He was a pneumatic chemist and collaborator of John Dalton, the famous English natural philosopher who revived the atomic theory of chemistry in the early nineteenth century. Although less remembered today than Dalton, Henry was renowned in his own time for his popular textbook *Elements of Experimental*

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[137] Haldane, 1800a, 242; Haldane, 1800b, 315-318.

[138] Haldane, 1800a, 242-243, Haldane, 1800b

Chemistry,[139] as an organizer and administrator of the *Manchester Literary and Philosophical Society*, and for his discovery that water (and other fluids) absorbs gas in proportion to the pressure of the gas at the surface of the solution.[140] Henry also conducted a series of experiments analyzing the composition of acids using electricity.[141]

With the advent of Lavoisian chemistry, new research avenues emerged. As Henry noted, one of the more questionable aspects of the French system was the explicit assumption that oxygen was a necessary component of acids.[142] In the late eighteenth century, many chemists undertook analyses of complex acids, such as fluoric (hydrofluoric) and muriatic (hydrochloric) acid, to determine whether oxygen was indeed one of its components. Muriatic acid was particularly problematic to study. Attempts to analyze it using common chemical procedures, such as distillation and precipitation, failed or were inconclusive. Many chemists believed the key was to find a known material that when mixed with muriatic acid and heated caused their decomposition and recombination of their elements. Ideally these new compounds would be more easily analyzable. In 1800, Henry entered the fray and attempted to decompose muriatic acid electrically using sparks and the voltaic pile.[143]

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[139] By 1831, Henry's *The Elements of Experimental Chemistry* was already in its eleventh edition in Britain and America. See, William Henry, *The Elements of Experimental Chemistry*, 2 vols. (Philadelphia: Robert Desilver, No. 110 Walnut Street, 1831).

[140] Henry, "Experiments on the Quantity of Gases Absorbed by Water, at Different Temperatures, and under Different Pressures."

[141] For an overview of Henry's life and work, see W.V. Farrar et al., "The Henrys of Manchester, Part 2 Thomas Henry's Sons: Thomas, Peter, and William," *Ambix* 21 (1974): 208-228; W.V. Farrar et al., "The Henrys of Manchester Part 3: William Henry and John Dalton," *Ambix* 22 (1975): 186-204.

[142] Henry, 1800a, 188.

[143] In modern notation, this reaction may take the form of: $A + BY \rightarrow AY + B$, or what Henry called a "single elective affinity", or $AB + XY \rightarrow AX + BY$, or what Henry called analysis by "complicated affinities". See Ibid, 201.

Henry argued that one of the difficulties in analyzing muriatic acid stemmed from its retention of “a large portion of water… introduc[ing] complexity [and] prevent[ing] any combustible substance that may be applied, from acting on the truly acid part”. For example, he observed that “when strong electrical shocks were passed through a portion of muriatic acid gas, confined in a glass tube over mercury” that “[t]he bulk of it, after 20 or 30 shocks, was considerably diminished; and a white deposit appeared on the inner surface of the tube”.[144] Chemical analysis of the remaining airs indicated the presence of hydrogen, while examination of the precipitate showed it “was not, like corrosive sublimate, soluble in water; but had every property of the less saturated salt, calomel [mercuric chloride].”[145] In addition to the reduction in gas volume and the formation of a precipitate, there was also a slight color change and an increase in the volume of mercury consistent with the formation of mercury oxide. As with earlier studies, Henry found his experiments did not decisively demonstrate “from whence this oxygen derived. It might either result from the decomposition of the acid gas, or of the water chemically combined with it.”[146]

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[144] Ibid, 190.

[145] Ibid, 191.

[146] To further examine muriatic acid’s reactivity with oxygen-containing compounds, Henry sparked mixtures of muriatic acid and water, common air, and pure oxygen gas. For instance, he applied to “1457 measures of muriatic acid gas, 300 electrical shocks […]. There remained, after the admission of water, 100 measures of permanent gas, (or not quite 7 [percent] of the original gas,) which, on trial, appeared to be purely hydrogenous.” In a second experiment, he placed “[a] mixture of common air and muriatic acid gas, in the proportion of 143 of the former to 116 of the latter” into a sparking tube and found that the mixture “was rapidly diminished by electrical shocks; 30 of which reduced the whole to 111 [measures]. The remainder [of the gas] consisted of muriatic acid and azotic [nitrogen] gases, with a small proportion of oxygenous gas. [A white] deposit [also] formed on the tube [and] was of the same kind as before, but much more abundant.” “[E]lectrifying muriatic acid with oxygenous gas”, he found that “the same appearances were occasioned, much more remarkably […]. At each explosion, a dense white cloud was seen in the tube, which soon settled on its inner surface, and was of exactly the same chemical composition as the [white deposit] already described.” The mercury also absorbed oxygen, as evidenced by the expansion of the

To extract extraneous oxygen, Henry tried mixing muriatic acid gas with other combustible substances known to attract oxygen. He noted, for instance, "that when electrical shocks are passed repeatedly through a confined portion of carbonated hydrogenous [charcoal] gas, the water held in solution by the gas, is decomposed by the carbon, which forms a constituent part of it; the carbonic acid is formed; and an addition made of hydrogenous gas." Lavoisier had performed similar experiments to decompose water by heating steam and charcoal to very high temperatures, using "the affinity of carbon for oxygen" to separate water into its components.[147] Henry combined "[eighty-four] measures [of carbonated hydrogenous gas]… with 116 of muriatic acid gas, dried by muriate of lime [calcium chloride, a material known to readily absorb water]. By 120 shocks, the mixture was a little dilated." The volume of the gas only increased by "7 measures, or about as much as might have been expected from [the sparking and expansion of] the muriatic gas alone". Although sparking the mixed gases produced a slight increase in volume, it was an insufficient amount to analyze.[148] This suggested that carbon's affinity for oxygen was less than the unknown element(s) of the muriatic radical. Henry wrote: "A great variety of similar experiments convinced me, that by

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metal, which "rose so as to touch the extremity of the platina [platinum] conductor." In each case, when electricity was applied to muriatic acid gas, hydrogen evolved. When mixed with an oxygen-rich gas, such as common air or pure oxygen, a precipitate formed and the mercury oxidized. These experiments, he argued, demonstrated the quandary: sparking caused the components of muriatic acid to react strongly in the presence of materials containing oxygen, making it impossible to determine if the acid itself contained oxygen. Ibid, 191-193, 191, 193.

[147] Ibid, 194-195.

[148] Ibid, 196.

electrifying together the carbonated hydrogenous and muriatic gases, not the smallest progress was made towards the decomposition of the latter."[149]

Henry then turned to the electrical action of the voltaic pile, applying the battery's electricity to acids, acid gases suspended over water or mercury, and to gaseous mixtures alone. Like Cruickshank, he was quickly convinced of the pile's efficacy in analyzing liquids. For example, he connected a pile composed of an equal number of half-crowns, zinc plates, and common saltwater to "[c]oncentrated sulphuric acid… in a glass tube, furnished with two platina [platinum] conductors, the open end of the tube being immersed in a cupful of the same acid."[150] Henry found that "[g]as was produced in great plenty [at both leads]." He subjected this gas to a series of examinations. First, he found that half of the total volume of gas "was absorbed by sulphuret of potash [potassium sulphate]". (It was well known that potassium sulphate absorbed sulphuric acid. This removed any sulphuric acid vapor that may have been produced by heating rather than electrical decomposition from the gas.) Chemical analysis of the residual gas revealed the presence of hydrogen and oxygen gases in a volume ratio of one to two. Henry noted: "But as the [amount of leftover] oxygenous gas was sufficient to have saturated twice the quantity of hydrogen gas evolved, one half of the former must have had another origin than water, and may be ascribed to the decomposition of the acid." In other words, sulphuric acid must contain oxygen.[151] Encouraged, Henry repeated the experiment with muriatic acid. He found that "424 parts of gas were evolved, of which 144 were

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[149] Ibid, 197.

[150] Ibid, 223.

[151] Henry also performed experiments on nitric acid, and found that it "consist[ed] of oxygenous and azotic [nitrogen] gases, in the proportion of 530 of the former to 151 of the latter." Henry, 1800b, 224.

oxygenous, and 280 parts hydrogenous. These gases had, doubtless, their origin from the decomposition of water" because the volume ratio of hydrogen to oxygen gas was almost two to one; again, a null result.[152]

Henry then tried applying the pile's current directly to various gases with surprisingly little effect. For example, directing its electricity through a mixture of hydrogen and oxygen gas did not produce water. Unexpectedly, the gases remained unaltered. He repeated the experiment with different gases, including phosphorated hydrogen (hydrogen phosphate) and "a mixture of muriatic acid and oxygenous gases". He observed no change in volume "or change of properties." He concluded that the pile's current was incapable of traveling through gases like common electricity. He wrote dejectedly: "The deficiency of the property of transmission [of the pile's electricity] through gases limits considerably the use of galvanism as a chemical agent, and has totally overturned my project of attempting, by its intervention, the analysis of muriatic acid."[153]

Henry was frustrated in his attempts to decompose muriatic acid. He wrote that these experiments indicated with "strong probability, that the basis of the muriatic acid is some unknown body; for, no combustible substance with which we are acquainted, can retain oxygen, when submitted, in contact with charcoal, to the action of electricity, or to a high temperature."[154] Furthermore, he noted that the current of the voltaic pile, a powerful chemical agent in liquids, did not affect substances in the gas state and that a

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[152] Ibid, 224.

[153] Henry, 1800a, 225.

[154] Ibid, 201.

more sophisticated type of analysis was needed to study muriatic acid. Although disappointed by his negative experimental results, Henry expressed his hope to Nicholson that "those who are practically engaged in investigating the properties of galvanism may derive, from a communication with each other through the medium of your journal, some of the advantages of personal intercourse and cooperation" towards a better understanding of the relationship between electricity and chemistry, and ultimately, the composition of complex acids.[155]

3.2.3 - The Inner Workings of the Pile: Davy's Radical Proposition

> M. Volta has supposed, that an electrical current is always produced by the mere contact of certain different conductors of electricity. But many of the British philosophers have denied this position; accounting for galvanism from the destruction of the equilibrium of electricity in galvanic circles, in consequence of the chemical agencies of the different bodies composing them.[156]
>
> Humphry Davy (1802)

The three articles briefly outlined in the last section added to a small, but growing literature re-emphasizing the relationship between electricity and chemistry in Britain in the early nineteenth century. Fabbroni and Haldane concluded that something more complicated occurred when two different metals and a wet conductor were brought into contact. Although Fabbroni did not systematically investigate whether specific combinations of metals oxidized in water also produced the most pronounced physiological effects, he argued that the absorption of oxygen was a key factor in galvanism. Haldane was convinced by the inactivity of a pile in vacuum that its effects had a strong chemical dependence. Henry also noted differences between friction-based

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[155] Ibid, 226.

[156] Davy, 1839k, 409.

electricity, which produced profound chemical changes in airs, and voltaic electricity. The pile's current altered the composition of liquids in unique ways, but appeared to have little to no effect on gases. While both Fabbroni and Haldane expressed their doubts that galvanic phenomena were truly electrical effects, Henry emphasized the pile's practical use in the chemical analysis of complex, aqueous solutions.

In addition to promoting a chemical interpretation of galvanism, these essays suggested two related lines of research to Davy involving gases and oxygen-rich compounds. First, Fabbroni's research indicated that the absorption of oxygen played a pivotal role in the production of galvanic phenomena, such as the physiological effects manifested by the contact of two different metals on organic tissues. Nicholson, Carlisle, and Cruickshank also observed the oxidation of the zinc plates used in the pile. Haldane further noted that a battery of silver, zinc, and water only generated current under atmospheric conditions; its electrical action diminished with decreasing air pressure. All of these experiments indicated that the presence of oxygen affected the pile's current. Davy did not believe this was a coincidence. He asserted that the relationship between oxygen and electricity warranted closer examination.[157]

Second, from his early trials with the pile, Davy thought of the battery as a series of electrochemical experiments. Rather than thinking of the pile's layers as silver, zinc, and water, he reordered its constituents: zinc, water, and silver. In this configuration, each unit within the pile became a testing ground for the chemical changes taking place between its components and its electrical output. Henry's research into the electrical

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[157] Davy referred to their research frequently. See, for example, Davy, "Early Miscellaneous Papers," on Haldane, 164, 167, 176, On Fabbroni, 155, 156, 164, 189, and on Henry, 139, 146, 149, 190, etc.

decomposition of complex acids in liquid and gaseous states encouraged Davy to experiment with different non-metallic wet conductors and, in particular, to try various acids in the construction of the battery. The results were surprising and informative.

Extending Haldane's research, Davy systematically studied the effects of placing a pile composed of units of zinc, water, and silver in a pneumatic trough with different gases. Haldane's experiments indicated that a common pile did not produce electricity in vacuum. It was well known that standing water absorbed gases from the atmosphere. Davy reasoned the pile's current was limited in vacuum because water alone did not facilitate the absorption of oxygen in metals. Water infused with air, however, did. To test this hypothesis, Davy was interested in determining which gases promoted the production of current. Like Haldane, he measured the pile's electrical activity by its ability to decompose distilled water: more gas indicated more current.[158]

Davy divided his trials into two groups: non-calcinating airs, including "hydrogen, nitrogen, nitrous oxyde, and hydro-carbonate",[159] and oxidizing gases, such as "atmospheric air, or oxygen, or nitrous gas, or nitrous acid, or marine acid [gas]".[160] He found that when the pile was immersed in one of the former, non-oxidizing gases, no current flowed: water was not decomposed and the zinc plates "were scarcely at all tarnished".[161] In each case, "[t]he action of the pile … [was] diminished immediately on its introduction into these gases … and [could] not be restored by admitting fresh gases of

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[158] Davy, 1839d, 155-156; Davy, 1839k, 408.

[159] Davy, 1839d, 157.

[160] Ibid, 158.

[161] Ibid, 157.

the same kind".[162] On the other hand, exposing the pile to one of the latter set of calcinating airs, he found that the zinc plates corroded and gas evolved. He further noted "[a] pile acted in atmospheric air, included in a gas cylinder over water for two days, till nearly all of the oxygen of the air was consumed." It then ceased to function.[163]

Haldane observed that a pile of zinc, water, and silver was incapable of decomposing water under vacuum. Davy not only confirmed Haldane's results, but also elaborated on his experiments, subjecting piles of various materials to low pressure. For example, he found that, although a pile of zinc, water, and silver did not produce current in the absence of air, a battery of zinc, nitrous acid, and silver under vacuum did generate enough electrical fluid to decompose water.[164] Davy asserted that these experiments indicated that "[*t]he galvanic pile of Signor Volta* [was] *incapable of acting when the water between the pairs of plates* [was] *pure*", i.e. when it did not contain an oxidizing gas or acid.[165]

Davy then compared the effects produced by the pile in different calcinating airs. He found that:

> The zinc [plates] oxydate less rapidly in nitrous gas than in atmospheric air, and less rapidly in atmospheric air than in oxygen: and the power of the action of the pile as known by its evolving gas from water is greater in oxygen than in atmospheric air, and greater in atmospheric air than in nitrous gas. The power of the pile to decompose water, and to give the shock is wonderfully increased after it has been dipped in marine acid, and still more increased after it has been dipped in weak nitrous acid…[166]

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[162] Ibid, 159.

[163] Ibid, 160.

[164] Davy, 1839f, 168.

[165] Davy, 1839d, 159.

[166] Ibid, 161.

He noted that the pile produced more current when exposed to gases containing free oxygen or if the wet conductor was mixed with an acid, in Lavoisier's framework, an oxygen-rich, corrosive compound. Because the pile's effects measurably increased in the presence of more reactive oxidizing agents, Davy concluded that the pile's electricity was *"in great measure, proportional to the power of the conducting fluid substance between the double plates to oxydate the zinc.*"[167]

He wrote: "Assuming the truth of this conclusion, it was easy to conceive, that a pile much more powerful than any hitherto constructed might be made, particularly supposing that the decomposition of water was not essential to the process."[168] Cruickshank hypothesized that the calcination of the zinc plates in solution was caused by free oxygen produced by the electrical decomposition of water at the silver plates. In contrast, Davy's experimental results diminished the importance of the production of hydrogen to galvanic processes, emphasizing instead the priority and uniqueness of the chemical changes occurring along the surfaces of the zinc plates. In short, Davy asserted that current did not flow unless the zinc calcined.

By focusing his attention on the reactions occurring at the positive plate and using materials that facilitated the absorption of oxygen in zinc, Davy created batteries producing significantly more current per galvanic unit than the standard pile of zinc, water, and silver. For example, he found that a pile constructed of eighteen units of zinc, muriatic (hydrochloric) acid, and silver was "at least equal" in "its capability of decomposing water" as "a common pile of seventy plates", while a pile composed of only

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[167] Ibid.

[168] Ibid, 162.

five units of zinc, nitrous acid, and silver produced a “shock [as] full as powerful as from the common pile of thirty plates.”[169] On the basis of these experiments, Davy argued: “It seems, therefore, reasonable to conclude, though our present quantity of facts we are unable to explain the exact mode of operation, that the oxidation of the zinc in the pile, and the chemical changes connected with it are *somehow* the cause of the electrical effects it produces.”[170]

To further bolster his argument, that electricity was produced by chemical changes in the pile, Davy extended his research on how different substances interacted to produce current. He warned other experimentalists, however, to take care when constructing new batteries. He initially made a pile of many more units of zinc, “diluted nitrous acid”, and silver. Upon touching each end of the pile with his hands, he found “the first shock was so powerful as to benumb [his] fingers for some seconds”. The experience was so unpleasant that he wrote: “I did not dare take another.” He also noted that chemical changes occurred at both metals. The silver plates especially corroded with such unexpected rapidity that he “was almost immediately obliged to throw the pile into [a nearby tub of] water to [dilute the acid and] prevent it [the silver] from being destroyed”. His previous experiments had focused on the oxidizing power of the wet conductor to calcine the zinc plates. He now more closely examined the reactions occurring at the silver plates. In addition to analyzing the materials that formed on or near the silver leads, he also experimented with the size and surface area of the plates.[171]

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[169] Ibid, 163.

[170] Ibid, 162.

[171] Ibid, 162-163.

Using different arrangements of “a series of twenty glasses with spring water, containing plates of silver and zinc, connected by brass wire”,[172] Davy found that the zinc plates corroded and oxygen gas evolved in each unit. At the silver plates, he noted that hydrogen gas evolved and each lead became coated with a “white pellicle”, which subsequent analysis showed to be ammoniac (ammonium), a compound of hydrogen and nitrogen.[173] Water exposed to the atmosphere absorbed common air, which contained nitrogen. Cruickshank hypothesized that ammoniac formed on the silver plate as electrically freed hydrogen interacted with nitrogen gas contained in the water, but he did not have enough of a sample to conclusively determine if this was the case. Davy’s experiment validated Cruickshank’s supposition. Davy further observed that “small oval, circular, and square plates, of nearly equal surfaces… produced precisely the same effects”: gas formed and, after some time, a thin film. Different surface areas, however, produced different amounts of gas and, therefore, electricity. For example, wires evolved significantly less gas than plates. There was also a limit to which the size of the plates increased the amount of gas produced. He observed that “whenever the surfaces of the silver plates did not exceed one-fourth of the quantity of the surface of the zinc plates… gas was always produced upon them”.[174] If they were larger than that, less gas evolved. Although he could not account for the effects of surface area, these experiments showed that the amount of hydrogen evolved in each galvanic unit affected the pile’s ability to decompose water. The galvanic units producing the most hydrogen decomposed the most

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[172] Davy, 1839f, 170.

[173] Ibid, 171.

[174] Ibid, 172.

water. Davy argued that the production of hydrogen did influence the electrical action of the pile: “the substances which are capable of rapidly oxydating the imperfect metals and of condensing nascent hydrogen at the same time, are those which produce the most powerful effects.”[175]

In trying to maximize the current produced by the pile, Davy gained valuable insight into the chemistry of the battery. Chemical changes occurred in every unit of the pile. Moreover, wet conductors promoting the oxidation of metals and the formation of hydrogen generated the most electricity. Davy now broadened the parameters of his experiments. Rather than focusing on the extent of galvanic phenomena produced by different piles, Davy shifted his research to examine which combinations of materials created a current capable of decomposing water. In particular, he asked whether two different, adjacent metals were necessary for electrical production? He began to speculate that “many [different material] arrangements could be made [electrically] active, not only when [the metals were] oxydating, but likewise when other chemical changes were going on”.[176] Table 3.4 provides an overview of his results.

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[175] Ibid, 179.

[176] Davy, 1839g, 184.

# of Units	Conducting material			Wires		Observations in Solution	
	1	2	3	1	3	1	3
20	Zinc	Sulphuric acid	Silver	O	H	Oxygen, Oxide	Hydrogen
10	Zinc	Sulphuric acid	Copper	O	H	Oxygen, Oxide	Hydrogen
13	Zinc	Red Sulphate of Iron	Silver	O	H	Green Oxyde of Iron	Brown Precipitate
8	Zinc	Pump-water	Iron	O	H	Oxygen, Oxide	Hydrogen
8	Iron	Pump-water	Silver	O	H	Oxygen, Oxide	Hydrogen
8	Zinc	Red Sulphate of Iron	Charcoal	O	H	Oxygen	Hydrogen
20	Copper	Nitrate of Mercury	Silver	O	H	Oxygen; Mercury Precipitate	Hydrogen
20	Silver	Nitrate of Mercury	Gold	O	H	Oxygen	Hydrogen
20	Water	Tin	Nitric acid	O	H	Hydrogen	Oxide
12	Sulphuret of Potash	Zinc	Acid; Sulphate of potash	O	H	Hydrogen on metal face in contact with Sulphuret of Potash	Oxygen, Oxide on metal face in contact with the Acid
8	Sulphuret of Potash	Copper	Water	H	O		
8	Sulphuret of potash	Silver	Water	H	O		
3	Sulphuret of Potash	Copper	Nitric Acid; Sulphate of Potash	O	H		
13	Sulphuret of potash	Silver	Nitric acid; sulphate of potash	O	H		

Table 3.4: A Brief Overview of Some of Davy's Experiments.[177] The first column indicates the number of units in each pile. The following three columns list the order and type of conducting materials used in each unit. As in previous experiments, gold wires were attached to each end of each pile and placed in water. Columns five and six indicate whether the gold lead produced hydrogen gas, denoted "H", or oxygen gas, denoted "O". When single metals were used, Davy attached one gold wire to the oxidizing surface of the metal plate and the other to its opposite face. He consistently noted that at the lead connected to the oxidizing surface, hydrogen gas evolved while the wire attached to the seemingly inert side of the plate produced oxygen gas and calcined. Columns seven and eight indicate any changes Davy observed in the pile's conducting materials.

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[177] Davy, "Early Miscellaneous Papers," 166-187.

Davy tried various arrangements of double and single conducting plates, separated by cardboard soaked with different fluids. For example, Davy's research indicated that piles with double plates worked most efficiently at decomposing water when one of the metals was easily oxidized while the other was not. A notable exception to this configuration was iron and zinc. Like Haldane, Davy found that both metals readily calcined and yet, together they acted in aqueous solution to produce significant amounts of current. It is interesting to note that, in units of iron, water, and silver, the iron oxidized and oxygen gas evolved. Near the silver, hydrogen gas was produced. In contrast, in units of iron, water, and zinc, the zinc calcined and oxygen evolved. Near the iron plates, hydrogen gas was produced. He also found that charcoal could be used in lieu of various metal plates, like silver, and the pile still decomposed water.

Davy grouped his results on single plates into "three classes", from those producing the feeblest to strongest galvanic effects. For example, the first and weakest class of batteries consisted of "single metallic plates" placed in series "with different fluids, one capable, and the other incapable of oxidating the metal"[178] and containing hydrogen, e.g. water, tin, and nitric acid. He attached two gold wires: one to the oxidizing surface of the tin at the bottom of the column and the other to its unscathed surface at the top of the pile. He placed each of the wire's free ends into a glass of water. He found that where the lead connected to the oxidizing surface entered the water, hydrogen evolved, whereas oxygen was produced at the lead attached to the top of pile. The second strongest group of piles were constructed of units of water, a single metallic plate "capable of

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[178] Davy, 1839k, 398.

acting upon… sulphurets", and "a solution of sulphuret"[179] (a compound containing sulphur and hydrogen, typically alkaline in nature). The third, and strongest class of batteries were composed of "metallic substances oxidable in acids, and capable of acting on solutions of sulphurets, [placed in series] as plates, with oxidating fluids [like acids] and solutions of sulphuret of potash"[180]. He later condensed these three groups of materials into two tables. (Table 3.5.)

Two Perfect and One Imperfect Conductor		
More Oxydable	Less Oxydable	Oxydating Fluids
Zinc	With gold, charcoal, silver, copper, tin, iron, mercury.	Solutions of nitric acid in water, of muriatic acid and sulphuric acid, etc.
Iron	-- gold, charcoal, silver, copper, tin.	Water holding in solution oxygen, atmospheric air, etc.
	-- gold, silver, charcoal.	
Tin	-- gold, silver.	Solution of nitrate of silver and mercury. Nitric acid, acetous acid.
Lead	-- gold, silver.	
Copper	-- gold.	
Silver		

Two Imperfect and One Perfect Conductor		
Perfect Conductors	Imperfect Conductors	Imperfect Conductors
Charcoal Copper Silver Lead Tin Iron Zinc	Solutions of hydrogenate alkaline sulphurets capable of acting on the first three metals, but not on the last three.	Solutions of nitrous acid, oxygenated muriatic acid, etc. capable of acting on all the metals.

Table 3.5: Davy's "Table[s] of Galvanic Circles". In each of the above tables, combining one material from each of the three columns produced an active voltaic pile, capable of decomposing water.[181]

In each case, however, the galvanic effects were short lived, as it only took a "few minutes" for the chemical changes to run their course. Thus, when the materials in the

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[179] Davy, 1839k, 400.

[180] Ibid, 400-401.

[181] These two tables were reproduced from Ibid, 404.

pile ceased to chemically interact, the galvanic effects also stopped.[182] He asserted that these experiments showed "how intimately chemical agencies are related to the production of galvanism."[183]

Davy asked: If chemical change was at the root of galvanic phenomena, did batteries of different materials decompose water in the same way?[184] He found in each case, irrespective of the pile's composition, that all batteries capable of producing current decomposed water into hydrogen and oxygen gas. Whatever electricity was, he concluded it was somehow generated by the chemical interactions between the pile's layered materials in a form that consistently acted on external substances in predictable ways. Although he could not explain some of his experimental results, e.g. how two oxidizable materials like iron and zinc worked together to generate current, Davy was convinced that it was the chemical interaction of substances that produced the electricity in the pile. In short, he argued, his numerous experiments demonstrated that if a chemical change did not occur, current did not flow. Electricity, therefore, must be generated by the chemical process itself, and not by the contact of two different metals alone.[185]

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[182] Ibid, 401.

[183] Humphry Davy, "Outlines of a View of Galvanism, Chiefly Extracted from a Course of Lectures on the Galvanic Phaenomena," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839h), 188-208, 192.

[184] In Davy's words: "I… engaged… to ascertain by experiments whether any differences exist in gases evolved from water by the galvanic current, when different oxydating substances form the medium of communication between the plates." Humphry Davy, "Extract of a Letter to Mr. Nicholson, Dated Oct. 23, 1800, Supplementary to the Preceding Paper on Galvanism," in *The Collected Works of Sir Humphry Davy*, ed. John Davy (London: Smith, Elder, and Co. Cornhill, 1839e), 163-165, 165.

[185] Davy reiterates this point in several places in his early papers. See, for example, Davy, "Early Miscellaneous Papers," 155, 162, 183, 190, etc.

Unlike many of his contemporaries, perhaps because he was largely self-taught, Davy's approach to the study of the voltaic pile was not hindered by the late eighteenth century discourse over matter theory, e.g. whether caloric and electricity were unique elements, immaterial, or one type of substance existing in multiple modes.[186] Although he promoted the idea that heat was an effect of matter in motion, he was not committed to a materialistic or mechanistic view of nature. Rather, he advocated detailed experimentation and the accumulation of "facts" before making theoretical claims about the causes of phenomena. He freely admitted that his interpretation of his experimental results contained some speculation. He also conceded that he did not have an adequate explanation for how chemical change produced electricity, but that did not negate his experimental results.[187]

Davy's argument that "chemical change [was] *somehow* the cause of [the pile's] electrical effects" was much more than a reiteration of Fabbroni's radical interpretation of galvanism in the early 1790s.[188] Davy recognized that "[t]he nature of this communication [was] incompatible with a detail of the opinions prevailing amongst natural philosophers, respecting the causes of the galvanic phænomena: they have been generally supposed to depend on the different powers of bodies to conduct electrical fluid."[189] He did not try to provide a theoretical account of the production, movement, or action of electrical fluid, but rather asserted that his experiments spoke for themselves.

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[186] On Davy's earliest approaches to scientific inquiry, see Fullmer, *Young Humphry Davy: The Making of an Experimental Chemist*, 153-171; Pancaldi, 2009.

[187] See, for example, Davy, 1839h, 205-209.

[188] Davy, 1839d, 162.

[189] Ibid, 155.

The standard voltaic pile of silver, zinc and water only decomposed water if immersed in a soluble, calcinating gas. In the absence of such an air, the pile produced no discernable current. If the contact of two metals was the cause of galvanism, the amount and type of gas in which the pile was placed should not have affected its ability to decompose water. Moreover, by concentrating his studies on the oxidizing abilities of the wet conductor, Davy was able to manipulate the pile's current, e.g. batteries constructed of zinc, muriatic (hydrochloric) acid, and silver decomposed more water than a pile of zinc, water, and silver in air. He was also able to construct piles out of single metals using two different fluid layers, one capable of oxidizing the metal and the other containing hydrogen. In contrast to contact theory, Davy argued this evidence strongly indicated that voltaic electricity was produced by chemical change.

Davy's experiments showed the importance of both the absorption of oxygen and the evolution of hydrogen to current production. Unlike Cruickshank's theory of electrical decomposition, in which the chemical changes occurring at the negative or silver wire affected the reactions observed at the positive or zinc wire, Davy asserted that two independent and unique sets of chemical reactions occurred at each lead. Furthermore, he showed that the rate and extent of those chemical changes could be manipulated and correlated to the electrical action of the pile. Volta argued that the pile embodied contact theory. It was an instrument that validated his theory that differences in the electromotive abilities of conductors affected the production of electricity.[190] In contrast, Davy's research indicated that the chemical reactions occurring between its

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[190] Mertens, 1998; Pera, 1992.

material layers controlled the pile’s current. In short, Davy argued that Volta was mistaken: the pile was, strictly speaking, a chemical device.[191]

3.3: Whither the Chemical Theory of the Pile? Objections to Davy’s Account

> That electricity is real matter, and not a mere property, seems to be evident from a variety of circumstances. When it passes between bodies, it divides the air, and puts it into those undulations in which sound consists. It emits the rays of light in every direction, and those rays are variously refrangible, and colorific, as other light is. And if light be acknowledged to be matter, it is contrary to reason and experience to suppose, that the thing which emits it should not likewise be material.[192]
>
> William Nicholson (1787)

Davy’s experiments and conclusions were generally considered thought provoking, but were by no means accepted. Eighteenth-century theory and experiment suggested that electricity was a substance. It was not clear how to reconcile Davy’s view that chemical changes were responsible for electrical effects and its materiality.

One of the difficulties resided in the concept of an electrical substance and the terminology reinforcing it. Davy was careful not to use the term electrical fluid in his papers. Rather, he discussed the chemical reactions taking place between the pile’s components and its associated electricity in terms of the amount of gas produced from the decomposition of water.[193] With an observable increase in the absorption of oxygen and the production of hydrogen in the pile’s units, more gas evolved from water. This indicated an increase in the pile’s electrical activity, but what that ‘power’ corresponded

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[191] Davy, 1839k, 409.

[192] Nicholson, *1787*, 304.

[193] In later essays, for example in his award winning Bakerian lecture *On Some Chemical Agencies of Electricity* published in 1807, Davy adopted the term electrical energy when discussing the electrical decomposition of compounds. Certain elements were drawn towards the positive wire, while others naturally gravitated towards the negative lead. See Davy, "1807."

to was a matter of some debate, e.g. did a more active pile produce a current of more substance or heightened intensity, or something all together new?[194] Also, by not directly addressing changes in the electrical fluid, Davy assigned it a less active role than either natural philosophers or chemists had traditionally. Chemists were particularly concerned by Davy's assertion that two independent sets of chemical changes occurred at the silver and zinc leads in solution. For instance, if the electrical fluid, leaving the pile at the zinc plate and entering water through its connecting wire, decomposed water causing the oxidation of metal and the production of oxygen gas, where did the hydrogen gas go? Why did it appear at the silver wire? If the absorption of oxygen released chemically bound electrical fluid from oxidizable metals, why was hydrogen gas released at the silver wire? Moreover, since the hydrogen gas likely came from the aqueous solution, what happened to the oxygen at the silver wire? What modifications did the electrical fluid undergo as it passed through these liquids? Did it facilitate or participate in these chemical changes? Davy made no attempt to answer this last question, which plagued late eighteenth-century chemists. By not committing to a materialistic view of electricity, his experimental results led him to restate the problem in novel ways, much to the consternation of his contemporaries. In his early papers, instead of asking how electricity interacted with and/or altered the composition of materials, he questioned how chemical changes affected electricity.

Of Davy's results, the one that garnered the most interest and support was his observation that the presence and absorption of oxygen was correlated with current

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[194] For example, Nicholson proposed that current was "a large quantity of electricity at a low intensity". See, Nicholson's commentary in Haldane, "1800a," 243-245, 244.

production. Lavoisier's theories and experiments on heat and acidity increased the perceived importance of oxygen to fundamental processes in nature, such as respiration, rusting, corrosion, and burning. As discussed in chapter one, many chemists also associated electricity with heat because of numerous similarities in their effects. It should be of no surprise, given the ubiquity and necessity of oxygen to a variety of thermal phenomena that electricity also fell under its purview. This section briefly examines some objections to Davy's theory and one other competing British chemical theory of the pile's electrical action, which emphasized the role of oxygen in current generation.[195]

William Wollaston was a well-known English physician turned chemist. Although he actively participated in the scientific community in optics, the discourse on Dalton's atomic theory, and the debates over the metric system, there has been no comprehensive study of his contributions to British science.[196] Rather, scholars have focused on his role in the palladium controversy, the dispute over whether a new element had been discovered in the process of refining platinum.[197] Wollaston's interest in metallurgy, however, also extended to the study of electricity, which indicated that current could be

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[195] A number of electrochemists promoted the idea that the oxygenation of metal affected current production. See, for example, Ostwald, 1980; Sudduth, 1980.

[196] See, for example, John A. Chaldecott, "Platinum and Palladium in Astronomy and Navigation: The Pioneer Work of Edward Troughton and William Hyde Wollaston," *Platinum Metals Review* 31 (1987): 91-100; Kiyohisa Fujii, "The Berthollet-Proust Controversy and Dalton's Chemical Atomic Theory 1800-1820," *British Journal for the History of Science* 19, no. 2 (1986): 177-200, 190-192; Brian Gee, "Through a Hole in the Windowshutter," *Physics Education* 18 (1983): 93-97; John H. Hammond and Jill Austin, *The Camera Lucida in Art and Science* (Bristol: Hilger, 1987).

[197] See for example John A. Chaldecott, "William Cary and His Association with William Hyde Wollaston: The Marketing of Malleable Platinum in Britain from 1805 to 1824," *Platinum Metals Review* 23, no. 3 (1979): 112-123; Melvyn Usselman, "The Wollaston/Chenevix Controversy over the Elemental Nature of Palladium: A Curious Episode in the History of Chemistry," *Annals of Science* 35 (1978): 551-579; Melvyn Usselman, "Merchandising Malleable Platinum: The Scientific and Financial Partnership of Smithson Tennant and William Hyde Wollaston," *Platinum Metals Review* 33, no. 3 (1989): 129-136; Luis Fermin Capitan Vallvey, "Export and Smuggling of Spanish Platina in the Eighteenth Century," *Annals of Science* 53 (1996): 467-487.

used to decompose and isolate metals from aqueous solutions. On the basis of his own experiments, he became committed to the position that "the oxidation of the metal [was] the primary cause of the electrical phænomena observed", but implicitly rejected Davy's argument that other types of chemical change also produced electricity.

In 1801, Wollaston wrote a short, but influential essay, *Experiments on the Chemical Production and Agency of Electricity*, in which he added his voice to Nicholson and Davy's in asserting that the pile's current was a form of electricity like friction-based electricity. His experiments were not particularly original, but unlike Cruickshank and Davy's papers, published in Nicholson's journal, Wollaston's essay appeared in the *Philosophical Transactions*, which had a longstanding international reputation and circulation.[198]

More specifically, Wollaston documented a set of experiments on metallic solutions using sparks and current. For example, he noted, like Cruickshank, that when wires were attached to each end of the pile and placed in a copper solution, copper formed on the lead connected to the negative plate. Reversing the wires, so that the lead formerly attached to the negative plate and covered in copper was now attached to the positive end of the pile, he found that the precipitate transferred. The copper on the positive wire slowly corroded and reappeared as a precipitate on the negative lead. He also experimented with single metallic plates in solution. It was well known, for instance, that if an iron bar was placed in a copper solution, copper precipitated onto the iron. By applying sparks from a friction machine to other metals suspended in a solution of

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[198] Davy and Wollaston became both friends and rivals over the course of the early nineteenth century. See, Knight, *1992a*, 135; Wollaston, 1801, 427.

copper, they attained the same "power" to precipitate copper as iron.[199] He also repeated Nicholson, Carlisle, and Pearson's experiments, and argued that both sparks and current caused the electrical decomposition of water: hydrogen and oxygen gas being produced. Wollaston contended that these likenesses-in-effect, i.e. that the application of sparks and current similarly caused the precipitation of metal and the decomposition of complex substances, demonstrated that friction-based and voltaic electricity were identical.[200]

Like Cruickshank, Wollaston tried to develop an overarching explanation for these phenomena. Cruickshank suggested that water was separated by electricity into its components at the silver or negative lead. Hydrogen gas evolved. The free oxygen then combined with the electrical fluid, and traveled through the conducting solution to the zinc or positive lead where it appeared as oxygen gas, metal oxide, and/or acid. In contrast to Cruickshank's theory and piggybacking on Davy's research, which demonstrated the importance of the absorption of oxygen to current production, Wollaston developed a theory emphasizing the chemical changes occurring at the positive or zinc wire.

More specifically, he wrote:

> We know that when water is placed in a circuit of conductors of electricity, between the two extremities of a pile, if the power is sufficient to oxidate one of the wires of communication, the wire connected with the opposite extremity affords hydrogen gas. Since the extrication of hydrogen, in this instance, is seen to depend on electricity, it is probably that, in other instances, electricity may be also requisite for its conversion into gas. It would appear, therefore, that in the solution of a metal, electricity is evolved during the action of the acid [an oxygen rich compound] upon it; and that the

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[199] Wollaston, 1801, 428-430.

[200] As Faraday suggested, Wollaston did not give proper credit to Pearson and Trootswyk and Deiman's research in his paper. See Faraday, 1833, 38; Wollaston, 1801, 430.

> formation of hydrogen gas, even in that case, depends on a transition of electricity between the fluid and the metal.[201]

In other words, as metal absorbed oxygen from the solution, it released electrical fluid. As the electrical fluid then passed through the liquid, it was free to combine with substances in the solution, like hydrogen, producing gaseous compounds.

Wollaston's theory borrowed heavily from the phlogistonist and calorist arguments of the late eighteenth century. For example, Priestley asserted that as metals rusted they lost phlogiston or electricity, their principle of conductivity. Wollaston also adopted the position that as metals absorbed oxygen (Lavoisier's explanation for calcination) they released electrical fluid. Once completely oxidized, they no longer transmitted electricity because they themselves were devoid of electrical matter. Drawing on Pearson and Lavoisier's account of gases, i.e. materials absorbed caloric to become aeriform, Wollaston argued that some of the freed electrical particles, in turn, interacted with the remaining components of the solution to produce gas, a compound of ponderable and imponderable matter, such as hydrogen and electricity or hydrogen gas. (Pearson suggested a similar model to explain how sparks interacted with water to produce hydrogen and oxygen gas.) As the electrical fluid was pushed and pulled by chemical changes taking place between the metals and liquid, it was diminished. Over time, the current eventually ceased to flow for one of two reasons: either the metals were saturated with oxygen, incapable of releasing any more electrical fluid, or the electrical fluid

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[201] Wollaston, 1801, 428.

completely combined with substances to form gaseous compounds, thus removed from the system entirely.[202]

Unlike Davy who clearly differentiated between the chemical reactions taking place at the two metal plates in solution, Wollaston lumped these chemical changes together. He thought Davy's argument added unnecessary complexity. Applying current to water produced hydrogen and oxygen gases respectively in a volume ratio of two to one and, therefore, had to come from the dissociation of water: what difference did a little distance make? He dismissed Davy's evidence on the grounds that Pearson's experiments showed that friction-based electricity also decomposed water into hydrogen and oxygen gas with no relative displacement. In short, his experiments and those of his contemporaries convinced Wollaston that friction-based electricity was identical to voltaic electricity. Because they were the same, the chemical account of the electrical decomposition of water by sparking had to coincide with the explanation for the behavior of current.[203]

Davy was not committed to this position. Although he also discussed the similarities between voltaic and frictional electricity, and asserted that these likenesses suggested there existed one type of electricity, his work was focused on the phenomena produced by the pile alone. For example, in a *Course of Lectures on Chemistry*, published in 1802 with the assistance of Thomas Young, he divided the study of electrical phenomena into two sections: one on friction-based electricity, the other on galvanism and the pile. He wrote:

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[202] Ibid, 432-434.

[203] Ibid, 427, 430, 434.

> Electricity is capable of being excited by the action of different conducting substances on each other; but the modes of this excitation, and its general connection with chemical changes, constitute a science which has hitherto been distinguished from common electricity, by the name of galvanism…[204]

Davy's early lectures and writings promoted the view that voltaic electricity or galvanism was a set of chemical phenomena related to static electricity, but with a different cause. While friction promoted the flow of electrical fluid between materials, electricity could also be excited by chemical change. Davy saw no incongruity in postulating that there existed one "electricity" capable of being excited by different means. He was primarily concerned with understanding and explaining the inner workings of the pile, which experiments indicated was a chemical instrument.[205]

For Wollaston, however, two sets of experiments needed to be accounted for by one explanation: sparking and applying current to water both caused its decomposition. Furthermore, eighteenth-century experiments and theory strongly indicated that electricity was a substance, albeit with special properties, capable of chemically combining with ponderable materials. In contrast to Davy, Wollaston contended that this was a necessary starting point for chemical accounts of electrical phenomena. Moreover, there was already a model in place. Lavoisier argued that as metals rusted, by absorbing oxygen from the air, heat or caloric was released into the surrounding medium. Davy's research clearly demonstrated a relationship between the rate of calcination and electrical production. Wollaston asserted that a process similar to combustion also gave rise to electricity: metals having a stronger affinity for oxygen than electrical matter. Particular

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[204] Davy, 1839k, 400.

[205] Ibid, 400-409, 400.

material combinations merely increased the rate of oxidation, making manifest electrical fluid and its associated phenomena.

Davy and Wollaston's disagreement over voltaic electricity reflected the eighteenth-century problem discussed in chapter one: did imponderable fluids, like heat and electricity, facilitate or participate as a substance in chemical change? With respect to heat, Lavoisier argued successfully for the latter: caloric was an element like oxygen or mercury. Davy attempted to avoid the question in discussing current production. His experiments indicated that electricity was generated by chemical changes taking place between the substances in the pile. Although Wollaston agreed with parts of Davy's research, he ultimately rejected his claim that there existed a general relationship between chemical change and the manifestation of electrical phenomena. It was well known that certain elements had predilections for specific materials, e.g. with the exception of gold and platinum, metals rusted by absorbing oxygen from the air, and releasing caloric. Wollaston believed a similar mechanism explained current production. Since the application of sparks and current to water caused its decomposition, Wollaston thought he had found a suitable model not unlike Pearson's: as metals absorbed oxygen they released electricity and, as electrical fluid passed through water, it combined with its constituents to form hydrogen and oxygen gas. Thus, within this framework, electricity was a chemical substance.

Although Wollaston promoted the view that electricity was a material, he recognized a key problem with chemical accounts in general. He wrote:

> Notwithstanding the power of Mr. Volta's electric pile is now known to be proportional to the disposition of one of the metals to be oxidated by the fluid

> interposed, a doubt has been entertained by many persons, whether this power arises from the chemical action of the fluid on the metal, or, on the contrary, whether the oxidation itself may not be occasioned by electricity, set in motion by the contact of metals that have different conducting powers.[206]

In short, he asked: did chemical changes produce current or did the motion of electrical fluid cause chemical change? Although he thought the latter unlikely, he conceded that Volta might be correct: a percussive force could potentially set electrical fluid in motion in conductors with different electromotive abilities. Current might then facilitate or accelerate the observed chemical reactions in the pile, especially the absorption of oxygen in metals.

Wollaston was not alone in expressing concern over the order of operations observed in the pile. Henry, for example, similarly wrote:

> On the whole, the electromotive power of the plates, and the chemical agency of the interposed fluids, appear to be the only circumstances, that can be brought to explain the efficiency of the Galvanic pile. To decide which is to be considered as the cause, and which as the effect, is a difficulty not peculiar to this case, but common to every other, where two events, that are invariably connected, are not distinguished by an appreciable interval of time.

The problem, Henry contended, could be boiled down to which came first: mechanics or chemistry? Like Wollaston, however, Henry still asserted that "the most defensible view of the subject [was] that which attributes the primary excitement of electricity to the chemical changes [observed in the pile]."[207] Drawing on Davy's research, he wrote:

> Why… when pure water forms a part of the arrangement, is the action of the pile suspended by placing it in an exhausted receiver, or in any of those gases that are incapable of supporting oxidation? Why is its efficiency increased by an atmosphere of oxygen gas, or by adding to the water in the cells several

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[206] Wollaston, 1801, 427.

[207] Henry, 1813, 268.

> fluids in a proportion not sufficient to change materially its conducting power? Why is the nitric acid, though a worse conductor of electricity than the sulphuric, more active in promoting the energy of the apparatus? Why is the power of these combinations proportional to the disposition of one of the metals composing them to be oxidized by the interposed fluids? These facts undoubtedly suggest that, in some way or other, the chemical agency of the fluids employed is essential to the sustained activity of the pile.[208]

Henry argued that regardless of what electricity was, whether it be a property or a substance, the production of current had strong chemical dependencies that contact theory could not adequately explain. He asserted that Haldane and Davy's investigations of how the pile behaved under vacuum and in different gases were most compelling. If the pile's electrical action was caused by the contact of dissimilar conductors, why did the chemical character of the ambient environment matter? He contended that these findings strongly indicated that chemistry trumped mechanics in current production.

Why were natural philosophers not convinced? Chemists' experimental results were, in part, overshadowed by the conceptual problems posed by the pile's chemical effects. For example, Johann Wilhelm Ritter, a German chemist who discovered ultraviolet radiation in sunlight, pointed out serious issues with the pile's alleged electrical decomposition of water. It was well known that water was a conductor. If electricity was a unique element, and if all conductors contained electrical fluid as Volta maintained, then water could not be a compound of hydrogen and oxygen alone. Wollaston proposed that electrical fluid entered a solution like water, and chemically combined with its constituents to form hydrogen and oxygen gas. Within this framework, electrical fluid contributed to the rarefaction of liquids in a similar manner as caloric:

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[208] Ibid, 263.

electrical particles' self-repulsion separated the particles of the liquid to form a gas. If water already contained electrical fluid, how was the process of vaporization to be understood? What were the consequences for current production?[209]

Jean Baptiste Biot was assigned to investigate and evaluate the purported causes of the pile's current by Napoleon Bonaparte. (Napoleon had met Volta in 1797 during his military campaign in the Italian States. Impressed by Volta, Napoleon became a patron and advocate for his science.[210]) Biot raised other objections to a chemical interpretation of the battery. The materials used in electrical instruments were chemically unaffected by the passage of electrical fluid. If chemical changes produced electricity, why did friction machines and electrical detectors, like Nicholson's doubler, not experience more rapid oxygenation or rusting. If frictional, animal, and voltaic electricity were different

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[209] Ritter's experiments, like Davy's, indicated that the oxygenation of metals played an important role in current production. Ritter compared conductors' abilities to absorb oxygen, including water, with Volta's measure of their electromotive properties. He noted that the most conductive metals were also the most susceptible to oxidation. He proposed re-evaluating the composition of water, modifying the phlogistic view. He suggested that many of the conceptual problems associated with the pile's electrical action and chemical effects could be explained if oxygen was a compound water and negative electricity. As oxidizable metals absorbed oxygen, water and electricity would be released. There is some debate amongst historians as to when British chemists first became aware of Ritter's studies. Fullmer suggests that Davy learned of Ritter's experiments from Thomas Beddoes as early as 1799. (Davy could not read German.) A brief discussion of Ritter's electrochemical experiments with water were published in 1801 in Nicholson's Journal in an extract of a letter to the editor by a little known physician named William Babington. Babington, at that time, noted two problems with Ritter's account. First, it "was written very obscurely, and was still more obscured by the language of the newer philosophy" (Ritter was a proponent of the controversial *natur philosophie* movement). Davy first referenced Ritter's work in a footnote in 1802, but did not discuss it in any great detail. Thus, more research is needed to illuminate the precise nature of the connection, if any, between Ritter and Davy's experiments prior to 1802. See: Fullmer, 2000, 284-287; William Bablington, "Extract of a letter from Dr. G.M. to Dr. William Bablington dated Freiberg, Dec. 17, 1800, On the State of Galvanism and other Scientific Pursuits in Germany", *Nicholson's Journal*, February (1801): 511-513, 512; and Davy, 1839, 200, 396. For a discussion of Ritter's life, work, and views on electrochemistry, see Christensen, 1995; Anja Skaar Jacobsen, "Spirit and Unity: Oersted's Fascination by Winterl's Chemistry," *Centaurus* 43 (2001): 184-218; Kleinert, 2002; Ostwald, 1980, 110-113, 158-168; Johann Wilhelm Ritter, *Die Begruendung Der Elektrochemie Und Entdeckung Der Ultavioletten Strahlen. Eine Auswahl Aus Den Schriften Des Romantischen Physikers.* (Frankfurt: Akademische Verlagsgesellschaft, 1968); Wetzels, 1990.

[210] See, Pancaldi, *2003*, 175-177, 234-240.

expressions of one type of electrical fluid, why did these three types of electricity cause dissimilar kinds of chemical change? Wollaston contended that for a chemical theory of electricity to be successful, it had to account for the decomposition of water by current and sparking. But as Henry noted, sparks and current sometimes caused different kinds of chemical change, e.g. current did not promote the synthesis of gases like nitrogen and oxygen, whereas sparking did. How were these differences in chemical effect to be reconciled?

Biot also criticized chemists' reliance on qualitative measures. Volta appeared before the French Academy of Sciences in 1801 to defend contact electricity. Cavallo, as discussed in chapter two, had pointed out experimental difficulties with Volta's theory: the contact of two different metals produced inconsistent, weak electrical discharges. Could this phenomenon reliably generate enough electricity to account for galvanic effects? In a demonstration hailed a tour de force, Volta confidently measured the electricity produced by the contact of two dissimilar metals in front of a large crowd of his peers. Using an electrometer, he also showed that after the pile's current had ceased to decompose water, but he was still able to detect electricity. Biot declared Volta's experimental results "irrefutable".[211] The percussion of two different metals created a measurable spark. Furthermore, the pile's electrical action persisted beyond its observed chemical effects. (Nicholson independently confirmed this result. [212]) Biot contended that

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[211] Biot, 1803, 8. Biot wrote: "La première, celle qui attribue tout à l'oxidation n'est pas admissible. Volta a prouvé d'une manière incontestable que des métaux isolés et mis en contact se retirent di contact dans des états électriques différens. Ce fair observé depuis par tous les physicians, ne peut être révoqué en doute." And "[L]'action du contact est tout; l'oxidation, rien."

[212] Nicholson in Haldane, 1800a, 243-245.

Volta's measurement of contact electricity was, therefore, more reliable and authoritative than Davy's experiments correlating the rate of oxygenation with the amount of current produced.[213]

Natural philosophers and chemists marshaled different kinds of experimental evidence to support either a chemical account of the pile's current or contact theory. For example, Henry emphasized the importance of Davy's experiments, in which piles of similar construction were placed in different gases. Batteries in non-calcinating airs lost their ability to decompose water, whereas piles placed in oxidizing gases readily separated water into its elements. Biot, on the other hand, stressed Volta's quantitative measures of electrical fluid. The contact of two different metals alone produced sparks. Did the pile's current reside in its metals: as a substance capable of being chemically displaced by oxygen as Wollaston contended; as an immaterial, but powerful chemical agent as Davy proposed; or as a fluid subject to the physics of neighboring charged bodies as Volta asserted?

Although they disagreed on the mechanism by which the pile produced current, scientists generally agreed that its chemical effects demanded further research. Could electricity cause chemical change? The answer was resoundingly yes. Was electricity a substance? With the exception of Davy, most electricians argued that it was. Did it facilitate or participate in chemical reactions? Were frictional, animal, and voltaic electricity different manifestations of the motion of one electrical fluid or many different

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[213] Biot, 1803; Pancaldi, 2003, 240-243.

types of electricity? These questions continued to shape electrical discourse long into the nineteenth century.[214]

3.4: Conclusion: The Nature of Chemical Change

> …as there are several invisible and permanently elastic fluids like common air, inflammable air, fixed air, &c. which are very dissimilar, though possessed of certain common properties; so there may be several sorts of more subtile fluids essentially different from each other, yet bearing some analogy to the electric fluid.[215]
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> Tiberius Cavallo (1795)

In 1802, Davy wrote that, at the ripe old age of nine years, the history of galvanism could already be divided into '4 epochs': "the publication of the fundamental galvanic fact" in the *Philosophical Transactions* by Luigi Galvani, namely that organic tissue produced electricity;[216] "the discovery of the existence of inorganic galvanism", by the Italian chemist Giovanni Fabbroni, which showed that electricity could be produced in minute quantities by the contact of oxidable metals; the invention of the pile or "galvanic battery" by Volta in 1799 for "distinctly exhibiting the analogy between galvanism and common electricity"; and the discovery by "British chemists" that there exists a "general connexion between the excitement of galvanic electricity and chemical

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[214] In an elegant and definitive essay in 1833, Michael Faraday evaluated the evidence in favor of one-electricity, citing disagreement amongst mainly British electricians as to the identity of the many fluids behaving like electricity. He concluded that these fluids: voltaic, animal, thermal, magnetic, and common or frictional were different manifestations of one form of electricity. The debate between contact theory and chemical accounts of current production, however, persisted throughout the nineteenth century. In 1888, Walter Nernst, a German physical chemist, published his "theory of the cell", which resolved many of the conceptual difficulties with a chemical explanation of the pile.

[215] Cavallo, 1795, 72. Wollaston, 1801, 427.

[216] Volta reported Galvani's experiments to the Royal Society in 1793 via Cavallo. Luigi Galvani and Alessandro Volta, "Account of Some Discoveries Made by Mr. Galvani of Bologna: With Experiments and Observations in Two Letters from Mr. Alexander Volta," *Phil. Trans.* 83 (1793): 10-44.

changes."[217] Davy, however, was unaware of the century long tradition of analyzing the origins of electricity and its chemical effects.[218]

In the early eighteenth century, British natural philosophers were concerned with the relationship between electricity and chemistry. As discussed in chapter one, Watson demonstrated that the sparking of airs caused chemical change (combustion). In the mid to late eighteenth century, many natural philosophers likened electricity to heat because of their numerous, similar effects. Priestley, for example, proposed that the relationship between electricity and chemical change, specifically the sparking of airs and the calcination of metal conducting wires, could be most easily explained by phlogiston theory. As Lavoisier's theory of heat, however, came to supplant phlogiston theory, the relationship between electricity and caloric became uncertain.

As scientists began to explicitly refer to their practice as either natural philosophical or chemical, however, distinctive theories were proposed to account for the behavior and action of electrical fluid. As discussed in chapter two, Volta developed a theory of electricity in which the distribution, intensity, and motion of one-fluid accounted for all electrical phenomena. With the invention of the voltaic pile, there was also renewed interest in explaining the chemical changes associated with electricity, especially in Britain.

In the late eighteenth century, Pearson tried to show that electrical studies and Lavoisier's theory of heat were not incompatible. Through a series of sparking

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[217] Davy, 1839h, 189-190.

[218] By 1807, Davy was much more aware of electrical studies conducted in natural philosophy, in addition to chemical research. See, Davy, 1807.

experiments, he demonstrated that electricity decomposed water. He subsequently used this result to argue that electricity was a form of concentrated caloric, capable of fracturing substances and chemically combining with their constituents to form gases in a manner similar to caloric.

With the invention of the voltaic pile, Nicholson and Carlisle demonstrated that, like sparking, current produced profound chemical changes in materials. As in Pearson’s experiments, for example, current could be used to decompose water into hydrogen and oxygen gas. Moreover, Nicholson and Carlisle’s research also suggested that the chemical interaction of the pile’s substances limited the amount of electricity it could produce. For instance, they observed in a standard pile constructed of silver, zinc, and water that the zinc plates tarnished and eventually stopped generating electricity when completely calcined.

Cruickshank’s research built on Nicholson and Carlisle’s observations. In one of the first systematic studies of the pile’s chemical effects, he found that the type of wire used to connect the pile to the solution, like water or lead acetate, affected the materials formed at each lead. Because hydrogen (and/or metal) was consistently produced at the wire attached to the negative end of a standard battery and oxygen (and/or acid) at the positive or zinc lead, he suggested that electrical fluid entered the liquid from the negative or silver side of the battery and fractured the components of the solution. The electrical fluid then combined with free oxygen in the liquid and traveled through the solution to the zinc wire, as evidenced by the appearance of metal oxide, oxygen gas, and/or acid at the positive lead. Furthermore, he observed that a similar set of reactions occurred between the layered materials in a standard pile, e.g. bubbles of hydrogen gas formed on the silver plates.

Davy then combined Cruickshank's studies with other known chemical facts about electrical behavior. For instance, Fabbroni observed in the 1790s that metals used in galvanic experiments were consistently and rapidly oxidized. Haldane also observed that the standard pile did not produce current under vacuum, and Henry added another class of substances known to react to electricity: acids, or in Lavoisier's framework, oxygen-rich compounds. Davy's research program subsequently concentrated on the relationship between oxygen absorption, hydrogen production, and current. He found that he could control the pile's ability to decompose water by manipulating the materials in the battery. For example, piles constructed of two different metals and an oxidizing fluid, like muriatic (hydrochloric) acid, produced significantly more gas per galvanic unit than a standard pile. On the basis of these experiments, Davy argued that voltaic electricity must be somehow produced by chemical change.

Modern readers of Davy's early papers – like me – will likely be readily convinced by his experiments and arguments that chemical change caused electricity. The majority of his contemporaries, however, did not endorse his theoretical conclusions. Henry and Wollaston argued that the main difficulty with Davy's theory was a chicken and egg problem: was electricity made manifest by chemical changes or were chemical changes caused by the passage of electrical fluid? It was also not clear how to reconcile Davy's view that chemical changes were responsible for electrical phenomena and its materiality. Even if chemical changes, like the absorption of oxygen, were paramount to the production of electricity, where did the electrical fluid come from? Was it a substance displaced by elements entering into chemical combination or some unknown form of matter?

Many theories privileged the role of oxygen in electrical production. Wollaston, for example, was committed to the position that "the oxidation of the metal [was] the primary cause of the electrical phænomena observed", but ignored Davy's claim that other types of chemical change also produced electricity. Instead, Wollaston suggested that the most likely explanation for voltaic electricity was that as metals absorbed oxygen, they released a proportional amount of electrical fluid.[219]

Although Wollaston and Davy disagreed about the primary cause of electricity, they were both committed to a chemical theory of current production. They were not successful, however, in convincing the natural philosophic community that chemistry affected electrical generation. Why were natural philosophers not persuaded by their experiments that chemical changes, like the absorption of oxygen in metals, produced current?

Davy considered himself to be both a natural philosopher and chemist, yet his approach to the study of electricity differed from the researches of Volta, Cavallo, and Nicholson. While they participated in the development of electrometers, instruments used to measure the properties of electricity in different contexts, Davy like Cruickshank and Wollaston emphasized the importance of accounting for the type, extent, and conditions under which chemical changes occurred. The former approach attempted to eliminate

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[219] Wollaston, 1801, 427.

some of the complexities associated with the study of electricity by providing a means of comparing charges on electrified bodies. Rather than relying solely on physiological responses as indicators of charge, instruments were used to mediate scientists' experiences of electricity, to provide a quantitative measure of electrical fluid. Davy used different methods to study electrical effects and their chemical dependences. It was generally acknowledged that the chemical changes associated with electricity were difficult to study. The properties of substances, such as color, acidity, flammability, and metallicity, were often profoundly altered by electricity, but challenging to compare rigorously. For Davy, changing an element of his apparatus or procedure played a pivotal role in determining the order of chemical operations and the kinds of chemical changes substances underwent when exposed to electricity. Natural philosophers and chemists, however, disputed the reliability and authoritativeness of these different approaches.

Furthermore, the pile's chemical effects produced an additional set of conceptual problems. If the contact of metals with different electromotive abilities was responsible for current production as Volta purported, why was the pile's electrical action adversely affected in vacuum and non-calcinating airs? Why were different substances drawn to either the positive or negative end of the battery? Why did current cause the decomposition of complex solutions, but not gases? Why did the substances in the pile undergo chemical changes, whereas the materials in friction machines did not? Did chemical change augment the flow of electrical fluid? Was it a by-product of the motion of electricity or was it the cause of current?

Volta asserted that, through contact theory, the physics of one fluid could be used to explain the generation of frictional, animal, and voltaic electricity. The chemical effects of the pile added more complexity to the phenomena under consideration. Perhaps voltaic and animal electricity were distinct from frictional electricity. Although they shared numerous similarities of effect, e.g. numbness, attraction, repulsion, heating, etc., there were many instances in which the analogy failed. It was generally acknowledged that neither contact theory nor the proposed chemical explanations adequately addressed the range of observed electrical phenomena. Which sets of experimental results were to be given priority in theory development? Volta, Biot, and other natural philosophers favored their experiments and measurements with multipliers and electrometers. Davy, Wollaston, and Henry promoted their chemical experiments and results. The community was divided.

In the late eighteenth and early nineteenth centuries, physics and chemistry were just emerging as independent fields of study; electricity thus belonged to physical science as a whole. Scientists, who referred to their practice as chemistry, natural philosophy, or both, actively debated and studied the same electrical phenomena. Although natural philosophers and chemists often studied the same subjects, they increasingly adopted different methods. For example, while Volta emphasized the importance of measuring the intensity and distribution of electrical fluid, Davy chemically analyzed the changes taking place in electrically active materials. By way of a conclusion, I discuss the role of analogy in this discourse, and how electrical studies affected the development of chemistry.

Conclusions: Analogical Reasoning, Chemical Studies of Electricity, and Methodology

> Mechanical philosophy, regarded as the science of the motions of the masses of matter, in its theories and practices, is to a certain extent, dependent upon chemical laws. How in fact can the mechanic calculate with accuracy upon the powers of solids, liquids, or gases, in communicating motion to each other, unless he is previously acquainted with their particular chemical affinities, or propensities to remain disunited, or to combine? It is to chemistry that he is indebted for the knowledge of the nature and properties of the substances he employs; and he is obliged to that science for the artificial production of the most powerful and most useful of his agents [heat and electricity].[1]
>
> Humphry Davy (1802)

In 1805, Georges Cuvier wrote of the late Joseph Priestley that he "was the father of modern chemistry, who never acknowledged his daughter."[2] It was a disparaging remark. At this time, chemistry was just in the process of being acknowledged as an independent physical science and women were often regarded as property. The implication of Cuvier's comment was clear: Lavoisier was a natural philosopher, while Priestley was a chemist. Historians have, in part, taken their cue from nineteenth-century researchers' perceptions of the burgeoning disciplinary landscape, some scholars arguing that Lavoisier ushered in a new age of quantitative chemistry by appropriating methods from experimental physics.

This dissertation, however, complicates Lavoisier's contribution to the chemical revolution by showing that many chemical practitioners were investigating topics belonging to "physics" during this period. For example, as discussed in chapters one and two, Priestley actively studied electrical phenomena. He was not only interested in its

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[1] Davy, "Early Miscellaneous Papers," 312.

[2] Schofield, 2004, xii.

physical properties as evidenced by his interest in electrometers, but also its chemical and biological effects. Similarly, Nicholson is often portrayed as a chemist in the historical literature, but he was also deeply invested in the study of electrical phenomena and electrical instruments. Moreover, he censured some of his contemporaries, most notably Lavoisier, for inappropriately assigning more significant figures than physically possible, arguing that the precision of an instrument needed to be taken into account in measurement and computation, a key element of modern experimental physics. Thus, this dissertation indicates that further research is needed not only to fully document Priestley and Lavoisier's respective roles in chemistry, but also to understand chemists' contributions to the development of quantitative physical science and what distinguished physics from chemistry during this period.

In the eighteenth and early nineteenth centuries, the study of electricity was the examination of the electrical properties and behaviors of substances in their various physical states. Chemists and natural philosophers learned that electricity was a powerful material agent. Like heat, it could be used in productive ways to learn more about chemical change. Friction machines, Leyden jars, electrometers, and the voltaic pile were common equipment in chemical laboratories. Electricity was also an important experimental tool, e.g. it could be used in both the analysis and synthesis of complex gases. Both chemists and natural philosophers recognized the significance of theoretically accounting for its actions. For instance, did it facilitate or participate as a substance in chemical change? How did bodies become charged? What properties of electricity did electrometers measure? In the process of debating these issues, electricians discovered new electrical and chemical effects, substantially adding to knowledge of matter in its various forms.

Given scientists' common interest in electrical phenomena during this period, I argued that differences in experimental practice provide more insight into disciplinary formation than does the classification of subject matter. Priestley, Cavendish, Nicholson, Cavallo, Volta, Davy, and others made significant contributions to the study of electricity. They were interested in similar questions, e.g. how do substances interact to produce charge, but they approached these problems using different experimental methods and standards of evidence. For example, Cavallo and Volta, as discussed in chapter two, both emphasized the importance of being able to measure and quantify weak electricity. They investigated how the electrical strength or tension of an electrified body varied under different conditions to learn more about the origin, motion, and distribution of fluids behaving like electricity. Davy, as we have seen in chapter three, took a different approach. Knowing that friction-based electricity affected gas composition and that electricians like Nicholson and Volta believed that the pile produced electrical fluid like the torpedo ray, Davy analyzed how current affected the chemical composition of solids and liquids and later how chemical changes in the pile's layered materials affected electrical production. Davy, like Cavallo and Volta, sought to identify the origins of current, but he used volume measurements, physiological responses, and other indicators of chemical change as evidence. Although they also conducted chemical experiments, Cavallo and Volta primarily relied on electrometers and multipliers, measuring the deflection angle of lightweight objects to determine the presence and strength of electrical fluid.

This suggests that early nineteenth-century chemical practitioners placed more emphasis on developing clarifying experimental procedures to elucidate complex chemical processes than they did on instrumentation. Priestley, for example, studied both electrical phenomena and the chemical changes associated with electricity. Davy accepted that the pile produced current. He was, however, more interested in understanding how current interacted with other materials, as manifested by changes in the chemical composition of substances, than in studying electricity as an independent phenomenon. Volta, in contrast, was less interested in documenting chemical change and more concerned with variations in the distribution and strength of electrical fluid. Volta's emphasis on developing sensitive and reliable electrometers stemmed from his interest in the electrical properties of solids, whereas Davy's emphasis on electricity's associated chemical changes stemmed from his fascination with chemistry.

These subtle, but important differences in experimental focus contributed to the debates over how the pile produced electricity. They are also suggestive of a burgeoning disciplinary divide between (physical) chemistry and (chemical) physics. An informative and necessary extension of this research would be to analyze the history of electricity through 1840 to see how chemical practitioners further contributed to the study of electrical phenomena and how their experimental methods compared to those of natural philosophers.

Nonetheless, it is clear that chemists and natural philosophers practicing chemistry were deeply concerned with and invested in electrical research. Thus, this dissertation demonstrates the need to revise our historical understanding of the study of electricity. Contrary to the literature, which suggests that analyses of electrical science elucidate the development of experimental physics, this work shows that the study of electricity belonged more to physical science in general than to any one discipline. Moreover, I have demonstrated that the study of electricity can also provide a vehicle with which to analyze the development of quantitative experimental science as a whole.

Although there is a large literature examining the history of the conceptual development of science and experimentation, missing from many of these accounts is a detailed understanding of how untidy, often non-linear reasoning and serendipitous observations develop into a set of experiments from whence a coherent theory of natural phenomena is created. Experimentation – the act of controlling or manipulating a set of criteria to gauge a system's response – provided information about natural processes that could not be easily deduced by other means.[3] It required knowing what elements participated in producing phenomena. As this dissertation showed, sometimes the design of an experiment was the subject of debate. Natural philosophers discussed why apparatuses and instruments behaved as they did under certain conditions and what they measured. For example, Cavallo challenged the veracity of various multipliers, arguing

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[3] Natural philosophers and chemists, for example, often referred to the electrical fluid produced by friction machines as *artificial*, recognizing that the process by which they manufactured electricity from metals, wax, and cloth did not naturally occur outside of the laboratory. Although electricians designed apparatus and instruments to investigate electrical phenomena, they asserted that the knowledge they gleaned from experiments could be applied to natural phenomena. Using similarity of effect, Benjamin Franklin, for example, made a cogent and compelling argument that lighting like laboratory sparks was electrical in origin.

that flaws in their construction caused their measurements to be ambiguous. It also required investigating the effects of minute changes to the system, like using silver instead of gold wires in electrochemical experiments. Cruickshank observed that although hydrogen and oxygen gas consistently formed at the negative and positive leads of wires placed in water, gold wires appeared to be unaffected by the passage of current, whereas silver wires were modified by electricity in aqueous solutions. With slight variations in experimental set-up and iteration, new knowledge of electricity was produced.

How did natural philosophers and chemists make sense of these diverse results? Detailed studies of scientific practice, especially experimentation, can provide insight into how natural philosophers marshaled evidence to develop and support theoretical claims about objects in Nature. This includes important information about the development of measurement, e.g. knowing how an instrument worked and what it measured; procedure, e.g. knowing how the order of operations affected experimental results; and how properties were assigned and weighted.

In particular, this dissertation demonstrated that analogy was a significant theoretical tool and that it was also used to develop experimental stratagems in electrical research. I argued that the likening of electricity to heat was representative of a broader trend in experimental philosophy, with many natural philosophers utilizing arguments by analogy to develop working theories of electrical action. For example, Beccaria and Priestley contended that because electricity and heat produced a number of similar effects, including fire and the calcination of metal, electricity was a form of heat.

Adopting “similarity of effect” as a conceptual method for constructing an experimental definition for a set of phenomena proved productive. Documenting the likenesses between electrical and thermal effects encouraged natural philosophers to design novel experiments to analyze the extent and validity of the relationship they believed to exist between heat and electricity. Priestley, for instance, compared the effects of sparking airs with gases exposed to a candle’s flame, and Nicholson examined how temperature affected conductivity in different materials. Through this research, they substantially added to knowledge of the physical and chemical properties of substances.

The act of articulating why the likenesses between phenomena should outweigh their differences, or vice versa, encouraged scientific discourse and rigorous evaluation of experiments and results. Through this dynamic interplay of experimentation, observation, measurement, and analysis, in which analogical reasoning played an important role, natural philosophers and chemists increased understanding / knowledge of electricity. Analogies came in four varieties. Although similarity of effect dominated discussion, e.g. whether the chemical changes occurring externally to the pile were identical to those observed within the instrument, they also used similarity of form, function, and cause to draw parallels between phenomena. For instance, while Cavendish could replicate the torpedo ray’s effects with a combination of Leyden jars, the phial did not bear a striking resemblance to the anatomy of the fish either structurally or materially. Nicholson and Volta, on the other hand, immediately recognized the pile as a device that mimicked the form of the torpedo’s electrical organ and its effects, lending credence to the idea that the fish produced electricity. Similarity of cause was only occasionally used. Some electricians, for example, asserted that because friction produced both heat and electricity that heat and electricity must be related. In these four different ways, analogies were used to make sense of diverse electrical phenomena and to devise experiments with which to validate or disprove apparent likenesses between cause and effect.

More research needs to be done on how natural philosophers and chemists utilized analogy in scientific practice. I have focused on its use in electrical studies in the eighteenth and early nineteenth centuries, but as discussed in the introduction, a quick survey of contemporary works in astronomy, zoology, and mechanics suggests that it was ubiquitously and productively used in other areas of study. Thus, analogical reasoning may provide a more general and compelling link between experimentation and theory construction than traditionally recognized by historians and philosophers.

This dissertation demonstrated that chemists were actively involved in electrical research. Their studies, for example, revealed the importance of electricity to fundamental chemical processes, such as synthesis and decomposition. Electricity was everywhere. It seemed to permeate all substances, and to be involved in a wide range of phenomena from storms to muscle contractions to combustion and chemical change. Its relationship to heat, light, and, later, magnetism begged further study. Its profound effects on substances sustained chemical practitioners' interest and investment in electrical research well into the nineteenth century. I have shown that the history of electricity and the variety of approaches to electrical research can provide insight into history of scientific practice, and I hope to extend this study. As Davy wrote in 1821:

> The production of heat and light by electrical discharges: the manner in which chemical attractions are produced, destroyed, or modified by changes

> in the electrical states of bodies: and the late important discovery of the connection of magnetism with electricity [in 1820], have opened an extensive field of enquiry in physical science, and have rendered investigations concerning the nature of electricity and the laws by which it is governed, and the properties that it communicates to bodies, much more interesting than at any former period in the history of philosophy.
>
> Is electricity a subtle elastic fluid? or are electrical effects merely the exhibition of the attractive powers of the particles of bodies? Are heat and light elements of electricity, or merely the effects of its action? Is magnetism identical with electricity, or an independent agent, put into motion or activity by electricity? – Queries of this kind might be considerably multiplied [and] the solution of them, it must be allowed, is of the highest importance…[4]

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[4] Davy, 1822, 64.

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Appendix I: Glossary of Some Key Chemical Terms

Name	Older Term	Meaning from 1770 to the Present			
		Priestley	Lavoisier	Davy	Modern
Acid	Sour, sharp, corroding ~1600	Simple substance	Containing oxygen ~ 1789	Containing hydrogen ~ 1808	Electron acceptor
Caloric	Fire, Sulphur	Phlogiston – inflammable principle	Caloric	Motion; Caloric	Energy (vibratory motion of particles) causing sensation of warmth
Dephlogisticated Air	Unknown	Dephlogisticated Air; Vital Air	Oxygen	Oxygen	Oxygen
Heat	Fire; Sulphur	Phlogiston – Inflammable principle	Caloric – material form of heat ~ 1783	Motion ~ 1799; Caloric - material form of heat ~ 1806	Energy (see above)
Hydrogen	Inflammable Air	Inflammable Air	Hydrogen or principle of water	Hydrogen	Hydrogen
Inflammable Air	Inflammable Air	Inflammable Air	Hydrogen	Hydrogen	Hydrogen
Marine Acid	Spirit of Salt	Marine Acid	Muriatic Acid	Hydrochloric acid	Hydrochloric acid
Muriatic Acid	Spirit of Salt	Marine Acid	Muriatic Acid	Hydrochloric acid	Hydrochloric acid
Nitrogen	Unknown	Phlogisticated Air; Mephitic Air	Azote	Nitrogen	Nitrogen
Oil of Vitriol	Oil of Vitriol	Vitriolic Acid	Sulphuric Acid	Sulphuric Acid	Sulphuric Acid

Name	**Older Term**	**Priestley**	**Lavoisier**	**Davy**	**Modern**
Oxymuriatic Acid	Unknown	Spirit of Marine Acid	Oxymuriatic acid	Chlorine (named for its color as a gas: pale green)	Chlorine
Oxygen	Vital air	Dephlogisticated air	Oxygen or acidifying principle	Oxygen	Oxygen
Phlogiston	Fire; Sulphur	Phlogiston – Inflammable principle	Caloric – material form of heat	Motion; Caloric	Energy (vibratory motion of particles) causing sensation of warmth
Phlogisticated Air	Unknown	Phlogisticated Air	Azote	Nitrogen	Nitrogen
Spirit of Salt	Spirit of Salt	Marine Acid	Muriatic Acid	Hydrochloric Acid	Hydrochloric Acid
Sulphuric acid	Oil of Vitriol	Vitriolic acid	Sulphuric acid	Sulphuric acid	Sulphuric acid

Appendix II – Survey of Articles in the *Philosophical Transactions* on Electricity

The following graph shows a survey of the number of articles published on or relating to electricity in the *Philosophical Transactions* between the years 1744-1795 and 1796-1825. In the latter half of the eighteenth century, approximately half of the essays made reference to heat, with approximately 20% referring to electricity as a type of electric fire.

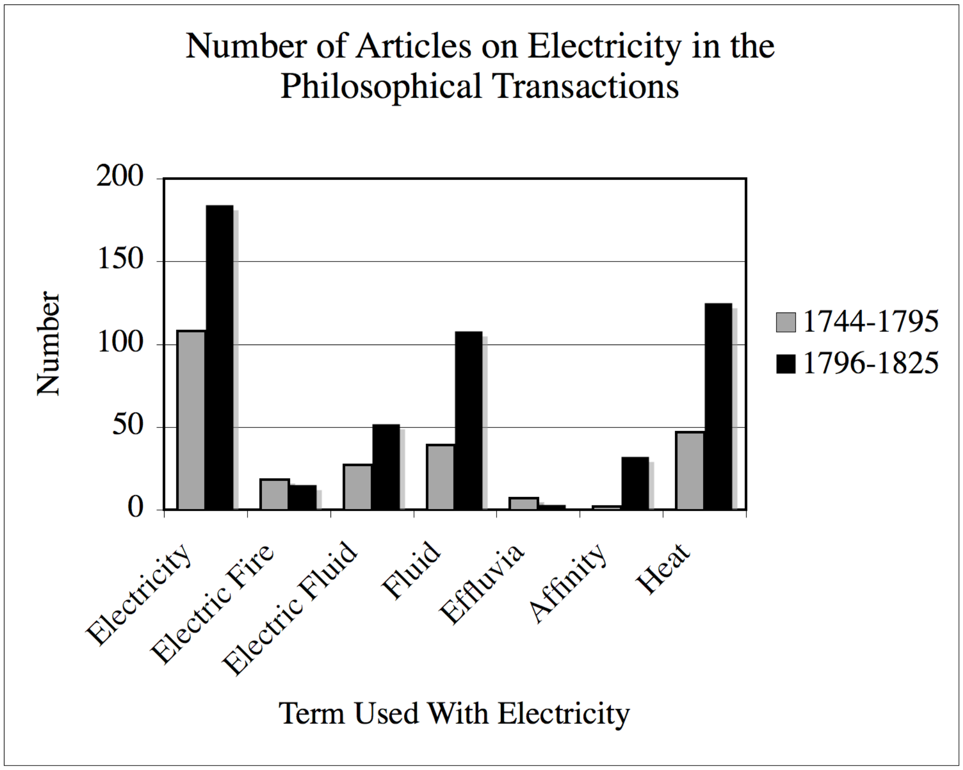


Figure 1: Bar graph representing the number of articles in the Philosophical Transactions containing the word electricity, electricity and electric fire, electricity and electric fluid, etc., between the years 1744-1795 and 1796-1825.

Appendix III: A Brief Overview of Some Electrical Terms in Use in the Late Eighteenth Century

Term	**~Year**	**Natural Philosopher**	**Definition**	**Approximate Modern Definition and/or Term**
Accidental Electricity	1775	Alessandro Volta	Electrical fluid made present by the proximity of a charged body	Induction - the creation of an electric state by the presence of a charged body
Atmosphere (Electric)	1751	Benjamin Franklin Giambatista Beccaria	A rarified, concentric, material vapor responsible for communicating electrical forces between charged bodies	Electromagnetic Field
Battery	1751	Benjamin Franklin	A series of Leyden jars, named for its resemblance to an artillery battery or a set of fortifications	Chemical battery or voltaic pile
Communication (Electric)	1795	William Nicholson	Means by which electrical fluid makes other charged bodies aware of its presence	Electromagnetic Field
Compensation	1787	William Nicholson	Electrical fluid made present by the proximity of a charged body	Induction - the creation of an electric state by the presence of a charged body
Conductor	1751	Benjamin Franklin	A material that allows the transmission of charge	A material that transmits electric current
	1795	William Nicholson	A material that allows the transmission of charge only at specific temperatures	
Electric	1751	Benjamin Franklin	A material that collects charge along its surface	A material that does not readily conduct electrical current

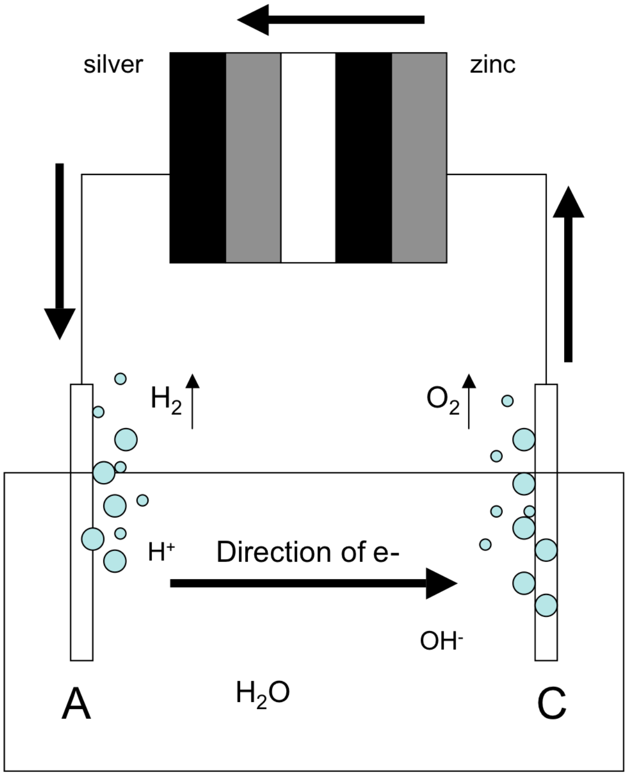
Term	~Year	Natural Philosopher	Definition	Approximate Modern Definition and/or Term
Electricity (s)	1750s	Abbe Nollet	Two fluids: resinous and vitreous	Electrons and protons; energy produced by the motion of charged particles
		Peter Mussenbroek	Two fluids: positive and negative	
		Benjamin Franklin	A material fluid (self-repulsive)	
	1770s	Henry Cavendish	The motion and action of charged particles (self-repulsive), which comprise a single fluid	
		Joseph Priestley	A single fluid akin to phlogiston	
		Giambatista Beccaria	A material fluid related to heat (self-repulsive)	
		Alessandro Volta	A material fluid comprised of self-attracting charged particles	
	1785	Charles Augustin Coulomb	Two fluids: positive and negative	
	1792	Giovanni Fabbroni	A complex set of phenomena produced by chemical change	
Franklin Square (simple Leyden jar)	1751	Benjamin Franklin	Three adjacent plates of metals, glass, metal	Capacitor – two conductors separated by an insulator in which electrical energy is stored
Insulator	1786	Tiberius Cavallo	A material that does not readily conduct electrical current	A material that does not readily conduct electrical current
	1795	William Nicholson	A material that does not readily conduct electrical current at specified temperatures	

Term	~Year	Natural Philosopher	Definition	Approximate Modern Definition and/or Term
Intensity	1788	Tiberius Cavallo	A measure of electrical strength or density	Voltage – electrical potential difference
	1787	William Nicholson	A measure of electrical strength	
	1795	Alessandro Volta	A measure of electrical strength or force tending to make manifest attraction (repulsion), sparks, etc	
Leyden jar or phial (Franklin Square)	1750	Peter Mussenbroek	A glass jar, with an outer metallic coating in which a metal chain is suspended in the middle of the jar	Capacitor – two conductors separated by an insulator in which electrical energy is stored
Resistance	1771	Cavendish	A measure of the degree of difficulty experienced by electric fluid as it passes through a substance that results in a change in the velocity of the electrical fluid	Resistance – the amount of energy lost by a current traveling through a substance (a measure of the opposition to current flow)
Tension	1778	Alessandro Volta	A measure of the forces acting on a charged point	Voltage – electrical potential difference
Vindicating electricity	1776	Giambatista Beccaria	Electric fluid made manifest in an object with unequally charged surfaces or by the proximity of a charged body	Induction – the creation of an electric state by the presence of a charged body

Appendix IV: A Brief Look at Modern Electrochemistry

There was much confusion as to how the voltaic pile caused the electrical decomposition of water. This appendix provides a very brief overview of the modern theory of electrolysis.

Figure AIV.1 depicts the electrolysis of water using gold connecting wires.



Water is an electrolyte, meaning that it contains charged ions, H^+ and OH^-, capable of conducting electrons. At the anode, *A*, electrons enter the solution and combine with hydrogen ions to form hydrogen gas. At the cathode, *C*, electrons leave the solution and oxygen gas and excess water molecules form. These reactions may be expressed in modern terms as:

$2H_2O \rightarrow 2H^+ + 2OH^-$
$2H^+ + 2e^- \rightarrow H_2\ (g)$
$4\ OH^- \rightarrow O_2\ (g) + 2H_2O + 4e^-$