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CHEMICAL AFFINITY IN EIGHTEENTH-CENTURY SCOTTISH PHYSIOLOGY AND AGRICULTURE

A DISSERTATION APPROVED FOR THE DEPARTMENT OF HISTORY OF SCIENCE

BY

Dr. Peter Barker, Chair

Dr. Kathleen Crowther

Dr. Richard Hamerla

Dr. Judith Lewis

Dr. Kerry Magruder

Dr. Rienk Vermij

Dr. Stephen Weldon

This dissertation is dedicated to my wife, Lisa, and our daughter, Evie,

for always believing in me and loving me.

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Abstract

The standard historiography of eighteenth-century chemistry focuses on the chemical revolution. French chemists, most notably Lavoisier, replaced the phlogiston theory of combustion with a new one based on oxygen and modernized the chemical nomenclature. This history has largely been treated as internal to the history of chemistry.

My dissertation decenters combustion and the French contribution by continuing modern work by Mi Gyung Kim (2003) and Georgette Taylor (2006) that locates elective attraction as the fundamental chemical theory in the second half of the eighteenth century. Also referred to as chemical affinity, this was an empirical theory that recorded the combining preferences of simples and compounds in order to understand and predict reactions. The development and demise of this theory extends well beyond the boundaries of chemistry as a technical subject.

I establish the existence of an important affinity school in Scotland centered in the work of William Cullen (1710-1790), Joseph Black (1728-1799), and their students. These lecturers applied affinity not only to inorganic chemistry but also to medicine, including respiration, and the treatment of syphilis and smallpox. The application of affinity theory in the medically important study of mineral waters, led to the advancement of chemical analysis techniques, but also to serious experimental and

theoretical problems for the affinity theory in the work of John Murray from 1815 to 1817.

Well before this, however, Scottish chemists had applied affinity theory to agriculture. The Scottish Improvement movement of the eighteenth century focused the advancement of agricultural yields. Led by the third Duke of Argyll and Lord Kames, the Scottish great landowners attempted to rationalize agriculture through chemistry, and in turn advanced the careers of important affinity chemists like Cullen and Black. Commercial and industrial applications of affinity theory included the production of manures, the production and sale of artificial mineral waters, and the preparation of soda and alkaline salts for bleaching, a key process in the textile industry. As a consequence, the history of affinity chemistry cannot be understood without reference to the political, social, and economic issues that come to the fore in this dissertation.

Chapter 1. Chemical Affinity in Eighteenth-Century Scottish Physiology and Agriculture

1.1 Introduction to Affinity

Chemical affinity theory provided a foundational understanding of chemical bonding from the sixteenth through twentieth centuries. Now obscured by many layers of supervening chemical theory, including molecular geometry, valency, and quantum chemistry, affinity theory at its heuristic core was the study of the various chemical substances' abilities to attract and bond with each other. The heyday of affinity theory came in the second half of the eighteenth-century. In 1790, American chemist John Penington defined the discipline of chemistry as "A science which teaches the laws of attraction between heterogeneous bodies in contact with each other."[1] In his *History of Chemistry* (1830), Thomas Thomson said, "Chemical affinity constitutes confessedly the basis of the science."[2] This dissertation examines the development and use of the chemical concept of affinity in the collateral fields of agriculture and physiology during the Scottish Enlightenment. Examining the use of affinity in these fields will demonstrate the interconnectedness of economic and scientific pursuits during the last half of the eighteenth century.

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[1] John Penington, *Chemical and Economical Essays: Designed to Illustrate the Connection Between the Theory and Practice of Chemistry, and the Application of That Science to Some of the Arts and Manufactures of the United States of America* (Philadelphia: Printed by Joseph James, 1790), 45.

[2] Thomas Thomson, *The History of Chemistry*, 2 v. (London: Henry Colburn and Richard Bentley, 1830), v. 2, 157.

The lectures of medical professors at Edinburgh and Glasgow demonstrate the permeability of disciplinary boundaries and illuminate the constellation of scientific fields that was unique to the late eighteenth and early nineteenth centuries. This study will also shed light on how farmers and physicians studied and appropriated chemical theory. From the patrons at the highest levels of British society through the professional classes and the yeomanry, chemistry was widely studied due to its utility in improving agriculture, medicine, and industry.

The professionalization of medicine, both in the reformation of medical education and the self-marketing of doctors, informs our understanding of the structure and mobility of the professional classes. The intellectual and social developments of Edinburgh during this period also carry historical consequences beyond understanding of Scottish society. "The Athens of the North," Edinburgh was an educational hub for English and American doctors, and the teachings of Cullen and Black were further disseminated through the Hunters in London and through Benjamin Rush (1746-1813) and Caspar Wistar (1761-1818) in Philadelphia. On the continent, Scotland was considered a shining example of the social and economic progress possible in the eighteenth century. One anonymous French writer said,

> No two countries have differed more widely from each other than Scotland has lately done from itself. It is not perhaps more than fifty years since the state of the country began materially to alter; but during

> that period, perhaps, no society has ever made such rapid steps in civilization and industry.[3]

In studying the intellectual, economic, and social advancements of the Scottish Enlightenment, we gain an understanding of the core goals of the broader, trans-national Enlightenment. The end of feudal agriculture, the rise of the professional classes, and an increased understanding of the processes of nature were goals shared by philosophers throughout Europe.

1.2 Diachronic History of Affinity

Michelle Sadoun-Goupil has written the most extensive diachronic history of affinity tracing the various chemical permutations of the term from the sixteenth through the twentieth centuries.[4] In the sixteenth century, the term affinity was used in conjunction with the concept of sympathies and antipathies. Girolamo Fracastoro (1478-1553) used the concept of affinity to express likeness between two substances. He combined affinity with the idea of sympathies and antipathies to express the idea

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[3] Originally Monsieur B-de, *Reflections on the Causes and Probable Consequences of the Late Revolution in France, with a View of the Ecclesiastical and Civil Constitution of Scotland, and of the Progress of Its Agriculture and Commerce* (Dublin: W. Wilson et al, 1790), 44. Quoted in Neil Davidson, "The Scottish Path to Capitalist Agriculture 2: The Capitalist Offensive (1747-1815)," *Journal of Agrarian Change* 4, no. 4 (2004): 411-460.

[4] Michelle Sadoun-Goupil, *Du Flou Au Clair? Histoire De L'affinité Chimique: De Cardan À Prigogine* (Paris: Ed. du C.T.H.S., 1991).

that like will attract like.[5] In *Magia Naturalis,* Gian Battista Della Porta (1534-1615) emphasized the vitalistic qualities of matter saying,

> When the things we have said come about from a property of a living substance are favorably rearranged, we may believe that we have seen that they co-operate through a simple affinity or struggle against each other because of a strange aversion.[6]

Again Della Porta uses affinity to express likeness between two substances. He asserts that the vitalistic property of substances will allow them to act on their sympathies and antipathies based on their affinity with other substances.

The study of sympathies and antipathies continued into the seventeenth century in the works of Kenelm Digby (1603-1665). Digby was best known for his Powder of Sympathy, a weapon salve meant to cure a wound by application to the weapon that caused the wound. Jan Baptiste van Helmont (1578-1644) also studied sympathies and antipathies but he reexplained the occult cause of the reactions, shifting it from a property of the physical body of the substance to the spiritual essence of that substance. Johann-Rudolph Glauber (1604-1670) used the term affinity in discussions on the generation and improvement of metals towards their

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[5] Girolamo Fracastoro, *De Sympathia Et Antipathia Rerum Liber Unus. De Contagione Et Contagiosis Morbis Et Curatione Libri Iii* (Venetiis: [Apud heredes Lucaeantonii Juntae Florentini], 1546), 40.

[6] As cited in Sadoun-Goupil, *Du Flou Au Clair? Histoire De L'affinité Chimique: De Cardan À Prigogine*, 38.

ultimate goal of becoming gold. In his "Work on Minerals," Glauber uses affinity to refer to the family resemblance or parentage between metals.[7]

In summarizing the various uses of the term affinity leading up to 1660, Sadoun-Goupil said,

> Le terme, exprime toujours la ressemblance de nature. La notion, ou l'idée de tendance à l'union, est considérée comme une qualité occulte---cachée ou dans le langage moderne potentielle---qui dérive du postulat suivant: le semblable attire et s'unit à son semblable. En conséquence, la réaction chimique est représentée comme une union, sans violence, une alliance ou un mariage, entre deux substances qui, tout en étant différentes ou mieux, non identiques, présentent entre elles une ressemblance, c'est-à-dire une similitude de nature.[8]

Sadoun-Goupil identifies the common thread in early notions of affinity as this occult quality of matter for the like to attract and unite to the like.

In the second half of the seventeenth century, the mechanists denied the existence of occult forces and disassociated affinity from sympathies and antipathies. Robert Boyle said,

> I look upon amity and enmity, as affections of intelligent beings, and I have not yet found it explained by any, how those appetites can be

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[7] For further information on Glauber's use of affinity see Sadoun-Goupil, *Du Flou Au Clair? Histoire De L'affinité Chimique: De Cardan À Prigogine*, 40-41.

[8] Sadoun-Goupil, *Du Flou Au Clair? Histoire De L'affinité Chimique: De Cardan À Prigogine*, 46.

> placed in bodies inanimate and devoid of knowledge, or so much as sense. And I elsewhere endeavour to shew, that what is called sympathy and antipathy between such bodies does, in great part, depend upon the actings of our own intellect...[9]

Actions at a distance, such as the sympathies of various chemical substances, were replaced with the physical interactions of corpuscles. Daniel Duncan proposed a typically mechanist understanding of chemical interactions saying, "Si les pointes de sels sont plus longues ou plus aigües, souvent il se produira en conséquence telle réaction ou telle autre."[10] The shapes of the various corpuscles affected their interactions, but corpuscles could not affect each other at distance. While the word affinity was still used to express likeness between two substances, these chemical substances could not interact except through physical contact.

Isaac Newton restored the use of active principles to chemistry with his famed Query Thirty-One in the Opticks:

> It seems to me farther, that these Particles have not only a *Vis inertiae*, accompanied with such passive Laws of Motion as naturally result from the Force, but also that they are moved by certain active Principles, such as is that of Gravity, and that which causes

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[9] Robert Boyle and Thomas Birch, *The Works of the Honourable Robert Boyle. In Six Volumes* (London: Printed for J. and F. Rivington, 1772), vol. 4, p. 289.

[10] Daniel Duncan, *La Chymie Naturelle, Ou L'explication Chimique Et Mécanique De La Nouriture De L'animal* (Paris: L. d'Houry, 1682), 35. As quoted in Sadoun-Goupil, *Du Flou Au Clair? Histoire De L'affinité Chimique: De Cardan À Prigogine*, 53.

> Fermentation, and the Cohesion of Bodies. These Principles I consider, not as occult Qualities, supposed to result from the specifick Forms of Things, but as general Laws of Nature, by which the Things themselves are form'd; their Truth appearing to us by Phaenomena, though their Causes be not yet discover'd. For these are manifest Qualities, and their Causes only are occult.[11]

Like gravity, chemical attraction was an observable law of nature. Although the causes of these active principles were unknown, their effects were undeniable.

> The parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. And for explaining how this may be, some have invented hooked atoms, which is begging the question; and others tell us that bodies are glued together by rest, that is, by an occult quality, or rather by nothing; and others, that they stick together by conspiring motions, that is by relative rest amongst themselves. I had rather infer from their cohesion, that their particles attract one another by some force, which in immediate contact is exceeding strong, at small distances performs the chymical operations above-mention'd, and reachs not far from the particles with any sensible effect... There are therefore agents in nature able to make the particles

[11] Isaac Newton, *Opticks: Or, A Treatise of the Reflexions, Refractions, Inflexions and Colours of Light* (London: Printed for S. Smith, and B. Walford, 1704), Query 31.

bodies stick together by very strong attractions. And it is the business of experimental philosophy to find them out.[12]

Newton thus laid out a research program for eighteenth-century natural philosophy to empirically chart the attractions between various substances and, if possible discover the underlying causes of such forces.

Etienne Francois Geoffroy began the task of charting the affinities of the various chemical substances with his *Tables des rapports* (1718). Primarily a pedagogic tool, Geoffroy's table (figure 1) lists common chemical substances in the first row. The column is then filled out with substances in descending order of their affinity for the header chemical. For example the spirit of acid in the first column has

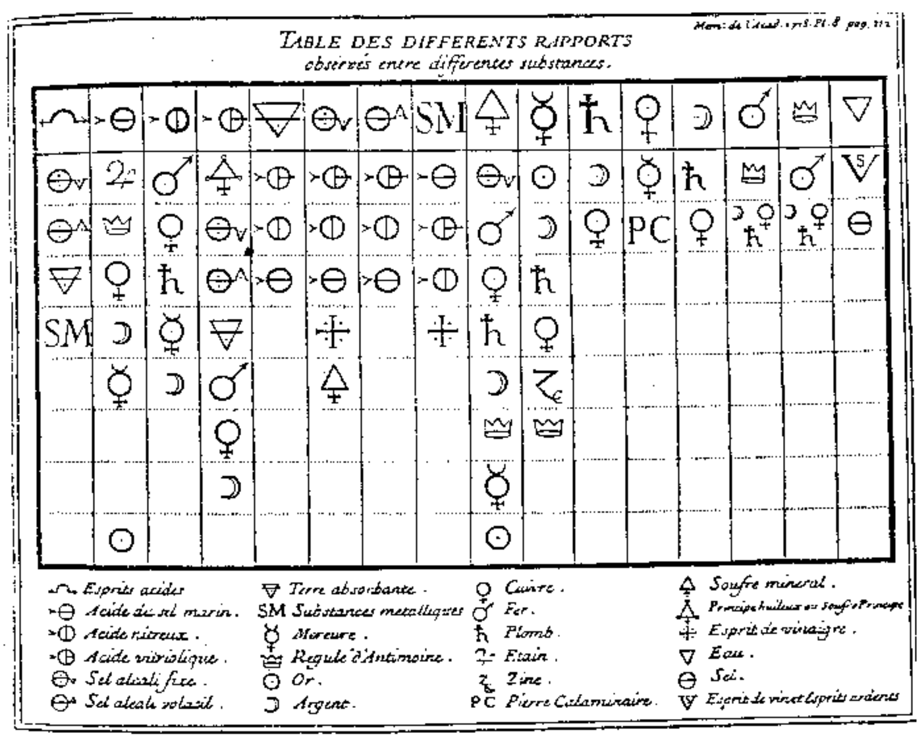

Fig 1: Etienne Francois Geoffroy, *Tables des rapports* (1718)

[12] Newton, *Opticks: Or, A Treatise of the Reflexions, Refractions, Inflexions and Colours of Light*, Query 31.

the greatest affinity for fixed alkali salts, followed by volatile alkali salts, absorbent earths,[13] and metallic salts. The table was useful in understanding chemical reactions, because substances that were higher in the column should be able to displace the substances beneath them in a displacement reaction. The third column thus informs the reader that iron will displace copper, lead, mercury or silver from a compound with nitrous acid.

Geoffroy's table was used into the 1750s before being replaced by increasingly elaborate and complex tables, culminating in the tables of Torbern Bergman.[14] Bergman produced two tables to indicate the difference between the affinities of chemical substances in solutions and when analyzed by heat. Each table had fifty-nine columns and twenty five rows, and the text that he prepared to accompany and explain the tables ran to three hundred eighty-two pages.

Much of the eighteenth-century work on affinity was in mapping the relations of the constantly growing list of known chemical substances. Theories explaining how affinity worked met with little success until the nineteenth-century, when electrical attraction and later valency provided some of the answers. The affinity theorists discussed in this dissertation were, for the most part, agnostic about the underlying causes of affinity. Some of the researchers held theories about chemical or physical atomism, some believed in phlogiston, others adopted the French oxygen

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[13] This was a mineralogical classification of earths that included limestone, chalk, and other earths that were rich in calcium.

[14] Torbern Bergman, *A Dissertation on Elective Attractions*, trans. Thomas Beddoes (London: J. Murray, 1785).

nomenclature, but all found affinity useful in understanding the properties of chemical substances and in predicting the outcomes of reactions in the lab and in the real world.

1.3 Chemical Affinity in the Eighteenth Century

Chemical affinity has had numerous meanings over the last four centuries. Even within a particular period, it is more appropriate to speak of a set of affinity theories recognizable through familial similarities than to a monolithic doctrine. The variety of eighteenth-century affinity theories were shaped by social, economic, and geographic influences. In Germany, mining and metallurgy necessitated a chemistry focused on ores and alloys with fire as the primary tool of analysis.[15] In France, the combination of pharmaceutical interests and the centralized research program of the Academie des sciences focused chemical studies on the analysis of salts in solution.[16] In Scotland, the economic importance of agriculture and the social importance of medicine for the burgeoning middle class produced a distinct set of Scottish affinity theories. Scottish affinity was marked by advanced techniques for soil and mineral analysis and the integration of pneumatic chemistry, theories of heat, and physiology.

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[15] See Ursula Klein, *Verbindung Und Affinität: Die Grundlegung Der Neuzeitlichen Chemie An Der Wende Vom 17. Zum 18. Jahrhundert* (Basel: Birkhäuser Verlag, 1994).

[16] See Mi Gyung Kim, *Affinity, That Elusive Dream: A Genealogy of the Chemical Revolution* (Cambridge (Mass.): MIT Press, 2003). And Frederic Lawrence Holmes, *Eighteenth-Century Chemistry As An Investigative Enterprise* (Berkeley: Office for History of Science and Technology, Univ. of California, 1989).

Affinity theorists rejected the principalist theory of chemical properties, which held that a compound had the same chemical properties as its constituent principals. Because knowledge of the chemical principals was insufficient to fully understand the vast array of compounds, chemists were forced to study and record the properties of each compound.

The leading chemical lecturers of the early- and mid-eighteenth century, Peter Shaw (1694-1764), William Cullen (1710-1790), and Joseph Black (1728-1799), made their livings as physicians, and the majority of their students were studying to become physicians. The chemical lectures and texts developed by these men should be understood, at least in part, as an existing tradition of medical chemistry descending from Paracelsus, Franciscus Sylvius, and Hermann Boerhaave. However, the secondary literature has tended to parse out and compartmentalize the physiological, mineralogical, agricultural, and chemical works of these lecturers. In the case of Cullen, his role in the development of medicine has been examined in a host of books and articles,[17] and his chemical theories have been explored separately

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[17] J. R. R Christie, "William Cullen and the Practice of Chemistry," in *William Cullen and the Eighteenth Century Medical World: A Bicentenary Exhibition and Symposium Arranged by the Royal College of Physicians of Edinburgh in 1990*, ed. Andrew Doig, Joan P. S. Ferguson, Iain A. Milne and Reginald Passmore (Edinburgh: Edinburgh University Press, 1993). Reginald Passmore, "Method of Study. William Cullen. An Introductory Lecture to the Course of the Practice of Physic Given at Edinburgh University in the Years 1768-89," *Proceedings of the Royal College of Physicians of Edinburgh* 17 (1987): 268-285. W. F Bynum, "Cullen and the Study of Fevers in Britain, 1760-1820," in *Theories of Fever From Antiquity to the Enlightenment*, ed. W. F. Bynum and V. Nutton (London: Wellcome Institue for the History of Medicine, 1981). R Stott, "Health and Virtue: Or, How to Keep Out of Harm's Way. Lectures on Pathology and Therapeutics by William Cullen C. 1770," *Medical history* 31 (1987): 123-142.

by Arthur Donovan and Georgette Taylor.[18] Cullen's agricultural work, almost entirely omitted from discussion of his nosology or chemistry, has only been studied by Charles Withers.[19] However, Cullen did not encapsulate his theories along disciplinary boundaries. Agriculture and mineralogy were taught in his chemistry courses, which were in turn part of the medical curriculum at Glasgow and Edinburgh. In parsing out these theories, historians have artificially imposed modern disciplinary boundaries on the past and obscured a knowledge system prevalent among eighteenth-century natural philosophers. This particular brand of chemical affinity used in the eighteenth century was challenged at the close of the century by the works of Claude Louis Berthollet (1748-1822) and John Murray (1786-1851).[20]

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[18] Arthur L Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black* (Edinburgh: University Press, 1975). Georgette Nicola Lewis Taylor, "Unification Achieved: William Cullen's Theory of Heat and Phlogiston As An Example of His Philosophical Chemistry," *British Journal for the History of Science* 39, no. 143 (2006): 477-502. Georgette Nicola Lewis Taylor, "Variations on a Theme: Patterns of Congruence and Divergence Among 18th Century Chemical Affinity Theories" (PhD diss., University of London, 2006).

[19] Charles Withers, "William Cullen's Agricultural Lectures and Writings and the Development of Agricultural Science in Eighteenth-Century Scotland," *Agricultural History Review* 37 (1989): 144-156.

[20] See Pere Grapi, "The Role of Chemistry Textbooks and Teaching Institutions in France at the Beginning of the Nineteenth Century in the Controversy About Berthollet's Chemical Affinities," in *Learning by Doing: Experiments and Instruments in the History of Science Teaching*, ed. Peter Heering and Roland Wittje (Stuttgart: Steiner, 2011). John Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water," *Annals of Philosophy* 6 (1815): 256-69, 347-63. John Murray, "A General Formula for the Analysis of Mineral Waters," *Annals of Philosophy* 10 (1817): 169-77.

1.4 Chapter Summaries

1.4.1 Affinity in Medicine

In chapter two, I argue that the growing prominence of chemical affinity in medical curricula in the Scottish Enlightenment allowed for the development of novel understandings the physiological processes of bodily fluids. Many of the physiological texts that were most widely used in Britain during the first half of the eighteenth century were translations of continental works. In London, Peter Shaw produced a relatively direct translation of Herman Boerhaave's *Elementa Chemiae*[21] in 1727, while William Lewis (1708-1781) translated and greatly extended the work of Caspar Neumann (1648-1715).[22] Shaw and Lewis were the first lecturers in Britain to use Geoffroy's table of affinities. John Elliot (1736-1786) appended a translated edition of Torbern Bergman's (1735-1784) table of elective attractions to his own work, *Elements of the Branches of Natural Philosophy Connected with Medicine*.[23] Many of the French texts on physiology were also widely used in

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[21] Herman Boerhaave, *A New Method of Chemistry; Including the Theory and Practice of That Art: Laid Down on Mechanical Principles, and Accomodated to the Uses of Life*, trans. Peter Shaw and Ephraim Chambers (3 pt. London: J. Osborn & T. Longman, 1727).

[22] Caspar Neumann and William Lewis, *The Chemical Works of Caspar Neumann Abridged and Methodized, with Large Additions: Containing the Later Discoveries and Improvements Made in Chemistry and the Arts Depending Thereon* (London: Printed for W. Johnston, G. Keith, A. Linde, P. Davey, B. Law, T. Field, T. Caslon, and E. Dilly, 1759).

[23] John Elliot, *Elements of the Branches of Natural Philosophy Connected with Medecine: Viz. Chemistry, Optics, Acoustics, Hydrostatics, Electricity, and Physiology. Including the Doctrine of the Atmosphere, Fire, Phlogiston, Water &C. Together with Bergman's Table of Elective Attractions* (London: J. Johnson, 1782).

Britain, although these were not usually translated, because it was assumed that students training for a medical degree could read French. Despite the prevalence of continental texts, Britain was by no means devoid of native works on physiology. Both Stephen Hales' *Vegetable Staticks* (1727)[24] and his *Haemastaticks* (1733)[25] were extremely influential in the later work of Black, Joseph Priestley (1733-1804), and Antoine Lavoisier (1743-1794). Although William Cullen published little, his courses at Glasgow and Edinburgh, along with his classification of diseases, shaped the thinking of the medical community of Great Britain in the second half of the eighteenth-century. His apprentice William Hunter (1718-1783) is remembered as one of the great anatomists of the period. Another of Cullen's students, Joseph Black, was one of the most influential medical professors of the century. By the 1770s, John Hunter (1728-1793),[26] John Caverhill (d. 1781),[27] and Adair Crawford (1768-1795)[28] had integrated chemical affinity into the physiological processes of animal heat, and

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[24] Stephen Hales, *Vegetable Staticks: Or, An Account of Some Statical Experiments on the Sap in Vegetables* (London: printed for W. & J. Innys, 1727).

[25] Stephen Hales, *Statical Essays; Containing Vegetable Staticks, Etc (Haemastaticks; Or An Account of Some Hydraulic and Hydrostatical Experiments Made on the Blood and Blood-Vessels of Animals)* (London: printed for W. Innys and R. Manby; and T. Woodward, 1733).

[26] John Hunter, "Experiments on Animals and Vegetables, with Respect to the Power of Producing Heat," *Philosophical Transactions of the Royal Society of London* 65 (1775): 446-458. John Hunter, "Of the Heat, &C. Of the Animals and Vegetables," *Philosophical Transactions of the Royal Society of London* 68 (1778): 7-49.

[27] John Caverhill, *Experiments on the Cause of Heat in Living Animals and Velocity of the Nervous Fluid* (London, 1770).

[28] Adair Crawford, *Experiments and Observations on Animal Heat, and the Inflammation of Combustible Bodies* (London: J. Murray; J. Sewell, 1779).

William Cruikshank (d. 1810)[29] and others had begun studying the chemistry of bodily fluids.[30]

In chapter three, I detail the use of affinity in the study of mineral waters, a popular medical commodity in the eighteenth century. Mineral waters provided an inexhaustible and ubiquitous source of materials, the analysis of each serving local medical and economic purposes and the advancement of a broader chemical research program. Cullen and his students used chemical affinity to analyze mineral waters in their courses on *materia medica*, chemistry, and later natural history. These chemical analyses provided information about the constituency, medical efficacy, and the natural and artificial formation of mineral waters. In turn, the precision required in isolating dilute salts in mineral waters drove the advancement of affinity theory and its analytical techniques. The recognition that gases and various non-soluble earths contributed to the medical efficacy of mineral waters but could not be studied in samples that had been bottled and shipped led to the rapid development of in situ experimentation. These volatile components along with the variation in chemical composition and concentration of the many spas emphasized the importance of locality and experiential knowledge in granting medical authority. The application of chemical affinity to the study of mineral waters is important because the literature on

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[29] William Cruikshank, *Experiments on the Insensible Perspiration of the Human Body, Shewing Its Affinity to Respiration* (London, 1779).

[30] For more on the history of animal heat in the eighteenth century, see Everett Mendelsohn, *Heat and Life: The Development of the Theory of Animal Heat* (Cambridge: Harvard University Press, 1964).

mineral water was the most published genre related to mineralogy or chemistry. Mineral water literature was a medium of advertising, for the water as a natural commodity, the spa as a medical resort, and the doctor as an authority. Doctors wrote pamphlets, articles, and monographs to gain the patronage of the gentry who owned or controlled the spas and to attract clients. In a period with no formal system of medical accreditation, these publications served as credentials demonstrating formal education, knowledge of a particular spa, and (through the dedication and list of subscribers) the patronage of the local gentry. Using the correspondence and mineralogical publications of Cullen and his students, I argue that affinity replaced the battery of tests that had been used in the sixteenth and seventeenth centuries to identify the constituents of mineral waters. I will also detail how these doctors gained patronage through their various publications.

1.4.2 Affinity in Agriculture

In chapter four, I describe the role of the land-owning classes in the establishment of the improvement movement. Agriculture, with its ties to the economics and power of the landed classes, was much discussed by the nobility and gentry throughout the eighteenth century. Changes in the price of grain and practices of farming, along with the political effects of the union and the failed Jacobite rebellion of 1745, fueled changes in tenancy that accelerated the disintegration of the clan system in the highlands and accelerated the urbanization of the lowlands. These changes were accelerated by powerful landowners like the Dukes of Argyll, who either owned or controlled much of the land in Argyllshire. Archibald Campbell, the third Duke of Argyll, also acted as a powerful patron placing men who would contribute to the continued development of agriculture in seats of political power and professorships within the universities.

Lord Kames, the patron of William Cullen, also includes affinity in his agricultural work, *The Gentleman Farmer*. Kames says,

> To be an expert farmer, it is not necessary that a gentleman be a profound chymist. There are however certain chymical principles relative to agriculture, that no farmer of education ought to be ignorant of. Such as appear the most necessary shall be here stated, beginning with elective attraction and repulsion, which make a capital article in the science of agriculture as well as of chymistry.[31]

Kames provides a detailed explanation of chemical affinity. He theorizes that plants chemically attract gases and liquids. The nutrients carried in solution by these gases and liquids provide plants with their nourishment.[32] Kames thus based his theory of plant nutrition on chemical affinity.

In chapter five, I discuss the development of affinity based agricultural chemistry in the Scottish universities. Although James Maxwell, secretary of the Society of Improvers, had proposed the foundation of a chair of agriculture as early as the 1720s, the first lectures on agriculture in the Scottish universities were given by

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[31] Henry Home, Lord Kames, *The Gentleman Farmer Being An Attempt to Improve Agriculture, by Subjecting It to the Test of Rational Principles* (Edinburgh: Printed for W. Creech, and T. Cadell, 1776), 293.

[32] Kames, *The Gentleman Farmer*, 298.

William Cullen in 1748. In the first half of the eighteenth century, agriculturalists were primarily concerned with mechanical alterations of the soil. Jethro Tull's Horse Hoeing Husbandry (1731) called for ploughing the land, pulverizing the soil, and drilling seeds. Even Cullen was primarily concerned with making sure that the soil had the right texture to convey water to the roots of a plant and to allow those roots to grow. However, Cullen's agricultural theories also suggested chemical improvements to the land that would accelerate the production of plant nutrients. Cullen's course was particularly influential because of his popularity as a teacher. Many of his students, including Joseph Black, Rev Dr John Walker,[33] and George Fordyce[34] included agriculture in their lectures. Francis Home's *The Principles of Agriculture and Vegetation* (1756) was the first book that used chemical affinity to explain agricultural principles. Home believed that fertile soils "consist of particles, which in part, or all together, attract acids."[35] Home used similarly atomistic, chemical conceptualizations of manures, air, and water to construct a chemical theory of agriculture that rivaled the mechanistic theory of Jethro Tull. Home so integrated

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[33] Charles Withers, "Improvement and Enlightenment: Agriculture and Natural History in the Work of the Rev. Dr. John Walker (1731-1803)," in *Philosophy and Science in the Scottish Enlightenment*, ed. Peter Jones (Edinburgh: J. Donald Publishers, 1988). Matthew D Eddy, "The Aberdeen Agricola: Chemical Principles and Practice in James Anderson's Georgics and Geology," in *New Narratives in Eighteenth-Century Chemistry*, ed. Laurence Principe (Dordrecht: Springer, 2007).

[34] Little has been written on Fordyce. See Noel Coley, "George Fordyce M.D., F.R.S. (1736-1802): Physician-Chemist and Eccentric," *Notes and Records of the Royal Society of London* 55, no. 3 (2001): 395-409.

[35] Francis Home, *The Principles of Agriculture and Vegetation* (Edinburgh: Printed for G. Hamilton & J. Balfour, 1756), 55-56.

chemical affinity into his agriculture that he ranked the efficacy of manures based on their affinity to acids in the air. The manure's ability to attract these acids allowed them to form salts that were, in his theory, the primary nutrient for plants.

George Fordyce's *Elements of Agriculture and Vegetation* (1771) provides another example of the use of affinity in agricultural texts. Part one of the book is entitled "Elements of Chemistry, Necessary to be understood for the explanation of the Principles of Agriculture." After an extended discussion of mechanical and chemical combinations, Fordyce includes a table of elective attractions listing in descending order the reactants for acids, alkalis, metals and air. He also includes several plates depicting the differences between mechanical and chemical combinations and comparing the relative forces of gravity and affinity. Though an interesting example of chemical atomism that predates John Dalton[36] by three decades, the book as a whole is as yet unstudied in the history of science. Fordyce's possibly novel representations of affinity relations and of atomic reactions may have been overlooked because of their publication in a work on agriculture.

Chapter six will provide a conclusion reviewing the novel findings of the dissertation and proposing possible extensions of this project.

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[36] John Dalton's chemical and meteorological work in the first decade of the nineteenth century is often identified as the foundation of the "modern" chemical atomism in which each chemical simple is thought to be elemental. For more on Dalton see Frank Greenaway, *John Dalton and the Atom* (Ithaca, N.Y.: Cornell University Press, 1966). Elizabeth Chambers Patterson, *John Dalton and the Atomic Theory; The Biography of a Natural Philosopher* (Garden City, N.Y.: Doubleday, 1970).

Chapter 2. Chemical Affinity and Physiology

2.1 Chemistry in the Medical Faculties

While studying the chemical affinity doctrine of William Cullen and Joseph Black it is important to remember that both of these men made their livings as physicians and lecturers and that the majority of their students were studying to become physicians. In exploring the interrelations of affinity doctrine and physiology, I argue that these pedagogues did not encapsulate their theories along disciplinary boundaries, but rather that chemistry informed their physiological works and vice versa.

In the early modern period, *physiologia* referred to non-Aristotelian natural philosophy, and this usage carried over into the first half of the eighteenth century. Benjamin Martin's *The philosophical grammar; being a view of the present state of experimental physiology, or natural philosophy* (1734)[37] is an example of this definition of physiology. By the mid-nineteenth century, "physiology" became associated with the experimental physiology of François Magendie (1783-1855) and Claude Bernard (1813-1878). Historians from Charles Sherrington[38] to Andrew

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[37] Benjamin Martin, *The Philosophical Grammar; Being a View of the Present State of Experimented Physiology, or Natural Philosophy* (London, 1734).

[38] Charles Sherrington, "Physiology: Its Scope and Method," in *Lectures on the Method of Science*, ed. T. B. Strong (Oxford: Clarendon, 1906).

Cunningham[39] have identified the beginning of the nineteenth century as the founding period for modern physiology. With this more modern definition of physiology in mind, J.E. Lesch says, “No one of these men [eighteenth-century experimenters, including William and John Hunter, William Cullen, William Cruikshank] was a specialized physiologist, and the term ‘physiology’ was not in general use.”[40]   While Lesch is correct that none of these men would have been perceived as a physiologist by their contemporaries, the term “physiology” was in general use during the late eighteenth century. William Cullen defines it as “the doctrine that explains the conditions of the body and of the mind necessary to life and health.”[41] The key difference between this late eighteenth-century physiology and the much ballyhooed developments of the early nineteenth century is the shift from the more philosophical explanations of the body to the experimental focus of Magendie and Bernard.[42] This chapter will focus on the interactions between the eighteenth-century physiological studies on humans and the affinity doctrine.

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[39] Andrew Cunningham, "The Pen and the Sword: Recovering the Disciplinary Identity of Physiology and Anatomy Before 1800. I: Old Physiology - the Pen," *Studies in the History and Philosophy of Biological and Biomedical Sciences* 33 (2002): 631-665.

[40] J. E. Lesch, *Science and Medicine in France. The Emergence of Experimental Physiology, 1790-1855* (Cambridge: Harvard University Press, 1984), 22.

[41] William Cullen, *Institutions of Medicine: Part I. Physiology* (printed for Charles Elliot; and T. Cadell, 1772), 7.

[42] For more on this distinction between eighteenth and nineteenth century physiology see Cunningham, "The Pen and the Sword."

In this chapter, I review the basic principles of affinity theory and demonstrate that the growing prominence of chemical affinity in medical curricula in the Scottish Enlightenment allowed for the development of novel understandings the physiological processes of bodily fluids. Although William Cullen published little, his courses at Glasgow and Edinburgh along with his classification of diseases shaped the thinking of the medical community of Great Britain in the second half of the eighteenth-century. By the 1770s, William Irvine and Adair Crawford[43] had integrated chemical affinity into the physiological processes of respiration and animal heat. John Haygarth melded Cullen's theory of fevers with a study of the affinities of smallpox miasmas to develop a theory of contagion and a system for hospitals treating fevers.[44] Helenus Scott studied the affinities of bile to understand the role of of mercuric oxides in treating liver obstructions and syphilis.[45]

2.2 Chemical Affinity in the Scottish Medical Schools

Within Britain, the integration of chemical affinity with medicine was the work of Scottish medical professor William Cullen and his students. Cullen's own medical education was a medley of university courses at Glasgow (1726-1729) and Edinburgh (1734-1736), apprenticeships to Glaswegian surgeon-apothecary John

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[43] Crawford, *Experiments and Observations on Animal Heat, and the Inflammation of Combustible Bodies*.

[44] John Haygarth, *An Inquiry How to Prevent the Small-Pox and Proceedings of a Society* (Chester, 1784).

[45] William Scott, "Account of the Effects of the Nitrous Acid on the Human Body," *Medical Repository* 1, no. Appendix 1 (1797): 141-146.

Paisley (1729) and London apothecary William Murray (1731), and practical experience gained serving as surgeon on a merchant ship trading in Jamaica and the West Indies (1730). While in London in 1731, Cullen may also have attended the chemical lectures of Peter Shaw[46] or William Lewis.[47] Upon returning to his hometown of Hamilton in the 1732, Cullen established a successful practice as a surgeon serving as medical attendant to James Douglas, 5th Duke of Hamilton, and much of the gentry of the area. From 1737-1740, Cullen mentored William Hunter (1718-1783),[48] and the two men remained close throughout their lives. Cullen

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[46] Cullen used Shaw's translation of Georg Ernst Stahl's *Philosophical Principles of Universal Chemistry* (London, 1730) in his lectures. For more on the possible connection between Cullen and Shaw see Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, 31.

[47] For more on the possible connection between Cullen and Lewis see Taylor, "Variations on a Theme: Patterns of Congruence and Divergence Among 18th Century Chemical Affinity Theories," 68.

[48] William Hunter became one of the leading anatomists of the eighteenth century. Along with his brother John, William established himself in London as a lecturer on anatomy and physician. See Jessie Dobson, "Hunter, William," in *Complete Dictionary of Scientific Biography* (Detroit: Charles Scribner's Sons, 2008), vol. 6, pp. 568-570.

received his MD from the University of Glasgow in 1740. When the Duke of Hamilton died in 1744, Cullen and his family moved to Glasgow.[49]

From 1744 to 1746, Cullen taught medicine as an extramural lecturer in Glasgow, and in 1746, he entered into an arrangement to teach the theory and practice of physic at the University of Glasgow for the absentee professor of medicine, John Johnstone (or Johnstoun). In 1747, he also taught courses on *materia medica* and botany. In the winter of 1747, Cullen and John Carrick were given the responsibility of lecturing on chemistry. However, Carrick became ill, so Cullen taught the course by himself. In 1751, Johnstone resigned from the chair of medicine and Cullen was named his successor. Cullen only held the position for four years, resigning in 1755 to become professor of chemistry at the University of Edinburgh. Cullen had been unable to develop a sufficient medical practice in Glasgow and despite his popularity as a professor, the student fees were inadequate to support his family.

In 1755, Andrew Plummer, the professor of chemistry at the University of Edinburgh who had lectured on the subject for twenty-eight years, fell ill and it

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[49] For Cullen's biography see John Thomson, *An Account of the Life, Lectures and Writings of William Cullen* (Edinburgh: Blackwood, 1832). Christie, "William Cullen and the Practice of Chemistry." On his career as a professor see Andrew Kent, *An Eighteenth Century Lectureship in Chemistry* (Glasgow: Jackson, 1950). W P D Wightman, "William Cullen and the Teaching of Chemistry," *Annals of Science* 11, no. 2 (1955): 154-165. Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*. Roger L Emerson and Paul Wood, "Science and Enlightenment in Glasgow, 1690-1802," in *Science and Medicine in the Scottish Enlightenment*, ed. C.W.J. Withers and P. Wood (East Linton: Tuckwell Press, 2002), pp. 96-97. Taylor, "Variations on a Theme: Patterns of Congruence and Divergence Among 18th Century Chemical Affinity Theories."

became apparent that a successor would need to be named.[50] Cullen, who may have attended Plummer's chemistry course during his studies in the mid-1730s,[51] was nominated for the position as were his former student Joseph Black and Francis Home. Cullen's prominence as a chemistry professor at the University of Glasgow provided him with a significant advantage over the other less experienced candidates, but his experience as a practicing physician actually worked to his disadvantage. The medical faculty were concerned (rightfully) that Cullen would draw away clients. They preferred Joseph Black, because he had never practiced as a physician. However, due in large part to the patronage of the Duke of Argyll, Cullen received the appointment and was made full chair of chemistry upon Plummer's death in July of 1756. Black succeeded Cullen as professor of chemistry at Glasgow and Home would eventually be made professor of *materia medica* at Edinburgh in 1758.[52]

Unlike Plummer who lectured on pharmaceutical chemistry, Cullen taught a broader philosophical chemistry targeted not only at medical students but also undergraduates and local farmers and artisans.

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[50] On the University of Edinburgh's faculty members, their duties, and their remuneration see Jack B Morrell, "The University of Edinburgh in the Late Eighteenth Century: Its Scientific Eminence and Academic Structure," *Isis* 62 (1971): 158-171.

[51] There is no record of Cullen having attended Plummer's course, but his interest in chemistry and his familiarity with Plummer's teaching would suggest that he attended the course while studying at Edinburgh in 1736 or 1737.

[52] This appointment and the patronage of the Duke of Argyll are discussed further in chapter five.

> Does the joiner want a particular glew? Does the mason want a cement? Does the dyer want the means of tinging a cloth of a particular colour? Or does the bleacher want the means of discharging all colours? It is the chemical philosopher who must supply these. In short, I need say but this one thing: Wherever any art requires a matter endued with any peculiar physical properties, it is the chemical philosophy which either informs us of the natural bodies possessed of these properties or induces such in bodies which had them not before, or lastly, produces new bodies endued with the necessary qualities.[53]

For Cullen, chemistry was a utilitarian science useful not only in medicine but in a broad array of industrial pursuits.[54] Arthur Donovan has noted Cullen's close friendship with David Hume and the similarity in the two men's epistemological view of science as the abstraction of general laws from experience. Scientific theories were not meant to discover the rationalist ultimate causes, but rather provide systematic descriptions of nature and useful predictions.

Cullen's focus on a broad practical chemistry and his practice of lecturing in English rather than Latin created an accessible and popular chemistry course.

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[53] Donovan cited this manuscript as GUL, Cullen MSS, no. 7 in Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, 60. However, the Cullen collections have been reorganized. The manuscript cited appears to be William Cullen, *Abstract of Dr. Cullen's lectures on agriculture* (MS Cullen 462).

[54] Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, 60.

Enrollment in Cullen's chemistry course increased from seventeen students in his first course at Edinburgh to fifty-nine in his second and peaked at one hundred forty-five in 1763/4.[55] That he was well liked as a lecturer is obvious from the rapid increase in the number of students attending his class, but the friendships that he formed with so many of his students are indicative of a deeper commitment to the advancement of each individual student. In his history of chemistry at the University of Edinburgh, Lyon Playfair said of Cullen,

> He saw that a science like Chemistry was not to be taught by mere lectures, but that there must be a free and unreserved communication between the teacher and the taught. He cultivated the personal acquaintance of his pupils, and zealously aided them to overcome those difficulties which we all experience in ascending the first steps of the ladder of knowledge. He taught professors of Chemistry to act as tutors as well as prelectors, and to descend from the elevated rostrum of the lecture table to mix with the students in the freedom of an individual intercourse. To his example we owe much of the modern success in the diffusion of our science.[56]

Cullen's extensive correspondence is filled with letters from his former students. This personal touch and ability to inspire further interest in chemistry contributed to the education and preparation of an entire generation of chemistry professors who

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[55] Thomson, *An Account of the Life, Lectures and Writings of William Cullen*, 97.

[56] Lyon Playfair, *A Century of Chemistry in the University of Edinburgh, Being the Introductory Lecture to the Course of Chemistry in 1858* (Edinburgh, 1858), 11.

would spread throughout Scotland, England, and America. Including his time at both Glasgow and Edinburgh, Cullen taught Joseph Black, Thomas Charles Hope (successor to Joseph Black at the University of Edinburgh), George Fordyce and William Saunders (extramural lecturers in London) Benjamin Rush and Caspar Wistar (University of Pennsylvania), Thomas Beddoes (Oxford), Samuel L. Mitchell (Columbia College), and numerous others who taught medicine, natural history, and other fields related to chemistry. Cullen and his network of students set the curricula for medicine and chemistry in much of the English speaking world in the second half of the eighteenth century.

Cullen included chemical affinity in his lectures as early as 1748. The outline for his course of chemical lectures for that year begins with a discussion of the general principles of chemistry and includes a discussion of "common and elective attraction" within the broader framework of "the primary causes of the changes of bodies occurring in chemical operations."[57] A set of lecture notes from 1766 provides Cullen's explanation of these chemical operations:

> The changes of the Qualities of Bodies, produced by Chy, are all of them produced by, Combination, or Separation. The Office of Chy is to induce new qualities on bodies, & take away old ones; & this, I say, it does by Combination & Separation.[58]

Cullen further explained combination and separation saying,

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[57] William Cullen, *The Plan of a Course of Chemistry* (MS Cullen 1069) (1748).

[58] William Cullen, *Notes Taken by Charles Blagden from Chemistry Lectures* (MS 1922, Blagden Papers) (1766), Lecture 9.

> Combination depends upon Attraction, and this upon Fluidity wch is employ'd in Solution or Fusion. Separation depends upon Elective Attraction or the Action of Fire.[59]

For Cullen, chemistry consisted of combining and separating substances using attractions.

After introducing the general principles, Cullen walked his students through the various classes of chemical substances, bodily processes, or diseases.[60] Affinity tables fit well with Cullen's taxonomic style of teaching in that each column provided a set of related elements and the columns could be grouped by acids and alkalis. From 1748 through 1750, Cullen used Geoffroy's 1718 table (fig. 1) in his classes and also referred to William Lewis's tables. In the late 1750s he began printing his own tables and in the 1760s he pinned a large extended table up during his lectures for students to copy into their notes (fig 2).[61] Cullen introduced his students to the affinity table early in his courses, establishing elective attraction relations before students had learned how to perform precipitations.

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[59] This quote is from an undated set of notes likely recorded in the 1760s. William Cullen, *Notes Taken from Chemistry Lectures* (MS/MSL/79a-c, Medical Society of London) (1760), ff. 66.

[60] Cullen's *Synopsis nosologiae methodicae* (1769), a classificatory scheme of diseases based on his medical lectures, went through four Latin editions during his life and was translated to English after his death.

[61] William Cullen, *Dr Cullen's Table of Elective Attractions* (MS 1920) (1765). For more on Cullen's tables see Taylor, "Unification Achieved: William Cullen's Theory of Heat and Phlogiston As An Example of His Philosophical Chemistry," 73.

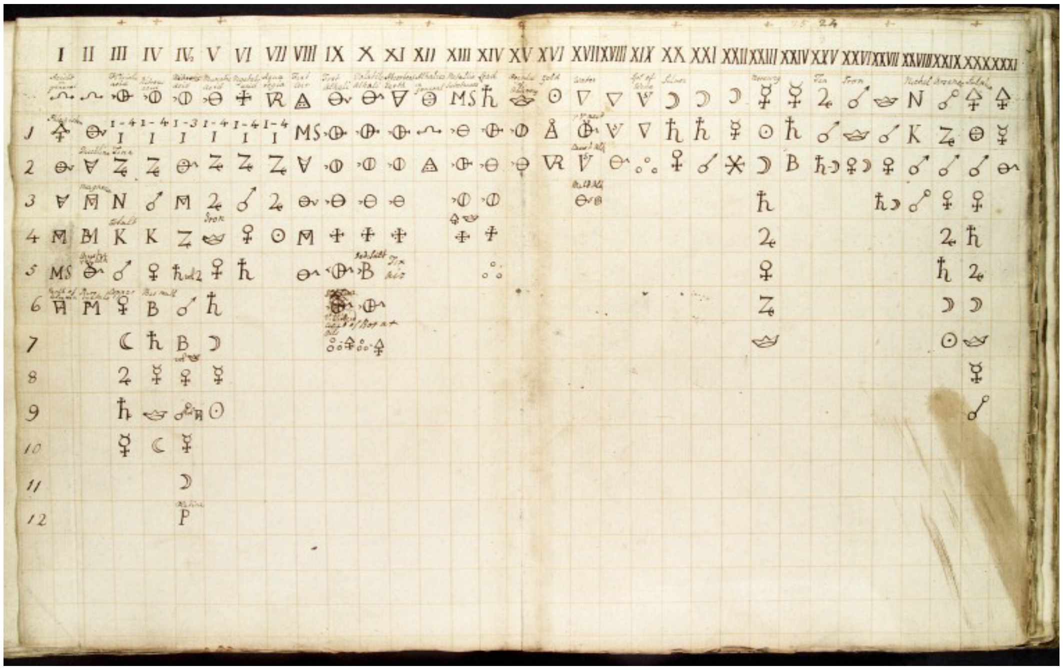

Fig 2: William Cullen, Affinity Table, 1765, MS 1920, Wellcome Library

In Cullen's lectures from 1757-1758, he used a visual notation for single and double elective attractions.[62] He listed the substances in two compounds and used arrows to indicate the rearrangement of these substances in a double displacement reaction. In this reaction, corrosive sublimate (mercuric chloride) enters into a

Fig 3: Darts diagram from Cullen's 1757 lectures

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[62] William Cullen, *Cullen's Chemical Lectures 1757-1758* (CUL/2/2/7) (1757), 40. As cited in Maurice Crosland, "The Use of Diagrams As Chemical 'Equations' in the Lecture Notes of William Cullen and Joseph Black," *Annals of Science* 15, no. 2 (1959); p. 77.

reaction with a solution of silver nitrate in aqua fortis. The spirit of salt A combines with silver D to form muriate of silver (silver chloride) while the aqua fortis B combines with mercury C to form mercuric nitrate. The "darts" as Cullen referred to them provided a visual short hand for noting a single or double displacement. In 1758, Cullen modified this notation to make the letters

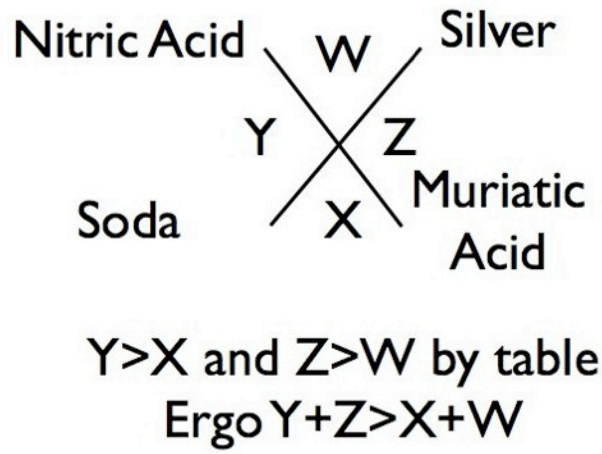

Fig 4: Cullen's lever diagram.

refer to the amount of attraction between each of the substances. This "lever diagram" shows the combination of nitrum argenti (a compound of nitric acid and silver) and common salt (a compound of soda and muriatic acid). Based on a table of affinities, Cullen knows that the attraction between nitric acid and soda is stronger than that between soda and muriatic acid. Similarly the attraction between muriatic acid and silver is stronger than that between nitric acid and silver. A double displacement reaction will thus occur rearranging the substances into two new compounds, nitrate of soda (sodium nitrate) and muriate of silver (silver chloride). Joseph Black and George Fordyce both adopted these lever diagrams and assigned numbers to represent the various attractions. However, both the letters and the numbers were more relational than actually indicative of any quantifiable attraction, so a precise algebra for double elective attractions remained elusive.[63]

Cullen's emphasis on affinity is repeated in Black's lectures on chemistry. Black said of elective attraction "upon the whole it accounts for the chief phenomena [of chemistry] in a far more complete and satisfactory manner than any that have been proposed before."[64] For Black heat and elective attraction were the two divisions of the doctrine of chemistry.[65] While Black introduced elective attraction after finishing his discussion of heat (often in lecture twenty-four or five) and included information on the affinities of the many substances discussed in the intervening lectures, the fullest exposition on affinity came towards the end of his course. In one set of undated lectures held by the Chemical Heritage Foundation, Black provides a history of elective attractions and an explanation of the affinity table in lecture 105. Black presents the affinity table as "a means of presenting to the mind a number of chemical operations and the principles on which they depend."[66] Black spent the next two lectures going row by row and substance by substance through his table of single elective attractions.

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[63] In a series of papers at the beginning of the 1780s, Richard Kirwan developed a mathematical system for measuring affinities based on saturation ratios between various compounds. Richard Kirwan, *Conclusion of the Experiments and Observations Concerning the Attractive Powers of the Mineral Acids* (London: J. Nichols, 1783), 40.

[64] Joseph Black, *Lectures on Chemistry* (MS Coll 129) (1775), Lecture 24.

[65] Joseph Black, *Lectures on Chemistry* (QD 14 .B533 1828) (1776), vol. 2 ff.85.

[66] Black, *Lectures on Chemistry*, vol. 6 ff.5.

In the middle of lecture 107,[67] Black introduced a new table of double elective attractions based on pairs of circles.[68] Black explained, “If a compound of any substance in the upper part of the first circle, and of the under part be mixed with a compound of any substance in the upper part and in the under part of the 2nd circle, the consequence will be that the two uppermost substances will unite and the two undermost so that two new compounds will be formed.”[69] Black included six common reactions that occurred in watery solutions, four that occurred in distillation or sublimation and require heat, and three that occurred in mixture by fusion. The first pair of circles in the row for watery solutions depicts the symbol for a generic acid compounded with either a generic earth, absorbent earth, or a metallic substance. The second circle depicts the symbol for a generic alkaline substance compounded with mephitic air. If these two compounds were mixed in a watery solution, the original compounds would be disassociated consisting of the acid with the alkaline substance and the generic earth, absorbent earth, or metallic substance with the mephitic air. In using the symbols for generic substances, Black was able to depict a set of common reactions in one diagram. His thirteen circle pairs thus represent a broad array of the most common types of double displacement reactions. Black’s two

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[67] Black, *Lectures on Chemistry*, vol. 6 ff.67.

[68] Maurice Crosland discussed Black’s double circle diagrams in Crosland, "The Use of Diagrams As Chemical 'Equations' in the Lecture Notes of William Cullen and Joseph Black," 85-90.

[69] Black, *Lectures on Chemistry*, vol. 6 ff.69.

tables were powerful pedagogical devices that summarized a significant knowledge of affinity relations.

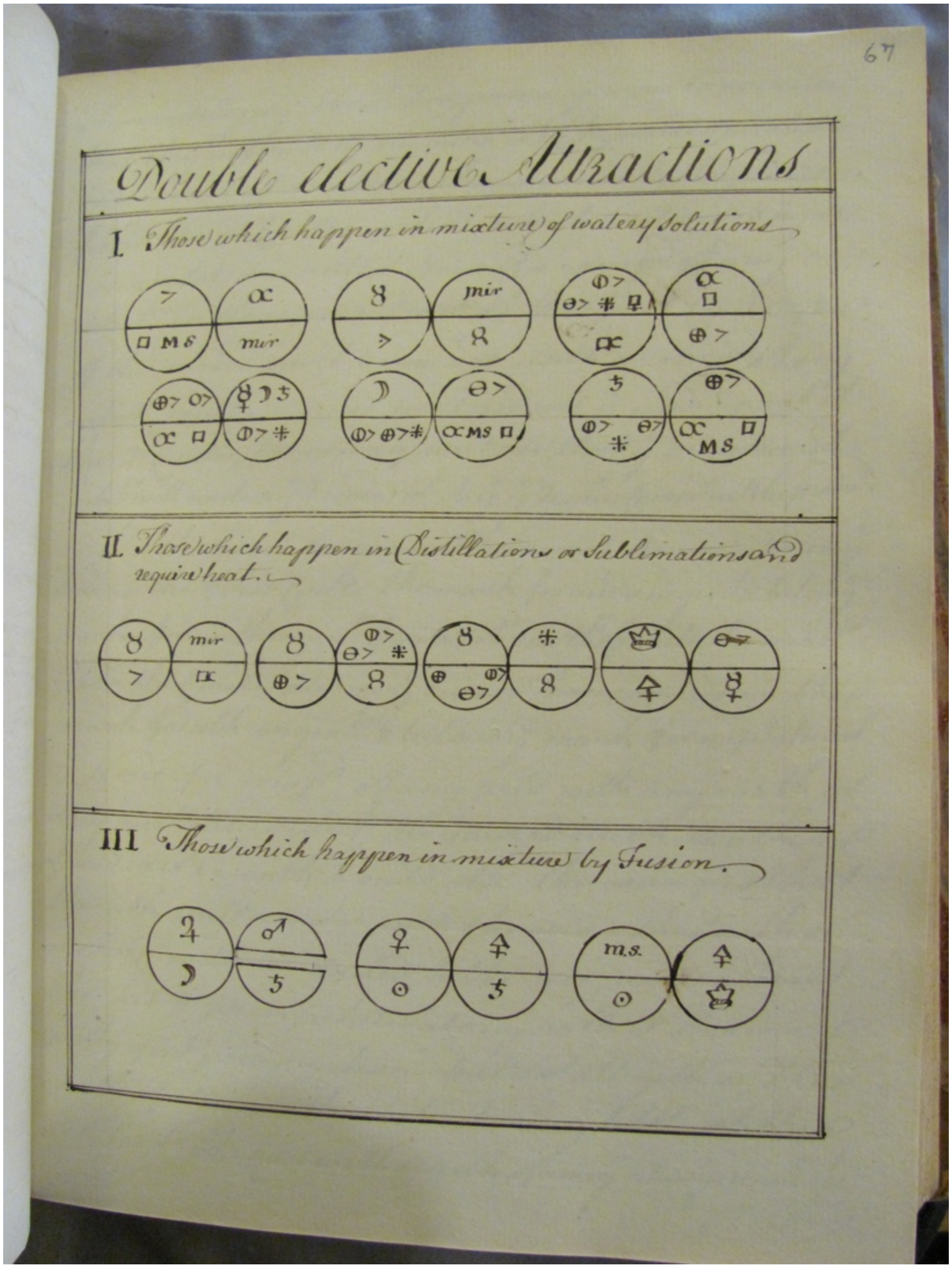

Fig. 5: Black's Double Elective Attraction Paired Circles Diagrams from *Lectures on Chemistry*, vol. 6 ff. 67.

Many of Cullen and Black's students went on to become chemical lecturers in their own rights. Their lecture notes demonstrate both their adoption of affinity theory and a broader agreement on affinity's central role in chemical pedagogy. George Fordyce received his MD from Edinburgh in 1758, and in 1760 he set up a medical practice in London and began lecturing extramurally. Fordyce began his chemical lectures with extensive affinity tables. In fact the first twenty-three pages of a note set recorded in 1765 are Fordyce's tables, and they are followed by Cullen's two page table.[70] After introducing these tables, Fordyce gave lectures modeled after Cullen's on the history and utility of chemistry before returning to a fuller explanation of affinity in his lectures on theory of chemical combination.[71] Thomas Charles Hope received his MD from Edinburgh in 1787 and at the University of Glasgow before succeeding Black at the University of Edinburgh.[72] Hope introduced his lectures on elective attraction by saying,

> The attraction of composition is that which is chiefly connected with chemistry; by its power it causes bodies to unite closely together, and form a quite different substance. It is with this last mentioned attraction, that the phenomena of chemistry are chiefly connected;

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[70] George Fordyce, *Elements of Agriculture and Vegetation* (Edinburgh, 1765).

[71] Fordyce, *Elements of Agriculture and Vegetation*, 46-61.

[72] Hope is best known for his discovery of the element strontium. For more on Hope see Jack B Morrell, "Practical Chemistry in the University of Edinburgh, 1799-1843," *Ambix* 16 (1969): 66-80. Jack Morrell, "Hope, Thomas Charles (1766-1844)," in *Oxford Dictionary of National Biography* (Oxford University Press, 2004), http://www.oxforddnb.com/view/article/13738 (accessed April 8, 2013).

> indeed it is almost the only attracting power which has any chemical effect.[73]

As chemistry professor at Edinburgh, Hope continued to teach chemical affinity well into the 19th century.

2.3 Affinity and the Animal Economy

In 1766, Cullen became chair of medicine at the University of Edinburgh, and Joseph Black succeeded him as chair of chemistry. The two men proved an extremely successful team in promoting the medical school in terms of national and international prestige. In addition to teaching the theory and practice of medicine, Cullen provided clinical instruction at the Edinburgh Royal Infirmary.[74] In his lectures on the practice of medicine Cullen maintained a role for chemistry in understanding the "human animal economy."

> I have in general observed that the human animal economy may be considered in three ways. First, with respect to its matter, whence it is considered as a mixt, liable to various changes in quality and consistence, and, as such a mixt it must be the object of chemistry, so it is called the chemical system. Next, it may be considered as an

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[73] Thomas Charles Hope, *Lectures on Chemistry, given at Edinburgh University, 1809-1810* (Gen 1398-1400) (1809), Lecture Dec 12th.

[74] Guenter B Risse, *Hospital Life in Enlightenment Scotland: Care and Teaching at the Royal Infirmary of Edinburgh* (Cambridge [Cambridgeshire]; New York: Cambridge University Press, 1986).

> organic body, or vascular system, in which various fluids are continually moving, and upon which most of the functions manifestly depend, and this part we call the hydraulic system. And thirdly, as an organic body, it is to be considered almost as an automaton, and here we are to consider those powers and properties with which it is endowed and upon which its several motions as an animal system depend; this is what we again call the nervous system of the animal economy.[75]

The chemical composition, the interactions of the various bodily fluids, and the regulation of the nervous system were all facets in a tripartite study of the human body. Cullen goes on to say that the chemical system had been given priority up until recent times when the hydraulic and nervous systems have been increasingly studied and integrated into the understanding of the animal economy.[76]

While chemistry played an important part in understanding the human body, chemical theory is largely absent from Cullen's medical lectures. His medical theories and his normal course of lectures focused more on the role of the nervous system in stimulating the various muscles and organs of the body. However, the absence of chemical theory from Cullen's lectures should not be misconstrued as the dismissal of the role of chemistry. Many of the students enrolled in Cullen's medical courses would have already taken chemistry with him, and he saw chemical

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[75] Cullen, *Notes Taken by Charles Blagden From Chemistry Lectures*, ff. 32-33.

[76] Cullen, *Notes Taken by Charles Blagden From Chemistry Lectures*, ff. 33.

principles as a prerequisite which did not need to be reexplained. At times in his lectures, Cullen simply asserted that chemistry was the causal force behind some bodily processes without going into a detailed explanation. One example of this can be found in Cullen's theory of taste, which he said may be in part due to an "elective attraction as being affected by particular parts of the substances dissolved."[77] Cullen also used affinity in his lectures on therapeutics as when he says that all astringents are likely acids based on their common affinities.[78] Cullen's medical lectures for the university are thus limited in what they can tell us about his integration of chemical affinity into his understanding of the human body.

However, Cullen occasionally provided private lectures to local artisans and gentry interested in chemical studies. On the 16th of December, 1763, Cullen gave a lecture on "The Chemical History of the Body."[79] His outline for this lecture begins with an assertion that the "employment of the study of chemistry [is] infinite" and that the "chemical history of bodies cannot be completed & much less the application in any course." These claims for the utility of chemistry are similar to his initial lectures in his chemistry courses. After brief discussions of the role of chemistry in pharmacy and pathology, the majority of the lecture was given over to "the chemistry of aliments." Cullen addressed the chemical constitution of food itself and the effects of cooking. He then turned to "the operation in the human body as chemical" and

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77 William Cullen, *Physiological Observations* (Dc.7.55) (1767), ff. 44.

78 William Cullen, *Therapeutic Observations* (Dc.7.55) (1767), ff. 14.

79 William Cullen, *Chemical History of the Body* (MS Cullen 250) (December 17, 1763).

"solution, diffusion, and assimilation." The rest of the lecture was a detailed description of the fermentation of foods in the stomach and the assimilation of nutrients into the body. Cullen's inclusion of explanations of basic chemical concepts like solutions, fermentation, and putrefaction indicate that he did not presume that his audience had attended a course on chemistry. It is unclear whether he used affinity language for this audience, but his extensive discussions of the various menstruums of the body, the role of acids and alkalis in fermentation and putrefaction, and the solutions generated in the stomach were all affinity based chemical processes.[80] The explicit use of chemistry in this lecture for chemical novices proves an extremely useful contrast with the implicit use of chemistry in the university lectures for medical students presumed to have already taken chemistry.

Because he was reluctant to write monographs, we are denied further insight into Cullen's use of chemical affinity in understanding the causes and treatments for particular illnesses. However, Cullen's popularity as a professor and his extensive influence in terms of number of students and the volume of material they wrote do provide insight into both Cullen's medical theories and the elaboration of those theories by his students.

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[80] Cullen discussed affinity in relation to these processes in lectures 20 and 30 of his 1765/66 lectures. Cullen, *Notes Taken by Charles Blagden From Chemistry Lectures*.

2.4 Affinities and Miasmas

John Haygarth (1740-1827) studied medicine at the University of Edinburgh from 1762 through 1765.[81] During this time, he attended William Cullen's lectures on both chemistry and clinical medicine,[82] and his theory of the transmission of small-pox reflects Cullen's teachings on both subjects. Like Cullen and most contemporary doctors, Haygarth subscribed to a miasma theory for the communication of fevers. Cullen taught that in addition to miasma brought on by the natural effluvia of marshes there were also contagion miasmas that arose from the bodily effluvia of people suffering from fevers, inflammation, eruption, hemorrhages, and fluxes. Haygarth attributed the communication of small-pox to the miasma created by variolous serum from the pus and scabs of the infected.[83] Haygarth said, "It is important to ascertain the mode of combination between the variolous poison and air. I apprehend that they are united by solution."[84] The moisture of variolous pus and scabs was soluble in air creating the small-pox miasma.

Haygarth argued this conclusion largely based on the transparency of pestilential air, saying, "When a clear menstruum has dissolved any substance, it

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[81] The only full length biography of Haygarth is Christopher C Booth, *John Haygarth, FRS (1740-1827): A Physician of the Enlightenment* (Philadelphia: American Philosophical Society, 2005).

[82] Booth, *John Haygarth, FRS (1740-1827): A Physician of the Enlightenment*, 24-26.

[83] On Haygarth's work on small-pox see Francis M Lobo, "John Haygarth, Smallpox and Religious Dissent in Eighteenth-Century England," in *The Medical Enlightenment of the Eighteenth Century*, ed. Andrew Cunningham (Cambridge; New York: Cambridge University Press, 1990).

[84] Haygarth, *An Inquiry How to Prevent the Small-Pox*, 17.

remains perfectly transparent."[85] To further assure the reader that small-pox was carried by chemical solution, Haygarth contrasted the transparency of solutions with the opacity of physical mixtures:

> But metals, earths, etc. are opaque bodies, yet when dissolved, in their proper menstrua, the solution is perfectly transparent. On the contrary, if two transparent substances, that have no chemical attraction for each other, be agitated together, they will become opaque, as, water and oil, or air supersaturated with watery vapour.[86]

Haygarth's argument was that small-pox is invisibly communicated by the air, and its invisibility was proof that it was in solution rather than physical mixture. Small-pox miasmas are thus a chemical compound of air and the variolous poison.

Having established that small-pox was soluble in air, Haygarth concluded that small-pox must have a chemical affinity for air. He said, "Chemical attraction is the cause of solution, as appears from the clear evidence of innumerable experiments."[87] Extending this thought, Haygarth expounded for his reader on the systematic study of affinities,

> Chemists have employed much labour and ingenuity to ascertain the various degrees of this attraction, between almost all the different substances that nature presents to their examination. The degree of

[85] Haygarth, *An Inquiry How to Prevent the Small-Pox*, 18.

[86] Haygarth, *An Inquiry How to Prevent the Small-Pox*, 18.

[87] Haygarth, *An Inquiry How to Prevent the Small-Pox*, 68.

attraction between the same substances, in the same circumstances, is always uniformly equal.[88]

Haygarth then set up a qualitative thought experiment to measure the relative affinity that small-pox had for air and for clothes.

> Now whether it be supposed that air attracts the variolous miasms more strongly than clothes, etc. do, or that clothes, etc. attract the miasms more strongly than the air does, the argument will be conclusive against this opinion. For if air attracts the miasms more strongly than clothes, etc. do, it is evident that the miasms could never be taken from the air in order to adhere to the clothes, etc. On the contrary, if clothes, etc. attract the miasms more strongly than air does, it follows that such miasms could never be taken from them by the air, and consequently they could never render it infectious.[89]

According to Haygarth, smallpox miasmas must have more affinity for the air than for clothes. Otherwise, clothes would constantly trap the miasma, and small-pox would not be communicable through the air. Clothes only absorbed the miasma when the air had become supersaturated, so Haygarth advocated ventilation and fresh air for the rooms and wards housing small-pox patients.[90]

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[88] Haygarth, *An Inquiry How to Prevent the Small-Pox*, 68.

[89] Haygarth, *An Inquiry How to Prevent the Small-Pox*, 68-69.

[90] Haygarth, *An Inquiry How to Prevent the Small-Pox*, 74.

Haygarth's understanding of the small-pox miasma as a finite solution originating from exposed variolous serum led him to argue that the miasma is only infectious within a small range of its origin. As it spreads out, it rapidly becomes diffused and innocuous. Because of this, he proposed that small-pox patients and fever patients more generally should be quarantined. By separating patients with fevers from those without, Haygarth sought to insure that the miasmas generated by the ill would be so diffused as to be non-contagious. He developed rules for cleaning fever wards thoroughly and for segregating both their bed linens and even plates and utensils from those of the general population of the hospital. These regulations proved effective and were adopted by many hospitals in the closing years of the 18th century.

While Haygarth's practices were widely adopted, his chemical theory of communication was not. In 1793, Haygarth published *A Sketch of a Plan to Exterminate the Casual Small-Pox from Great Britain*, and he included correspondence from several prominent doctors on issues of small-pox and fever. Thomas Percival and John Aikin, who were both friends of Haygarth and fellow Edinburgh students, found his argument based on the transparency of small-pox miasmas unconvincing. Aikin, along with Glasgow chemistry professor and fellow Cullen protege William Irvine, dismissed Haygarth's claims about the relative affinities of small-pox for air and clothes.[91] Haygarth defended his chemical conception of the small-pox miasma, but his theory never caught on. Haygarth's appropriation of affinity was something of an overreach. However, the application of affinity to small-pox is noteworthy, because it demonstrates the use of affinity with miasma theory and because it inspired quarantine procedures.

2.5 Combustion, Respiration, and Asthma

Cullen's students also used chemical affinity to construct new theories about animal heat and respiration. Cullen himself denied that respiration was chemical relying instead on blood to convey heat in a vitalistic process regulated by the nervous system.[92] However, Joseph Black taught that respiration was a chemical process analogous to combustion. While he did not publish his theory, his student Daniel Rutherford summarized his teachings:

> As the life of animals depends on the free use of air, so this is altogether necessary for the support of flame and fire. But no less by fire than by respiration is it so changed as to be unfit for either use and contrary to both. And as the effects are nearly the same, what I have

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[91] John Haygarth, *A Sketch of a Plan to Exterminate the Casual Small-Pox From Great Britain, and to Introduce General Inoculation; To Which Is Added, a Correspondence on the Nature of Variolous Contagion, with Mr. Dawson [Et Al.]* (London: Printed for J. Johnson, 1793), 198, 218.

[92] Cullen, *Institutions of Medicine: Part I. Physiology*, 218-223. See Mendelsohn, *Heat and Life: The Development of the Theory of Animal Heat*, 112-113.

> brought forward as to respiration may be repeated as to combustion.[93]

The analogy developed by Black and Rutherford was reformulated into a theory of respiration and heat exchange by Black's student William Irvine and Irvine's student Adair Crawford. Irvine modified phlogiston theory by claiming that it was not the substance of heat. Phlogiston was instead inversely related to heat capacity. Those substances with little or no phlogiston, like dephlogisticated air (oxygen) had a high heat capacity, while phlogisticated air had a low heat capacity. Whenever phlogiston was added to a substance, that substance's heat capacity was lowered, driving out sensible heat. Combustion was the rapid combination of dephlogisticated air with phlogiston. This process created fixed air and a large amount of sensible heat.[94]

Crawford studied medicine with Irvine at the University of Glasgow from 1775-1777 and also took medical courses at the University of Edinburgh in 1776. His *Experiments and Observations on Animal Heat* (1779) demonstrates how Irvine's conceptualizations of phlogiston and heat could be used to understand respiration:

> It has been already observed, that the arterial blood has a strong attraction to phlogiston, and that by its union with this principle, in the course of the circulation, it is obliged to give out that heat which it had received in the lungs. In the state of health, the velocity of the blood

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[93] Daniel Rutherford, "Daniel Rutherford's Inagural Dissertation," *Journal of Chemical Education* 12 (1935); pp. 373-374.

[94] John A Stewart, "The Reality of Phlogiston in Great Britain," *HYLE* 18, no. 2 (2012); p. 11.

> through the different parts of the system, and the quantities of phlogiston with which it is supplied in those parts, are adjusted to each other in such a manner, that the heat is equally diffused over the whole.[95]

Crawford indicated the role of affinity when he said that "arterial blood has a strong attraction to phlogiston." The role of affinity in this reaction was more explicitly described by John Aitken in his summary of Crawford's theory for his textbook *Principles of Anatomy and Physiology* (1786). Aitken said:

> Many reasons may be alleged to make it probable that animal heat is derived from the air in the lungs, or from the atmosphere, perhaps in consequence of a chemical action between the blood and the air. Thus it is contended, that the blood gives out phlogiston, which unites with air so as to expel its fire, and that this is attracted by the blood, in consequence of superior affinity; or, in other words, a double elective attraction is continually going on, connected with respiration, or any analogous action in animals.[96]

In this theory, the body naturally produced phlogiston which was absorbed and removed by the blood. As the blood absorbed phlogiston, its heat capacity was lowered, releasing heat into the tissues of the body. The blood then transported the

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[95] Crawford, *Experiments and Observations on Animal Heat, and the Inflammation of Combustible Bodies*, 89.

[96] John Aitken, *Principles of Anatomy and Physiology* (London: Printed for J. Murray, 1786), 161.

phlogiston to the lungs where a double displacement reaction occurred. Phlogiston had greater affinity for air than for blood, so it combined with air displacing heat. This heat then joined the blood to be redistributed throughout the body.

The chemical exchange of heat for toxic phlogiston was one of the primary purposes of the respiratory and circulatory systems. If the body's circulation were sped up or slowed down, illness could ensue:

> But, if by any irregularity, the balance be destroyed; if, by the increased action of the vessels, the blood be urged with greater violence than usual through any particular part, or, in consequence of a greater tendency to putrefaction, be more copiously supplied with phlogiston, it is manifest, that a greater quantity of heat will be extricated in that part, in a given time. This heat will stimulate the vessels into more frequent and forcible contractions, by which the velocity of the blood, and the consequent extrication of heat will be full farther increased. On this principle we may probably account for the partial heats which are produced by topical inflammations, and for those which arise in hectic and nervous diseases.[97]

For Crawford, the chemical exchange of heat for phlogiston was an inescapable result of chemical affinity, so the even distribution of heat was reliant on the even flow of blood throughout the body. When the circulation was uneven, the chemical release of

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[97] Crawford, *Experiments and Observations on Animal Heat, and the Inflammation of Combustible Bodies*, 89.

heat could produce inflammations or diseases. Crawford has thus combined chemical and physiological processes to explain the production of inflammations and several diseases.

Robert Bree (1759-1839)[98] drew on Crawford's theory of respiration in proposing an affinity based theory of asthma.[99] Bree updated Crawford's theory of respiration with a hybrid nomenclature that combined phlogiston theory with recognition of oxygen, hydrogen, and carbon.

> In healthy respiration the oxygen having a stronger attraction to the carbon of the blood than to the other components of atmospheric air, is absorbed through the soft and vascular membrane of the air cells, and combines with carbon, to be exhaled as carbonic acid in expiration.[100]

Bree was not replacing Crawford's phlogiston cycle with carbon but rather saying that the phlogiston accumulated by the blood as it passes through the body is present in the form of carbon. Bree said that for asthma patients "the blood will be more

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[98] Bree studied medicine at Edinburgh under John Brown in 1780-81. Arthur H Grant and Joan Lane, "Bree, Robert (Bap. 1758, *D.* 1839)," in *Oxford Dictionary of National Biography* (Oxford University Press, 2004), http://www.oxforddnb.com/view/article/3307 (accessed March 15, 2013).

[99] For more on Bree in relation to eighteenth century theories of asthma, see Mark Jackson, *Asthma: The Biography* (Oxford; New York: Oxford University Press, 2009), 83-86.

[100] Robert Bree, *A Practical Inquiry on Disordered Respiration: Distinguishing Convulsive Asthma, Its Specific Causes, and Proper Indications of Cure* (Birmingham; Sold by G.G. & J. Robinson ... London, and Creech, Edinburgh: Printed for the author, by M. Swinney ;, 1797), 243.

phlogisticated, and have more carbon to discharge in respiration....”[101] In the phlogiston nomenclature, charcoal was thought to be a rich source of phlogiston. This association between carbon and phlogiston was further supported by pneumatic theory. The combination of dephlogisticated air with phlogisticated air produced fixed air. In the new nomenclature, dephlogisticated air was oxygen and fixed air was carbon oxide, so the phlogisticated air must have been (or at least contained) carbon. Bree was thus employing the same double displacement affinity reaction as Crawford and Aitken had, but was using the new nomenclature to describe it.

To support his theory of asthma, Bree employed arguments from authority citing everyone from Hippocrates and Galen to anatomists Thomas Willis (1621-1675) and Giovanni Battista Morgagni (1682-1771) to argue for the presence and importance of black mucus in irritating the lungs.[102] What was novel in Bree's theory, was his claim that this black mucous serum in the lungs blocked the natural chemical reactions of respiration. “If the air cells are obstructed with serous fluid, the oxygen cannot be attracted to enter into this new combination,” said Bree. “The carbon must therefore remain in the blood in greater quantity than was usual.” Asthma “is chiefly characterized by a low temperature, weak solids, and watery fluids; in other words, hydrogen holding carbon in solution predominates in the

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[101] Bree, *A Practical Inquiry on Disordered Respiration: Distinguishing Convulsive Asthma, Its Specific Causes, and Proper Indications of Cure*, 241.

[102] Bree, *A Practical Inquiry on Disordered Respiration: Distinguishing Convulsive Asthma, Its Specific Causes, and Proper Indications of Cure*, 89-147.

system, and gives to the arterial too much of the colour and quality of venous blood."[103]

2.6 The Affinities of Bile

In 1793, Helenus Scott (1758-1821),[104] a surgeon for the East India Company, began experimenting on the chemical affinity between bile and various oxides of mercury in order to better understand mercury's utility in treating liver obstructions and syphilis. In heating the resin of bile with mercuric oxides, Scott found that the bile combined with oxygen to form a salt, but the bile did not combine with mercury. Scott tentatively concluded that in dissolving liver obstructions, the active medical ingredient in mercuric oxide was not mercury, as was generally supposed, but rather oxygen.

> The experiments that I had made on the base of the bile, inclined me to wish to take myself a quantity of pure air, united to a substance for which it has no great attraction. I reflected on the different ways that are employed by chemists to oxygenate inanimate matter; for I believed, that the same chemical attractions would produce a similar

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[103] Bree, *A Practical Inquiry on Disordered Respiration: Distinguishing Convulsive Asthma, Its Specific Causes, and Proper Indications of Cure*, 243-244.

[104] Helenus Scott studied at Marischal College from 1773 to 1777 and studied medicine at Edinburgh from 1777 to 1779. For a biography of Scott see Patrick Wallis, "Scott, Helenus (Bap. 1758, D. 1821)," in *Oxford Dictionary of National Biography* (Oxford: Oxford University Press, 2004), http://www.oxforddnb.com/view/article/24873 (accessed March 19, 2013).

> effect in the living body, although they might be disturbed in their operation by the vitality of the principles of which it is composed.[105]

Here Scott extended the role of affinity from the laboratory into the body, and acknowledged that the results might not be exactly the same because of vitalistic processes. Scott continued:

> The nitric acid, as may be supposed, was one of the first substances that occurred to me as fit for my purpose; for it is known to contain about four parts of vital air, united to one of azote, with a certain proportion of water. These principles can be separated from each other by the intervention of many other bodies, as chemists find every day in their operations. I was led, besides, to give a preference to the nitric acid, from observing, that it dissolves very completely the resinous base of the bile.[106]

Scott's research into the efficacy of nitric acid demonstrates the interplay between chemistry and materia medica. In order to understand the medical efficacy of mercuric oxides, Scott conducted in vitro chemical research on the affinity between mercuric oxides and bile. The chemical results led Scott to conclude that oxygen dissolved bile resins. Combining medical knowledge of the toxicity of mercury with

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[105] Scott, "Account of the Effects of the Nitrous Acid on the Human Body," 142-143. It is unclear why Helenus Scott published the 1797 paper under the name William. However, he explicitly confirms that he was the author in Helenus Scott, "On the Internal and External Use of the Nitro-Muriatic Acid in the Cure of Diseases," *Medico-Chirurgical Transactions* 8 (1817); pp. 175-176.

[106] Scott, "Account of the Effects of the Nitrous Acid on the Human Body," 142-143.

chemical knowledge of compounds and affinities, Scott substituted nitric acid for mercuric oxide because it contained a large amount of oxygen, and it was easily disassociated from the inert (or at least benign) nitrogen component.

American Philip Gendron Prioleau promoted Scott's use of nitric acid for syphilitic patients in his dissertation for the University of Pennsylvania Medical School.[107] Prioleau dedicated his dissertation to his mentor Caspar Wistar, a student and correspondent of Cullen. Prioleau's dissertation collected medical cases to confirm the efficacy of nitric acid in cases of syphilis. Prioleau also agreed with Scott that the efficacy of nitric acid was due to its chemical constituents:

> The nitric acid is known to be composed of an active principle, Oxigene, and an inert one, Nitrogene. Its beneficial effects in diseases, have by Mr. Scott been attributed to the active principle alone.[108]

Scott's work on nitric acid had opened the door to study similar compounds that were high in oxygen and easily disassociated. Prioleau extended Scott's work by experimenting with oxigenated muriatic acid.

> The muriatic acid, is capable of combining with a very large quantity of oxigene, forming then, what by Chemists is called, Oxigenated Muriatic Acid, or the Dephlogisticated Marine Acid (HClO). From

[107] Philip Gendron Prioleau, *An Inaugural Dissertation on the Use of the Nitric and Oxigenated Muriatic Acids, in Some Diseases* (Philadelphia: Printed by John Bioren, 1798).

[108] Prioleau, *An Inaugural Dissertation on the Use of the Nitric and Oxigenated Muriatic Acids, in Some Diseases*, 54.

> this Oxiginated Muriatic Acid containing a very large proportion of oxigene, and from the facility with which it is decomposed. It appeared to me to be well calculated for the oxigenation of the system.[109]

Having provided the chemical reasoning for suspecting its utility, Prioleau confirmed the efficacy of oxigenated muriatic acid through medical case studies. Aware of the probable chemical interests of his readers, Prioleau had warned on the initial page that he would not spend time discussing the affinities of his acids, because they were already so thoroughly studied in chemical books.[110] That he included such a disclaimer and nonetheless cited the affinities of his chemical remedies demonstrates the extent to which chemical affinity and *materia medica* were intertwined.

As is often the case with graduate students, Prioleau had planned to experiment with other oxygenated compounds but ran out of time before his defense.

> It was my intention when I first undertook it, to have ascertained the effects of a number of other substances, which contained a large proportion of oxigene and are easy of decomposition: as oxigenated

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[109] Prioleau, *An Inaugural Dissertation on the Use of the Nitric and Oxigenated Muriatic Acids, in Some Diseases*, 54.

[110] "In treating of these acids, it may be necessary to premise, that it is not my intention to speak of their chemical affinities to the substances which surround us. As this is very accurately and minutely taken notice of, in every system of chemistry, I mean to confine myself to their medical properties, and their effects on the human body, as this part is that, which which physicians are, as yet, least acquainted," Prioleau, *An Inaugural Dissertation on the Use of the Nitric and Oxigenated Muriatic Acids, in Some Diseases*, unnumbered.

> vinegar, oxalic acid; oxigenated muriate of potash, and many other substances, all of which I am persuaded will be found to possess nearly the same medicinal properties.[111]

In a footnote, Prioleau cited François-Xavier Swediaur's just published article in the *Medical Repository*, which contained information on the efficacy of oxygenated muriate of potash, superoxygenated muriate of potash, and citric acids.[112] Swediaur was one of several French investigators of oxygenated compounds as *materia medica.* In England Thomas Beddoes was conducting similar research. The research circle was completed with the 1829 edition of Cullen's *First Line of the Practice of Physics* which included the line, "Perhaps the most important addition to the internal remedies in the treatment of syphilis, is the nitric or nitrous acid, either taken internally, or in the form of the warm bath impregnated with it, or the nitro-muriatic acid."[113]

2.7 Conclusion

For William Cullen, chemistry was the study of combination and separation of natural substances, and elective attractions causally explained those reactions. From his first chemistry courses in Glasgow through his last at Edinburgh, elective attractions were a foundational subject and affinity tables a key pedagogical device in

[111] Prioleau, *An Inaugural Dissertation on the Use of the Nitric and Oxigenated Muriatic Acids, in Some Diseases*, 71-72.

[112] Francois-Xavier Swediaur, "On Nitric Acid in Syphilis," *Medical Repository* 1, no. 4 (1797): 579-580.

[113] William Cullen, *First Lines of the Practice of Physic*, ed. James Craufurd Gregory (Edinburgh: Printed for Bell & Bradfute, and Adam Black, 1829), vol. 2, p. 430.

teaching his students to predict the results of solution based analysis. If Cullen's lectures provide an insight into the role of affinity in his system of chemistry, those of his students provide evidence that they adopted and expanded affinity theory. Affinity theory's role in Cullen's lectures on physiology and the physiological works of his students has gone largely unnoticed in the historiography of eighteenth century chemistry and medicine. Haygarth's use of elective attraction in describing the affinities of smallpox and fevers has not received any attention, though it informed his well known work in developing protocols for preventing contagion in fever hospitals. While respiration as an affinity based chemical process has been studied, in part because of Lavoisier's contributions to the subject, the conceptualization of asthma as a breakdown in this chemical process has gone unnoticed. Likewise Helenus Scott's promotion of nitric acid in the treatment of liver obstructions and syphilis has been mentioned, but Scott's initial research into the affinities of bile and his larger theory about oxygen delivery using weakly attracted oxygen compounds are only noticed when we foreground the use of chemical affinity in physiology.

In the next chapter, I will demonstrate the role of affinity in understanding one of the most commonly used eighteenth-century *materia medica*, mineral waters. Doctors used chemical affinity to analyze mineral waters into their constituent components, correlate these components with medicinal applications, and produce artificial mineral waters. The dilute nature of mineral waters required chemists to develop more precise analytical techniques to measure trace components. Their volatile components, most notably fixed air, also led to increased study of the affinities of airs and their abilities to make medically efficacious chemical substances more soluble. I will also discuss how John Murray's study of mineral waters in the early nineteenth century cast doubt on the epistemic foundations of chemical affinity and triggered a crisis for the entire theory.

Chapter 3. Affinity in Mineral Waters

3.1 Mineral Waters as *materia medica*

During the eighteenth century, naturally occurring mineral waters were used to treat a variety of ailments including gout, stones, stomach complaints and skin diseases. With the advent of chemical affinity, mineral waters became a key substance for chemists in testing and improving their analytical techniques. William Cullen's 1765/66 *Clinical Lectures* promoted the use of mineral waters as a medicinal substance and provided his students with the chemical procedures for analyzing the salts found in mineral waters. Chemical analyses by Cullen and his students provided information about the constituency and formation of natural mineral waters and provided recipes for the formulation of artificial mineral waters. In turn, the precision required in isolating dilute salts drove the advancement of affinity theory and its analytical techniques. The recognition that gases and non-soluble earths contributed to the medical efficacy of mineral waters but could not be studied in samples that had been bottled and shipped also led to the rapid development of *in situ* experimentation. Cullen[114] in Scotland, and Torbern Bergman[115] in Sweden, developed and promoted new analytical techniques for evaporation of sample waters, weighing sedimentary remains and separation of the salts found in them. Using the lectures, publications and correspondence of Cullen's network, this chapter will elucidate the mutually

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[114] William Cullen, *Fragment of a Lecture on Saltpetre, Aquafortis, and Elective Attractions, Separating and Combining* (Cullen Papers, MS 1060) (1749).

[115] Torbern Bergman, *Physical and Chemical Essays*, trans. Edmund Cullen (London: J. Murray, 1784). Bergman, *A Dissertation on Elective Attractions*.

beneficial relationship that developed between affinity and balneology in the second half of the eighteenth century. University trained doctors like John Walker, Joseph Black, Francis Home, George Fordyce, and their many students used their chemical education to bolster their own credentials and to buttress the reputations of their local wells. In the universities, affinity based analysis of mineral waters became a ubiquitous part of chemistry lectures, a common subject of dissertations, and an important tool in securing patronage and permanent positions. This chapter will also argue that John Murray's work on mineral waters in 1815 through 1817 challenged the theoretical foundations of elective affinity and ultimately proved fatal to this chemical theory. Like the tail that wagged the dog, balneology was a sub-discipline of chemistry that drove both the rise and fall of affinity theory.

3.2 Using Affinity to Analyze Spa Waters

The growth of specialized medical faculties in the Scottish universities during the middle of the eighteenth century led to an increased focus on *materia medica* and medical chemistry. Mineral waters fell naturally under the purview of these subjects. At both Glasgow and Edinburgh, William Cullen and his students conducted affinity based chemical analyses of the various waters, just as they did with so many other mineral and biological *materia medica*. Cullen's students (and students of students) wrote several dissertations on mineral waters[116] along with articles for the *Philosophical Transactions*[117] and other academic journals. After graduation, many doctors continued to publish on mineral waters.[118] These publications served both as an educational credential and as an appeal for patronage from the towns and lords associated with the growing number of spas in Scotland and England. The chemical study of mineral waters contributed to the local economies of spa towns, and also the national economy through the isolation and industrial production of constituent chemical substances, most notably fixed alkali. However, some doctors argued that the attribution of medical efficacy based solely on a mineral water's chemical

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[116] Joseph Black, *Experiments Upon Magnesia Alba, Quicklime and Some Other Alcaline Substances* (Edinburgh: Printed for J. Balfour, 1756). Joshua Walker, *Dissertatio Chemica Inauguralis, De Aqua Sulphurea Harrowgatensi* (Edinburgh: Balfour, Auld, and Smellie, 1770).

[117] John Walker, "An Account of a New Medicinal Well, Lately Discovered Near Moffat, in Annandale, in the County of Dumfries," *Philosophical Transactions of the Royal Society of London* 49 (1757): 117-147. Donald Monro, "An Account of the Sulphureous Mineral Waters of Castle-Loed and Fairburn, in the County of Ross; And of the Salt Purging Water of Pitkeathly, in the County of Perth, in Scotland," *Philosophical Transactions of the Royal Society of London* 62 (1772): 15-32. Matthew Dobson, "A Description of a Petrified Stratum, Formed From the Waters of Matlock, in Derbyshire," *Philosophical Transactions of the Royal Society of London* 64 (1774): 124-127.

[118] Thomas Dancer, *A Short Dissertation on the Jamaica Bath Waters: To Which Is Prefixed, An Introduction Concerning Mineral Waters in General: Shewing the Methods of Examining Them, and Ascertaining Their Contents* (Kingston: Printed by D. Douglass & Alex Aikman, 1784). A Fothergill, *A New Experimental Inquiry Into the Nature and Qualities of the Cheltenham Water* (Bath: Printed by R. Cruttwell, and sold by W. Taylor, 1788). William Saunders, *A Treatise on the Chemical History and Medical Powers of Some of the Most Celebrated Mineral Waters; With Practical Remarks on the Aqueous Regimen: To Which Are Added Observations on the Cold and Warm Bathing* (London, 1805).

contents was an oversimplification that would lead to potentially injurious self-medication. During the second half of the eighteenth century, the debates over chemical studies of mineral waters ranged from the relative importance of medical theory versus empirical experience to the utility of a chemically reductivist understanding of waters and an epistemological challenge to Cullen's system for the analysis of solutions. However, the very presence of these debates indicates the central importance of chemical analysis in the understanding of mineral waters as a medical commodity. From the time Cullen began lecturing in 1748 through the end of the century and into the second decade of the nineteenth century, affinity based analyses were used to determine the constituents, efficacy, and the natural and artificial formation of mineral waters. In turn, the precision required in isolating dilute salts in mineral water research drove the advancement of analytical technique.

While the efficacy of mineral waters had been attributed to the healing powers of various local saints in the Middle Ages,[119] the waters were secularized in the sixteenth and seventeenth centuries and their efficacy was attributed to their chemical properties. Doctors and natural philosophers sought to identify the acidity or alkalinity of mineral waters in order to use them as part of a neohumoral regimen to balance the patient's constitution. In the early modern period, tasting substances was an important skill in both medicine and chemistry. An acidic substance would taste bitter or sour while an alkaline substance could be identified by its sweetness. Waters

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[119] Ruth Morris and Frank Morris, *Scottish Healing Wells: Healing, Holy, Wishing, and Fairy Wells of the Mainland of Scotland* (Sandy: Alethea Press, 1982).

known to contain iron salts (iron based compounds) tasted bitter and were thus deemed acidic. This connection between metallic salts and bitter waters become such a commonplace, that Nathaniel Highmore proposed that all chalybeate waters (those containing metallic salts) were acidic.[120] This correlation of metallic salts and acidic waters was normalized in the last decades of the seventeenth century and was asserted as common knowledge in Charles Leigh's *The Natural History of Lancashire, Cheshire, and the Peak of Derbyshire* (1700).

In the eighteenth century, focus shifted from using mineral waters as an acid or alkali in a neohumoral regimen to the medical properties of the constituents of the waters. In one of the more widely read eighteenth-century books on medical spas, *Domestic Medicine* (1769),[121] William Buchan divided the therapeutic substances found in mineral waters into four categories: ferruginous, gaseous, sulfurous, and saline. Ferruginous or chalybeate wells and springs had been studied and used since the seventeenth century. These waters contained vitriol of iron, also known as salt of iron, a combination of iron and an acid. Iron, whether consumed in solution or as

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[120] Nathaniel Highmore, "Some Considerations Relating to Dr. Wittie's Defense of Scarborough Spaw Together with a Brief Account of a Less Considerable Salt-Spring in Somersetsh[ire]," *Philosophical Transactions of the Royal Society of London* 4, no. 56 (1668-1669) (1669): 1128-1131.

[121] Buchan's *Domestic Medicine* went through nineteen authorized editions with between five and seven thousand copies per edition. With additional pirated editions and translations, Buchan's book was a best-seller. Alastair Durie, "Medicine, Health and Economic Development: Promoting Spa and Seaside Resorts in Scotland C. 1750-1830," *Medical history* 47, no. 2 (2003); p. 195. *Domestic Medicine* is also analyzed in Charles E Rosenberg, "Medical Text and Social Context: Explaining William Buchan's *Domestic Medicine*," *Bulletin of the History of Medicine* 57 (1983); pp. 22-42.

iron shavings, was considered a stimulant and was one of the most widely used mineral medications. Gaseous waters contained some form of air and were used to treat weakened nervous systems and bladder stones. Sulfurous waters most often contained sulfur, but this category also included waters that contained pyrites or other inflammable materials. Saline substances were usually the combination of an acid with a base but could also include the metallic salts, salts that contained fixed air, and salts that contained inflammable substances. Chemists working on mineral waters used affinity based analysis to identify the salts present in solution, and, towards the end of the century, provide a quantitative description of these waters.

The utility of chemical affinity in studying mineral waters was illustrated in William Falconer's 1770 book-length study of the waters of Bath.[122] Falconer had attended William Cullen's 1765 chemistry course and graduated from Edinburgh with a medical doctorate in 1766.[123] He then studied with Hieronymus David Gaubius and Bernhard Siegfried Albinus at the University of Leyden before receiving a second MD in 1767. He set up a practice and served as physician to the Chester Infirmary from 1767-1770. Falconer's publication of his *Essay on the Bath Waters* coincided with his relocation from Chester to Bath in 1770. As an advertisement, the essay was a success, helping Falconer to establish a successful practice. In 1773 he was elected to the Royal Society of London, and in 1774 he was elected physician to the Bath

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[122] William Falconer, *An Essay on the Bath Waters in Four Parts. Containing a Prefatory Introduction on the Study of Mineral Waters in General* (London: Printed for T. Lowndes, 1770).

[123] Will Falconer, *Notes of William Cullen's Chemistry Lectures* (MS 1921) (1765).

General Hospital, a position he would hold until 1819.[124] Falconer cited Cullen's opinions throughout his book making *An Essay on the Bath Waters* a prime example of Cullen's students participating in his affinity research program.

Falconer began the book by discussing the theoretically possible constituents of mineral waters. He stated that only those substances that are both naturally occurring and soluble in water can be expected to exist in natural mineral waters. However, Falconer did note that some substances with extremely low solubility, like argillaceous earths (clay, marl, etc.), had been found in solution in mineral waters, and that other earths were sometimes found diffused, though not dissolved, in waters.[125] Having provided those caveats, he launched into a study of salts, noting their defining quality of solubility. Here, Falconer applied his second restriction, that salts must be naturally occurring to appear in mineral waters. "Hence the nitrous and vegetable acids are to be rejected and the acid of sea salt, though a fossil production, yet as it is never known to be found in a separate state, so it never can, by itself, impregnate a Mineral Water."[126] The acid of sea salt, more commonly referred to as muriatic acid or in modern terms hydrogen chloride, does occur naturally but is so reactive that it always forms non-soluble compounds before entering into solution.

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124 Anne Borsay, "Falconer, William (1744-1824)," in *Oxford Dictionary of National Biography* (Oxford: Oxford University Press, 2004), http://www.oxforddnb.com/view/article/9118 (accessed February 22, 2013).

125 Falconer, *An Essay on the Bath Waters*, 28.

126 Falconer, *An Essay on the Bath Waters*, 29.

Falconer used the same reasoning for limiting the likelihood of finding a mineral water impregnated with free vitriolic acid.[127] "The vitriolic acid, from its almost universal distribution through the bowels of the earth, has been more generally supposed to do so. But then its attractions are so general, and so potent, as to prevent its remaining long unassociated."[128] Here, Falconer explicitly used affinity theory to explain the rarity of finding vitriolic acid in solution in a mineral water. Vitriolic acid's high affinity for many different substances made it likely that it would bond with a mineral or earth as the water passed through the ground. It was only when a dissociative reaction occurred near a spring that vitriolic acid would be found in solution. Falconer provided the example of sulfurous pyrites, which are "subject to deliquescence on exposure to the air. Hence if they are exposed in any subterraneous cavern, the vitriolic acid may be thus separated, and if this decomposition takes place not far distant from the surface, it may impregnate the spring before it be prevented by an fresh attraction."[129] Falconer's text used chemical affinity for the analysis and identification of mineral waters and also as a chemical description of unseen geological processes.

In his section on metallic impregnations, Falconer turned his attention to iron and copper. Iron has a high affinity for vitriolic acid, and the salt formed from their combination is soluble. Falconer said that most chalybeate waters contain this

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[127] Vitriolic acid is now known as sulfuric acid, H_2SO_4.

[128] Falconer, *An Essay on the Bath Waters*, 29.

[129] Falconer, *An Essay on the Bath Waters*, 30.

particular salt in varying amounts. Copper also has a high affinity for vitriolic acid, and the salt produced is again soluble. However, this copper salt is not commonly found in mineral waters, because vitriolic acid has a greater affinity for iron than copper. Iron displaces copper whenever both are present, and produces the common chalybeate water. Thus, Falconer used the chemical properties of metals to explain the geological question of why iron salts are more commonly found in mineral waters than are copper salts. However, this focus on affinity also raised a new question, as Falconer wondered why zinc salts are not more common in mineral waters. Zinc is naturally abundant and it displaces both copper and iron from combinations with vitriolic acid. Falconer was unable to explain the dearth of zinc salts in mineral water analyses and concluded that zinc compounds had been understudied.[130]

If chemical affinity could be used to identify the possible constituents of mineral waters, it could also be used to explain the false identifications in prior chemical analyses. Falconer said,

> An accurate knowledge of chemistry is likewise requisite in the examination of waters, to distinguish their original contents from those which are only the product of the experiments. From inattention to this circumstance, many mistakes have been committed, and many supposed discoveries have been made, of impregnations which never had any existence in the water before these were made.[131]

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[130] Falconer, *An Essay on the Bath Waters*, 57-60.

[131] Falconer, *An Essay on the Bath Waters*, 11.

Falconer cites the confusion over the presence of sulfur in mineral waters as an example of the mistakes of chemically undereducated analysts. Many analysts had found that sulfur was present in the waters of noted German spa Aix-la-Chappelle (now known as Aachen). Falconer assures the reader that sulfur is not present in naturally occurring mineral waters but rather was absorbed from the pipes supplying Aix-la-Chappelle.[132] During the second half of the eighteenth century, affinity became central to the analysis of mineral waters. Falconer's analysis of the Bath waters is typical of those produced by Scottish trained physicians. In the competition between the growing number of spa towns, the chemical constituents of a water helped to establish the spas medical efficacy, but the comparison of spas extended beyond the chemical analysis of their waters.

3.3 The Chemical Commensuration of Spas

Although Moffat had been a popular spa since the mid-seventeenth century, the growth and heyday of the Scottish spas occurred during the second half of the eighteenth century. Spas at Peterhead, Pannanich, Strathpeffer, and Pitkeathly rose to prominence, and a partial list in the the 1819 edition of William Buchan's *Domestic Medicine* included thirty active springs in Scotland. The relative success of the various spas rested on several factors including anecdotal evidence of their medical efficacy, the scientific analysis of the composition of the waters, and the spa's social

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[132] Falconer, *An Essay on the Bath Waters*, 49.

status. The gentry who controlled spas and the doctors who promoted them used affinity to compete with each other in each of these factors.

A respectable chemical analysis of a mineral water was a necessary credential for a spa and could be used in determining and advocating medical efficacy. Scientific verification of mineral waters was key in minimizing the folk traditions of healing wells. While the Kirk could not condone superstitious traditions of healing wells, waters that had been scientifically analyzed and confirmed as medically efficacious *materia medica* were acceptable. As historian Alexander Durie said, "In authenticating the claim of any waters to medical virtue (a much-used word), no spa could progress to resort status unless 'proofed' by an analysis."[133] A chemical analysis could also be used to compare the waters of a new spa to other known mineral waters. A common strategy for Scottish spa towns and their advocates was to associate themselves with successful English or continental spas that had similar mineral waters. In reviewing the sulfureous waters of Castle-Loed in County Ross, Donald Monro compared them to the waters of Harrogate, in Yorkshire, concluding, "It may often be used with more advantage than the purging sulphureous waters, as they sometimes purge people of weak constitutions too freely, and weaken them too much."[134] Castle-Loed's waters were similar to those of Harrogate in that sulfur was

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133 Durie, "Medicine, Health and Economic Development: Promoting Spa and Seaside Resorts in Scotland C. 1750-1830," 197.

134 Monro, "An Account of the Sulphureous Mineral Waters of Castle-Loed and Fairburn, in the County of Ross; And of the Salt Purging Water of Pitkeathly, in the County of Perth, in Scotland," 24.

the active purgative in both, and Monro suggested that Castle-Loed's waters might even be preferable in that they are less concentrated and thus more suited to those with weak constitutions.

The comparison of Scottish spas to their English and continental equivalents also served a social function by assuring clients that they would be as comfortably housed and entertained as they would be in the more established spas. In a travel memoir written in the 1770s, David Loch said, "Peterhead is the Scarborough of North Britain, and has excellent accommodation for bathing. The mineral waters are much in vogue, and the inhabitants obliging and industrious."[135] Before embarking on a medical pilgrimage into the rural parts of Scotland, members of the gentry and the middle classes wanted reassurance that they would be comfortable and entertained. Spa treatments could last for weeks or even months so society, food, and entertainment were significant in determining the success of a spa resort. Satirist Thomas Rowlandson depicted the counter-productive nature of these amenities in a series of cartoons called the *Comforts of Bath*. In "Gouty Gourmands at Dinner," Rowlandson presented two patients suffering from gout. The gluttony that made them sick is still in full force and has ironically been extended to their consumption of the many bottles of mineral water in the foreground. As this and the other cartoons in Rowlandson's series suggest, many patrons of the various spas took the waters while

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[135] David Loch, *A Tour Through Most of the Trading Towns and Villages of Scotland* (Scotland, 1778), 120.; quoted in Matthew D. Eddy, *The Language of Mineralogy John Walker, Chemistry and the Edinburgh Medical School, 1750-1800* (Farnham; Burlington (Vt.): Ashgate, 2008), 214.

simultaneously continuing the eating and drinking that led to gout or stones. In one extreme case of a spa being advertised on the merits of its amenities, Reverend J. Barrett recommended the waters of Malvern, admitting that they did not contain any medically efficacious mineral component, but insisting that clients would benefit from the purity of the rural air and the beauty of the scenery.[136]

3.4 Artificial Mineral Waters

Valentine Seaman, best known for his map of yellow-fever deaths in Manhattan, published an analysis of the mineral waters of Saratoga Springs in 1793. Seaman said, "One great advantage resulting from the analysis of mineral waters is, the being enabled thereby to make artificial waters similar to them, whence all their virtues may be obtained at pleasure; and at any place, without the inconvenience or expense of attending the springs."[137] Artificial mineral waters had been produced

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[136] J., Rev. of Colwall Barrett, *A Description of Malvern, and Its Environs. Comprising An Account of the Efficacy of the Malvern Waters, and the Accommodation of Strangers in That Delightful Neighbourhood. A Sketch of the Natural History of the Malvern Hills, and Concise Account of the Gentlemen's Seats, Scenery, and Picturesque Views in Their Vicinity: With Many Other Interesting Particulars* (Worcester: printed for the author by T. Holl, 1796), 39-42.

[137] Valentine Seaman studied with Benjamin Rush at the University of Pennsylvania in 1791. Valentine Seaman, *A Dissertation on the Mineral Waters of Saratoga; Containing, a Topographical Description of the Country, and the Situation of the Several Springs; An Analysis of the Waters, As Made Upon the Spot, Together with Remarks on Their Use in Medicine, and a Conjecture Respecting Their Natural Mode of Formation: Also, a Method of Making An Artificial Mineral Water, Resembling That of Saratoga, Both in Sensible Qualities and in Medicinal Virtue* (New York: Printed by Samuel Campbell, 1793), 38.

since the mid-seventeenth century,[138] but advancements in chemical analysis in the second half of the eighteenth century allowed for precise identification of the constituents of spa water. After identifying the medically efficacious components, chemists could use affinity to imitate the waters by choosing the proper solutes accounting for the affinity reactions that would occur in solution.

The main limitation for both artificial waters and bottled spa waters had been that they lacked the "mineral spirit," that unknown substance that made mineral waters sparkle and bubble. In his work on lime-water, Joseph Black found that this substance was fixed air. Subsequent investigations by William Brownrigg[139] and Henry Cavendish[140] confirmed the role of fixed air in mineral waters. Even with this understanding and improved bottling techniques, natural philosophers and doctors had difficulty in preserving fixed air within their mineral water samples. One alternative that proved successful was artificial aeration at the point of analysis or consumption. In 1770, Joseph Priestley suggested a system to control the introduction of fixed air into liquids. By combining chalk and vitriolic acid, Priestley could create a source of fixed air. This air was then collected in a pig bladder and pumped into a separate chamber with the water, temporarily aerating the sample.

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[138] Noel G Coley, "The Preparation and Uses of Artificial Mineral Waters (Ca. 1680-1825)," *Ambix* 31, no. 1 (1984); p. 32.

[139] William Brownrigg, "An Experimental Enquiry Into the Mineral Elastic Spirit, or Air, Contained in Spa Water; As Well As Into the Mephitic Qualities of This Spirit," *Philosophical Transactions of the Royal Society* 55 (1765): 218-243.

[140] Henry Cavendish, "Experiments on Rathbone-Place Water: By the Hon. Henry Cavendish, F. R. S," *Philosophical Transactions of the Royal Society* 57 (1767): 92-108.

Scottish physician John Nooth (1737-1828) commercialized this apparatus,[141] replacing the pig bladder with an arrangement of glass receivers.[142] Nooth's apparatus gained widespread use in the closing decades of the eighteenth century. In his *Zoonomia*, Erasmus Darwin suggests using Nooth's apparatus to prepare a carbonated alkaline water to treat urinary stones.[143]

In addition to its utility in treating stones, fixed air also served to hold other medically efficacious substances in solution. William Falconer explains the reasoning behind the preparation of a fixed alkaline salt saturated with fixed air.

> Fixible Air seemed to him adapted to this purpose in every respect, as it forms with the alkali a neutral salt, agreeable to the taste and stomach, and powerfully antiseptic. At the same time their combination is so loose, that the alkali is easily separated from the air by any other acid it may meet with.[144]

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[141] One catalog of scientific instruments from 1797 listed a "glass machine for impregnating water with fixed air and apparatus" for £2 12s. 6d. W. Jones and S. Jones, *A Catalogue of Optical, Mathematical, and Philosophical Instruments, Made and Sold by W. And S. Jones, No. 135, Next Furnival's-Inn, Holborn, London* (London, 1797), 11.

[142] John Mervin Nooth, "The Description of An Apparatus for Impregnating Water with Fixed Air; And of the Manner of Conducting That Process," *Philosophical Transactions of the Royal Society of London* 65 (1775): 59-66.

[143] Erasmus Darwin and Robert Waring Darwin, *Zoonomia; Or, the Laws of Organic Life* (London: J. Johnson, 1796), vol. 2, p. 45.

[144] William Falconer and Matthew Dobson, *On the Use of the Solution of Fixed Alkaline Salts Saturated with Fixible Air, in the Stone and Gravel* (London, 1785), 8.

William Falconer, who became a successful doctor in Bath in the last three decades of the eighteenth century, marketed this artificial alkaline mineral water as a lithontriptic (a treatment for stones), offering a dozen servings for six shillings.[145] Though still expensive, this cost of sixpence per serving was equivalent to a meal of cold meat, bread and porter. Even after the multiplication of spas in the eighteenth century had made them more accessible for the English and the Scots, the expense of traveling, lodgings, and food, often for several weeks or months, made spa treatment an expensive medical option. For the lower classes, spas were a last resort due to their expense. By eliminating the need to travel, artificial mineral waters provided a much cheaper option.

It was not necessary that an artificial water precisely replicate the original mineral water but rather that it imitate the original's medically active constituents. In studying an imitation of the Bath mineral water, William Falconer noted that the artificial water had nearly fifty times as much iron as the original. This relatively high level of iron made it unsuitable to people suffering from stomach conditions or fevers, but was perhaps more beneficial than the original water for people suffering from skin conditions. Falconer also suggested that the artificial water could be beneficial for people suffering from colica Pictonum (lead poisoning).

> If it should be found efficacious here, it would be a discovery of great importance, as this disease is chiefly confined to the lower rank of

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[145] Andreas-Holger Maehle, *Drugs on Trial: Experimental Pharmacology and Therapeutic Innovation in the Eighteenth Century* (Amsterdam; Atlanta, GA: Rodopi, 1999), 94.

people, artificers especially, whose circumstances and employment would not permit them to make use of the waters themselves.[146]

Falconer's remarks, like those of Valentine Seaman two decades later, demonstrate that these chemists were conscious of the social and economic benefits of being able to create artificial mineral waters and use chemical analysis to predict their medical qualities.

One large-scale application of artificially prepared waters during the eighteenth century was the preservation of water for sea voyages, an important concern for the navies and merchant marine of Europe. A proposal that received attention and even a trial in the French navy was to drop quicklime into the water casks. The resultant limewater was potable and did not putrefy, and the superfluous limestone would settle at the bottom of the cask. The most significant problem with this scheme was the objectionable taste. Manchester surgeon-apothecary Thomas Henry FRS[147] proposed an affinity based process to remove the lime before consumption. Pouring vitriolic acid onto limestone or marble would release fixed air, and the fizzing marble could be dropped into the cask. Lime has higher affinity for

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[146] Falconer, *An Essay on the Bath Waters*, 263. See also Coley, "The Preparation and Uses of Artificial Mineral Waters (Ca. 1680-1825)," 35.

[147] Thomas Henry credited his friend Thomas Percival with introducing him to natural philosophy. Percival had studied under Joseph Black in Edinburgh, so Henry can be seen as a member of the extended Edinburgh chemical network. This connection was further confirmed when Thomas Henry apprenticed his son William to Percival and later sent William to Edinburgh to study under Joseph Black. Thomas Henry was also a founding member of the Manchester Literary and Philosophical Society. See E. L. Scott, "Henry, Thomas," in *Complete Dictionary of Scientific Biography* (Detroit: Charles Scribner's Sons, 2008).

fixed air than for water, so the fixed air would attract and precipitate the lime, thereby restoring the water.[148]

As in the case of preserving water for ocean voyages, affinity chemistry applied to mineral waters had important economic implications. The creation of artificial mineral waters led to new industries including bottled water companies like Schweppes. A further example, showing the centrality of affinity chemistry to the Improvement movement, is the analysis of civic water supplies.

3.5 Analyzing Civic Water Supplies

In addition to studying the various remote wells and the more popular spas, Joseph Black exercised and expanded the authority of the university chemist by offering analyses of civic water supplies. As compared to the analysis of mineral spas, the stakeholders in civic water supplies hoped for different chemical constituents. The medically efficacious iron compounds that were so important to spas were not necessary for civic water and were thought possibly harmful when consumed constantly. Sulphur and other volatile constituents along with many pneumatic compounds would dissipate in the piping or bottling of water for transportation. The very qualities that attracted pilgrims and required *in situ* experimentation, limited the importance of chalybeate spas and wells for civic water

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[148] Thomas Henry, *An Account of a Method of Preserving Water, at Sea, From Putrefaction, and of Restoring to the Water Its Original Pleasantness and Purity, by a Cheap and Easy Process: To Which Is Added a Mode of Impregnating Water. In Large Quantities, with Fixed Air, for Medicinal Uses, on Board Ships, and in Hospitals: And Likewise a Process for the Preparation of Artificial Yeast* (London: W. Eyres for J. Johnson, 1781).

concerns. Civic water primarily needed to be wholesome, visually appealing (clear, free of flora, fauna and other pollutants), and soft. This softness was observable in the water's ability to dissolve soap and measurable as the number of particulates per given volume of water. Joseph Black used a standard of forty grains per gallon of water as the maximum threshold for soft water. Chemical analysis of these waters focused on isolating and identifying the constituent particulates.

On June 18th, 1770, Richard Lambert, a surgeon in Newcastle upon Tyne, wrote to Joseph Black asking for his analysis of water samples from the nearby well at Coxlodge and a spring at Fellon. Newcastle was to be supplied from one of the waters, but the town's prior efforts to have the waters analyzed had returned conflicting reports. While their choice of Black is not explained in Lambert's letter, it does speak to his personal authority and the reputation of the chemists of the University of Edinburgh that the people of Northumberland would look to Black as an arbiter.

Lambert sent samples of the waters on August 5th, and Black returned an analysis on August 27th. Black focused his examination on the water from Coxlodge. He deemed the water "sufficiently pure for use and it contains no particles but what are perfectly wholesome."[149] Having returned this favorable judgment, Black continued,

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[149] Joseph Black, *Letter to Richard Lambert, surgeon in Newcastle upon Tyre* (182/1/36) (August 27, 1770).

> If I were writing to the Gentlemen who are to determine and direct in this matter, I should certainly stop here well knowing what perplexity is often occasioned by speaking to people a language which they do not easily understand. But as I address myself to you, I shall add the reasons of my opinion, particularly of my examination of these waters and comparison of them with the water of Edinburgh.[150]

Black acknowledged the difficulties presented by technical language for lay readers and also recognized that as a medical professional, Lambert had sufficient understanding of chemistry to follow Black's experiments on the water and his reasoning. Starting with an evaporation test, Black calculated that the Coxlodge waters had twenty-eight grains of particulates per gallon and that the Fallon waters had sixteen while the Edinburgh water had just eight. All three samples were within the contemporary parameters for soft water. In the Fallon samples, half of the particulates were calcareous earth while the rest was a mixture of fixed alkali and soluble earths. In the Coxlodge sample, the calcareous earths accounted for five grains and fixed alkali accounted for the remaining twenty-three grains.[151] That the calcareous earths were benign or even salubrious was implicit in this analysis and presumably obvious for a surgeon like Lambert. Black did explicitly state that the fixed alkali was probably no more harmful than gypsum or other particulates common to drinking water and that sulphur, which was detectable by smell at the springs, was

[150] Joseph Black, *Letter to Richard Lambert, surgeon in Newcastle upon Tyre* (182/1/37) (August 27, 1770).

[151] Black, *Letter to Richard Lambert, Surgeon in Newcastle Upon Tyre*.

thought by many to be beneficial for common medical purposes. Black also said that the waters would prove useful "for all oeconomical purposes & for bleaching linen."[152] His focus on the economic uses of water, and particularly bleaching linen, show how ingrained the improvement movement was in Black's thoughts and how intertwined medicine, chemistry, and the industrial arts had become.

In 1782, the police commissioners of Leith wrote to Joseph Black and John Robison asking them to analyze Lochend (also written Lough end) water. As with the Newcastle water sources twelve years earlier, Black compared the water samples to the better known water supply of Edinburgh. As it was important to establish the commonalities between Scottish spa waters and more established spas in England or the continent, it was likewise important to establish a city's water supply as meeting the standards of Edinburgh. In analyzing a water sample from Leith, Black reports,

> To the taste it was sweet. In dissolving soap it was rather softer than Edinburgh Pipe water. 7000 grains weight of it was evaporated & left only 3/4 of a grain of solid matter which was saline and earth, the nature of it was very nearly the same as that of the solid matter contained in the Edinburgh Pipe water. N[ote] B[ene] Edinburgh Pipe water contains 1 1/2 grains of this matter in 7000 grains of the water, and the best waters contain more or less. N[ote] B[ene] I made two experiments on Edinburgh water, the first gave 1 3/4 of residue, and

[152] Black, *Letter to Richard Lambert, Surgeon in Newcastle Upon Tyre*.

> the 2nd 1 1/2 grains. But in September, I tryed it again, weather dry & water very clear, it gave just 1 grain.[153]

In response to another inquiry from the commissioners of Leith on the waters from Salsberry Rock, Black responded, "They do not dissolve soap quite so well as Edinburgh pipe water & have therefore a degree of hardness which is equall in all the three." He then provided a table to express the hardness of various water samples:

> Edinburgh pipe water has a very small degree of hardness which may be represented by the number 1.00
>
> River of Leith Water 0.50
>
> St. Katherine's Well 1.33
>
> Lough End water 2.50
>
> Springs at foot of Salsberry Rock 3.33
>
> Hard Pump water in Edinburgh 5.70[154]

Edinburgh's water supply was notably soft, but the constant comparisons and the use of Edinburgh water as a standard also indicate something else. Whether it was civic pride or positioning with patrons, Black's repeated references to Edinburgh are a consistent theme of his work on civic water supplies and a reminder of the city's lead role in the improvement of Scotland and Northern England.

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[153] Joseph Black, *Black's Draft Report on the Purity of the Water of Leith* (182/2/182) (July, 1784).

[154] Black, *Black's Draft Report on the Purity of the Water of Leith*.

3.6 The Crisis of Doubt for Affinity

John Murray dealt a severe blow to affinity theory with an epistemological challenge presented in a pair of articles on mineral waters published in 1815 and 1817.[155] Murray argued that the process of analyzing waters could trigger chemical reactions, so that the salts identified by analysis might not match the salts in solution. Murray went on to suggest that the chemical combinations most likely to be present in solution were those that were most soluble. The first article entitled "An analysis of the mineral waters of Dunblane and Pitcaithly; with general observations on the analysis of mineral waters and the composition of Bath water," began as a standard contribution to the mineral waters genre providing a chemical analysis of the newly discovered waters of Dunblane and comparing it with an original analysis of the better known waters of Pitcaithly. He noted that both waters likely originated from red sand-stone deposits in the foot hills of the Grampians, that they were both diuretics and purgatives, and that the active medicinal constituents of both were muriate of lime and oxide of iron. In his comparative analysis, Murray evaporated the waters, weighed the sediments, and separated out the various salts using the same analytical techniques that had been promoted by Cullen and Bergman.

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[155] Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water." Murray, "A General Formula for the Analysis of Mineral Waters." Murray's theories on mineral waters are discussed in Christopher Hamlin, *A Science of Impurity: Water Analysis in Nineteenth Century Britain* (Berkeley: University of California Press, 1990), 75-78.

Despite having utilized the standard analytical operations in his analysis of mineral waters, in his "General Comments" section, Murray challenged the epistemological foundations of chemical analysis. He said,

> The obtaining certain saline compounds from a mineral water by evaporation leads no doubt at first to the conclusion that they are its ingredients; it is the conclusion, accordingly, which has hitherto been always drawn, and we are disposed to regard this as evidence establishing this conclusion, in some measure, in opposition to any different view of the composition. But this is merely oversight or prejudice. If it can be shown that the elements of these compounds may equally exist in the water in a different state of combination, which the evaporation must change, the conclusion that they do exist in such a state is *a priori* as probable as the conclusion that they exist in the state in which they are actually obtained.[156]

Here, Murray challenged the assumption that the salts identified through chemical analysis of mineral waters were the same salts that were present in solution. He undermined affinity theory's central tenet that chemical substances always acted upon empirically determined preferences for chemical combination, and he claimed instead that salts can avoid affinity triggered decomposition if a solution is dilute enough. Murray argued, "If [reactants] be in binary combinations, the most probable

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[156] Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water," 354.

conclusion with regard to this, as I have already endeavored to show, is, that the combinations are those which form the most soluble compounds...."[157] Solubility not affinity was the key property of dissolved salts. Although affinity could precipitate chemical substances from solution, the salts in solution were likely to be those that were most soluble.

Murray acknowledged that his theory could not be confirmed by direct analysis, because "the concentration by the evaporation must in many cases change the state of combination and the salts obtained are hence frequently products of the operation, not original ingredients."[158] Murray turned to his analysis of the Dunbland water as an example saying,

> The ingredients obtained are muriate of soda, muriate of lime, and sulphate of lime. Now it is possible that the sulphate of lime may be a product of the operation, not an original ingredient. The sulphuric acid may exist rather in the state of sulphate of soda, and when, in the progress of the evaporation, the liquor becomes concentrated, this salt may act on a portion of the muriate of lime, and by mutual decomposition form corresponding portions of muriate of soda and sulphate of lime.[159]

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[157] Murray, "A General Formula for the Analysis of Mineral Waters," 174.

[158] Murray, "A General Formula for the Analysis of Mineral Waters," 94.

[159] Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water," 348.

Here, Murray argued that the standard analytical process of dehydration by evaporation could trigger a displacement reaction. Although stable in the naturally dilute mineral water, sulphate of soda and the muriate of lime entered into a double displacement reaction, because concentration allowed sulphuric acid to displace the muriatic acid and form the sulphate of lime. The remaining muriatic acid bonded with soda to form muriate of soda.

Although direct analysis was inconclusive, Murray did provide some experimental evidence to support his argument. Murray added up to thirty grains of sulphate of soda to four ounce samples of the Dunblane water. Based on the affinity between sulphuric acid and lime, sulphate of lime should have been formed and should have precipitated from solution. However, no precipitation occurred, even with some evaporation, so Murray concluded, "Sulphate of soda may exist with muriate of lime in solution without decomposition, in the state of dilution which this mineral water affords." Murray acknowledged that the experiment did not prove his theory, but it did reinforce that his was "the more probable opinion."[160]

Doubts about the ability to identify salts present in solution based on chemical analysis led Murray to suggest that knowledge of the salts in solution was epistemologically underdetermined. Murray embraced this epistemological uncertainty saying, "All that can be done with precision is to estimate the elements, and then to exhibit their binary combinations according to whatever may be the most

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[160] Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water," 349.

probable view of the real composition."[161] While the salts in solution could not be identified with certainty, their constitutive elements could through simple affinity based precipitations. "Nothing is easier, for example, than to estimate the total quantity of sulphuric acid by precipitation by barytes, or of lime by precipitation by oxalic acid."[162] Once the constitutive elements had been identified, an analyst could choose between accepting the traditional affinity assumptions of direct analysis or inferring the presence of the most soluble salts that could be formed.

Having established that the choice between the two systems was experimentally underdetermined, Murray turned to medical instrumentality as a measure of the probability of the two systems. "A question of this kind is not merely one of speculation, but the solution of it may sometimes throw light on the properties of mineral waters, particularly on their powers of affecting the living system." Drawing on his analysis of the Dunblane mineral water, Murray continued,

> Sulphate of lime is a substance apparently inert. If it exist, therefore, as such in the water, it can contribute nothing to its efficacy. But in the other state of combination which is supposed, both the quantity of the muriate of lime, the more active ingredient, will be greater, and the

[161] Murray, "A General Formula for the Analysis of Mineral Waters," 95.

[162] Murray, "A General Formula for the Analysis of Mineral Waters," 95.

> presence of sulphate of soda will in part account for the purgative operation which the water exerts.[163]

For the Dunblane waters, Murray's solubility thesis suggested that muriate of lime and sulphate of soda were the salts present in solution. The purgative action of sulphate of soda and the commonly accepted diuretic effects of muriate of lime correlated well with the known effects of the Dunblane water. The salts identified through direct analysis, sulphate of lime and muriate of soda, were much less active and did not explain the medicinal qualities of the water. Murray generalized his analysis and argued that the affinity reactions triggered by evaporation often produced these relatively inert salts.

> Sulphate of lime has been often stated as an ingredient existing in mineral waters with muriate of soda and muriate of lime. It is almost superfluous to remark, that it is probable the original ingredients in all such cases are sulphate of soda and muriate of lime, and that the sulphate of lime is a product of the operation, or rather that the portion of it equivalent to the quantity of muriate of soda has this origin.[164]

In generalizing his findings on sulphate of lime and muriate of soda, Murray staked a claim on two very common products of mineral water analysis. He argued that the

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[163] Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water," 348.

[164] Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water," 352.

assumption that these salts were present in solution had long misled medico-chemical analyses of mineral waters.

Murray cited the waters at Bath as a prime example of this type of water. The empirically observed medical efficacy of the Bath waters had not been satisfactorily explained based on its chemical constituents of sulphate of lime, muriate of soda, and sulphate of soda. However, if the analysis were reinterpreted according to Murray's method, muriate of lime and sulphate of soda would explain the diuretic and purgative effects of the Bath waters. Reiterating his appeal to medical instrumentality, Murray noted that many had questioned the utility of chemical analysis of mineral waters "from finding examples of waters possessed of active powers, in which analysis does not detect any ingredients of adequate activity."[165] Murray advocated his system as a way to reestablish the credibility of chemical studies of mineral waters by providing a better correlation between the salts in solution and the established medically efficacious salts.

In comparing the chemical constituents of the waters of Dunblane and Pitcaithly to the more established spa at Bath, Murray was fulfilling the promotional aspect of the mineral waters genre. Murray also suggested that the Scottish spa waters could be altered to more closely match the medicinal qualities of the Bath water. The concentration of muriate of lime in the waters at Bath were associated with a tonic effect while the higher concentrations in the Scottish spa waters triggered

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165 Murray, "An Analysis of the Mineral Waters of Dunblane and Pitcaithly; With General Observations on the Analysis of Mineral Waters, and the Composition of Bath Water," 353.

a diuretic effect. By simply diluting the waters of Dunblane and Pitcaithly with warm water, you could match the concentrations found naturally at Bath. A patron could then choose between using the waters as they naturally occurred or the diluted Bath imitation. Murray's focus on concentration as a variable thus opened new pathways for the artificial production or modification of mineral waters.

Murray also claimed that his soluble salts thesis allowed for the production of alkaline carbonated waters, which were popular on the continent but did not occur naturally in Great Britain. The waters of Spa, Pyrmont and Selzer were noted for their characteristic carbonic acid gas (CO_2) and carbonate of soda, and direct analysis of these alkaline waters identified carbonate of magnesia, carbonate of lime, and muriate of soda as ingredients. Murray reinterpreted the active ingredients of these waters to be carbonate of soda, muriate of magnesia, and muriate of lime. Drawing on Selzer water as an example, Murray said that the affinity based interpretation of its ingredients could not account for its medicinal efficacy or satisfactorily describe an artificial preparation of it. Under Murray's system though, the mineral water could be artificially created by combining water, muriatic acid, and the carbonates of lime, magnesia, and soda in a closed container. The muriatic acid would displace the carbonic acid to bond with the lime, magnesia, and soda. The displaced carbonic acid would take the form of carbonic acid gas. Affinity theorists would predict that the muriatic acid would react preferentially with the carbonate of soda, leaving the carbonates of lime and magnesia intact. Murray's success in producing artificial

Seltzer water provided experimental support for his system and cast further doubt on the tenability of affinity based analyses of solutions.

John Murray's attack on affinity based analysis of solutions completed the earlier work of Claude Louis Berthollet. From 1798 to 1803, Berthollet had developed his theory of mass action. Frederic Holmes explained this concept in his analysis of Berthollet's theory saying, "If two substances are competing to combine with a third substance for which they have unequal affinities, a relatively larger quantity of the substance with weaker affinity can exert an attractive force equal to or greater than a small quantity of the other substance."[166] This problematization of affinity theory shook the theory's epistemic foundations, but it was not immediately recognized as a decisive blow. Holmes noted,

> In the 1804 and 1807 editions of his *System of Chemistry,* Thomas Thomson presented Berthollet's laws about mass, cohesion, and volatility as revisions of the standard affinity theory, factors previously overlooked or considered only as special cases. But, in the edition of 1817, he called Berthollet's affinity theory the complete opposite to that of Bergman.[167]

While Murray disagreed with Berthollet's idea of partial displacement, his work on salts in solution did support Berthollet's larger argument about the multiple variables

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[166] Frederick Lawrence Holmes, "From Elective Affinities to Chemical Equilibria: Berthollet's Law of Mass Action," *Chymia* 8 (1962); p. 110.

[167] Holmes, "From Elective Affinities to Chemical Equilibria: Berthollet's Law of Mass Action," 115.

affecting reactions in solution. Murray's work on the solubility of salts proved particularly damning for affinity theory, because solution analysis had been at the center of affinity theory. Even if the proprietors of the various spas continued to desire the legitimacy offered by direct chemical analysis and the comparison of salts to more established spas, chemists increasingly recognized that there was no epistemic certainty regarding the salts that were active in solution. This epistemic uncertainty plagued the analysis of mineral waters throughout the first half of the nineteenth century and was still being debated as John Snow (1813-1858)[168] and Edward Frankland (1825-1899)[169] shifted the analysis of waters towards their biological contents.[170]

3.7 Conclusion

Balneology benefitted significantly from the articulation of affinity theory in the second half of the eighteenth century. Mineral waters had long been a natural medical commodity used to treat clients with skin conditions, ulcers, gout, or stones. However, advances in chemical analysis allowed for the identification of medically

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[168] John Snow, *On the Pathology and Mode of Communication of Cholera* (London, 1849).

[169] Edward Frankland and Chemical Society Britain), *On Some Points in the Analysis of Potable Waters* ([London]: [Harrison and Sons, Printers in Ordinary to Her Majesty], 1876).

[170] For water analysis in the nineteenth century see Christopher Hamlin, "Chemistry, Medicine, and the Legitimization of English Spas, 1740-1840," in *The Medical History of Waters and Spas*, ed. Roy Porter (London: Wellcome Institue for the History of Medicine, 1990).

efficacious salts and the artificial manipulation and production of mineral waters. For a chemical theory centered on the study of salts in solution, mineral waters were a readily available, socially important substance. Doctors in spa towns produced a significant body of literature on mineral waters advertising both the qualities of particular spa towns and their own chemical and medical skills. However, as chemical analyses of mineral waters became more advanced, the chemical and medical communities began to debate the sufficiency of chemical analysis in understanding the medical efficacy of mineral waters.[171] Many medical writers expressed concern that patients would self-medicate based on the chemical constituents of the various known mineral waters. To assert their claim to authority, doctors emphasized experience recognizing disease and prescribing proper dosages of the highly variable mineral waters.

Ultimately John Murray's challenge to the epistemic certainty of mineral water analysis triggered a crisis of doubt for the entire affinity research program. The analysis of aqueous solutions was the heart of affinity research, and if chemical reactants could not be proven to conform to their presumed affinities, then the theory had little utility. Thomas Charles Hope continued to teach affinity at the University

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[171] David Harley, "A Sword in a Madman's Hand: Professional Opposition to Popular Consumption in the Waters Literature of Southern England and the Midlands, 1570-1870," in *The Medical History of Waters and Spas*, ed. Roy Porter (London: Wellcome Institute for the History of Medicine, 1990). Hamlin, "Chemistry, Medicine, and the Legitimization of English Spas, 1740-1840." Durie, "Medicine, Health and Economic Development: Promoting Spa and Seaside Resorts in Scotland C. 1750-1830."

of Edinburgh well into the 1810s[172], but empirically determined affinities were already being replaced by the electrical theories of Jacob Berzelius. The complexities of Bergman's great affinity tables were for the moment replaced with much simpler assumptions about the attraction between positive and negative atoms, reminiscent of the dualistic seventeenth-century theories that focused on acids and alkalies.

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[172] Hope's lecture notes from the 1810s show that he continued to use affinity throughout his tenure at Edinburgh. Hope, *Lectures on Chemistry, Given at Edinburgh University, 1809-1810*.

Chapter 4. Improving Chemical Agriculture

4.1 The Age of Improvement

For Scottish agriculture, the eighteenth-century was the "Age of Improvement."[173] Enclosure and changes in tenancy enlarged the land size of the average farm while reducing the number of agricultural proprietors. New crops like the potato proved profitable even in the poor soils of the Highlands, and the turnip provided fodder for the animals while replenishing the soil. Afforestation to the tune of more than ten million trees provided wind breaks and prevented erosion while growing into a profitable crop for the timber starved British Isles. During the second half of the century, agriculture was introduced in the universities through both

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[173] The literature on agricultural improvement in eighteenth-century Scotland is extensive and multi-faceted. G. E. Fussell wrote on agricultural improvement in England and the rest of Great Britain from 1921 until 1971. Most pertinent to this chapter is G E Fussell, *Crop Nutrition: Science and Practice Before Liebig* (Lawrence, Kan.: Coronado Press, 1971). On the socio-economic history of the Improvement movement, see T. M. Devine, "Social Responses to Agrarian "Improvement": The Highland and Lowland Clearances in Scotland," in *Scottish Society, 1500-1800*, ed. R. A. Houston and Ian Whyte (Cambridge; New York: Cambridge University Press, 1989). And Neil Davidson, "The Scottish Path to Capitalist Agriculture 1: From the Crisis of Feudalism to the Origins of Agrarian Transformation (1688-1746)," *Journal of Agrarian Change* 4, no. 3 (2004): 227-268. On patronage and politics in Scotland during the improvement movement, seeRoger L Emerson, *Academic Patronage in the Scottish Enlightenment: Glasgow, Edinburgh and St Andrews Universities* (Edinburgh: Edinburgh University Press, 2008). On Lord Kames' interest in agriculture, see William Christian Lehmann, *Henry Home, Lord Kames, and the Scottish Enlightenment: A Study in National Character and in the History of Ideas* (The Hague: Martinus Nijhoff, 1971). On agricultural lecturers see Withers, "William Cullen's Agricultural Lectures and Writings and the Development of Agricultural Science in Eighteenth-Century Scotland." And Eddy, "The Aberdeen Agricola: Chemical Principles and Practice in James Anderson's Georgics and Geology."

chemistry and natural history courses in an attempt to appropriate science to improve the fertility of the soil and the value of the land.

Improvers looked to chemistry to explain the processes behind plant nutrition and to create a more controlled, more precise agriculture. Worried that Scottish farmers were, "led by custom in chains and in instances without number [were] fettered against interest,"[174] agriculturalists appropriated the authority of science to argue for newer, more modern farming methods. This push for more agriculture in the Scottish universities coincided with the growth of chemistry as a science and the emergence of affinity at the core of chemistry. Chemical affinity proved useful in explaining what substances plants needed to grow, how soils interacted with water, how to avoid soil exhaustion, and even what crop rotations were most effective. Because of the interconnectedness of Scottish society and the permeability of academic disciplines during the eighteenth century, agricultural chemistry became a subject of interest for doctors, natural historians, politicians, philosophers, and economists. Agricultural chemistry and the improvement movement more broadly were appropriated by multiple levels of society and helped shape the science of the Scottish Enlightenment.

4.2 Patrons of Agricultural Chemistry

In the seventeenth and eighteenth centuries, agricultural improvement was supported by the state in England, the Low Countries, and Scandinavia. In Denmark,

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[174] Kames, *The Gentleman Farmer*, ix.

a special Royal Commission was established in 1757 to study agricultural methods and make recommendations for improvement, which were then enacted by royal decrees and government funding.[175] The Scottish improvement movement lacked similar governmental support and was driven instead by the landed classes. As land holders, these gentlemen farmers stood to profit by increasing the fertility of their lands and the rents of their tenants. Though rarely found guiding a plow through their fields, members of the landed classes promoted new crops like the turnip, the potato, and madder. They drained bogs to bring more land into cultivation and planted trees as both wind breaks and sources of lumber. In addition to studying the practices of the field, the improvers also rethought the relationship between the landowners and their tenants. Longer-term, guaranteed leases replaced yearly leases, and enclosure of lands was accelerated. Beginning with The Honourable the Society of Improvers in 1723, societies were formed to support agricultural innovation and disseminate best practices. These societies in turn funded county and nation wide surveys like Andrew Wight's *The Present State of Husbandry in Scotland* (1778). The landed classes of Edinburgh and the Scottish lowlands were an "audience for science."[176] As Steven Shapin has argued, "This public, institutionalized alliance between agricultural improvement, powerfully urged by the august landed audience, and the rationalizing

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[175] Devine, "Social Responses to Agrarian "Improvement": The Highland and Lowland Clearances in Scotland," 150.

[176] Steven Shapin, "The Audience for Science in Eighteenth Century Edinburgh," *History of science; an annual review of literature, research and teaching* 12, no. 2 (1974): 95-121.

impulse of scientific intellectuals proved to be an enduring and pervasive one in the social relations of Edinburgh culture."[177] In this section, I will elaborate on this alliance, first chronicling the patronage of the Duke of Argyll in the early improvement movement, and then documenting the improvers' appeals to science as a means of "rationalizing" agriculture and promoting a nationalistic socio-economic agenda.

4.3 The Duke of Argyll

One of the most powerful patrons in eighteenth-century Scotland was Archibald Campbell (1682-1761),[178] first Earl of Ilay (1706-1743) and third Duke of Argyll (1743-1761). Archibald, like his elder brother John, second Duke of Argyll,

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[177] Shapin, "The Audience for Science in Eighteenth Century Edinburgh," 102.

[178] No book length biography of the third Duke of Argyll has been published, but Roger L. Emerson has studied Argyll's life and involvement in science. The Duke of Argyll's scientific interests are treated in Emerson, "The Scientific Interests of Archibald Campbell, 1st Earl of Ilay and 3rd Duke of Argyll (1682-1761)," *Annals of Science* (2002): 21-56. His library is studied in Roger L Emerson, "Catalogus Librorum A. C. D. C., or the Library of Archibald Campbell, Third Duke of Argyll (1682-1761)," in *The Culture of the Book in the Scottish Enlightenment*, ed. Paul B Wood (Toronto: Fisher Rare Book Library, University of Toronto, 2000). His patronage of medicine and science is addressed in Emerson, *Academic Patronage in the Scottish Enlightenment: Glasgow, Edinburgh and St Andrews Universities*. Roger L. Emerson, "Medical Men, Politicians and the Medical Schools at Glasgow and Edinburgh 1685-1803," in *William Cullen and the Eighteenth Century Medical World: A Bicentenary Exhibition and Symposium Arranged by the Royal College of Physicians of Edinburgh in 1990*, ed. Andrew Doig, Joan P. S. Ferguson, Iain A. Milne and Reginald Passmore (Edinburgh: Edinburgh University Press, 1993). And Jan Golinski, *Science As Public Culture: Chemistry and Enlightement in Britain, 1760-1820* (Cambridge: Cambridge University Press, 1992). Argyll's impact on politics and society has been recognized in several sources including Bruce Lenman, *Enlightenment and Change: Scotland 1746-1832* (Edinburgh: Edinburgh University Press, 2009).

gained much of his power by serving as an agent of the crown in negotiating the Treaty of Union in 1705 which ultimately led to the Act of Union in 1707. For his part in the negotiations, Archibald was made Lord Treasurer of Scotland in 1705, a post that would prove the first in a long line of political ascension. Lord Archibald was also made first Earl of Ilay in 1706. Acting first as an agent of the crown and later for Prime Minister, Sir Robert Walpole, Ilay became a government manager helping to identify those politicians that would support the crown. During this period, Scotland was represented by forty-five members in the House of Commons and sixteen peers in the House of Lords. While these representatives were nominally elected, the candidates with government backing won almost every election up through the 1760s. In 1734, a set of peers protested against this "King's list" and Ilay, who they identified as the political manager pulling the strings.[179] Despite their protests, the members of the King's list swept the elections of 1734, and Ilay was rewarded with an appointment to the Keepership of the Great Seal.

However, by 1740 Ilay had withdrawn his support from Walpole's government, and his power was somewhat diminished. Ilay's power was further diminished when Walpole's successors as Prime Minister began playing the two leading Scottish factions, the Argathelians (Argyll's supporters) and the Squadrone, against each other. However, Squadrone Secretary of State for Scotland, the Marquis of Tweeddale, proved such a poor leader during the rebellion of 1745, that the Argathelians once again became the dominant party in Scotland. Despite being

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[179] Lenman, *Enlightenment and Change: Scotland 1746-1832*, 26-29.

distrusted and disliked by the Duke of Newcastle, the long serving Secretary of State who succeeded his brother Henry Pelham to become Prime Minister in 1754, Campbell, now third Duke of Argyll, was too powerful in Scotland to be circumvented. By the time of his death in 1761, Archibald Campbell had enjoyed more than fifty years as one of the most powerful patrons in Scotland. When Argyll died in 1761, Newcastle begrudgingly called him "the absolute Governor of one of His Majesty's Kingdoms."[180]

Argyll's importance in the development of Scottish agriculture is twofold. As one of the single largest land holders in Scotland the Duke could implement improvements over vast stretches of western Scotland. Second, the Duke was one of the most powerful patrons in Scotland, controlling seats in the judiciary and government bureaucracy. As head of their own Campbell clan, the Dukes of Argyll owned more than five hundred square miles, and they were the feudal lords of another three thousand square miles. On these lands Archibald Campbell experimented with and encouraged the adoption of new crops including timothy, alfalfa, and flax. At his estates in Peebleshire, he drained waste-land bogs and also reclaimed lands on his estate near Hounslow Heath.[181] His efforts at afforestation resulted in the planting of several million trees across Argyllshire.

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[180] Emerson, "The Scientific Interests of Archibald Campbell, 1st Earl of Ilay and 3rd Duke of Argyll (1682-1761)," 23-24.

[181] Emerson, "The Scientific Interests of Archibald Campbell, 1st Earl of Ilay and 3rd Duke of Argyll (1682-1761)," 32.

The Dukes of Argyll were also active in the enclosure and renegotiation of tenancy in former clan lands in the Highlands. In the seventeenth-century, the Argylls leased their lands to gentry level "tacksmen" from the Campbell clan who were responsible for letting the land to tenants and raising these tenants to fight in times of war. In the opening decades of the eighteenth-century, the second Duke of Argyll opened up land to the highest bidder, regardless of kinship. In removing the tacksmen from the picture, Argyll broke the feudal hierarchy, but at the same time increased the rents on the land. Argyll argued that the higher rents would be offset, because renters no longer had to perform labor services for the tacksmen. These included "ploughing, harrowing or harvesting on the mains or home farm; moving grain supplies for the lord ('carriage'); cutting, drying and bringing in the peat supply; quartering the lord's livestock; and helping maintain the estate mill, to which they would also have to take their grain for grinding ('thirlage'), before paying the lord in kind for the privilege of doing so ('multure')."[182] Nonetheless, the increase in sheep and cattle grazing along with rapid population growth led to increases in rent of two hundred to three hundred percent from 1725 to 1775.[183] Insolvency forced many highlanders to emigrate to the coasts, the growing lowland industrial cities, America, and Europe. Over the course of a half-century, the Argylls shifted from being clan chiefs to landlords. While the

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[182] Davidson, "The Scottish Path to Capitalist Agriculture 1," 238.

[183] Eric Creegen, "The Changing Role of the House of Argyll in the Scottish Highlands," in *Scotland in the Age of Improvement: Essays in Scottish History in the Eighteenth Century*, ed. N. T. Phillipson and Rosalind Mitchison (Edinburgh: University Press, 1970), 14.

Duke no longer controlled a feudal army of five thousand men, he now had a revenue stream of more than five thousand pounds a year, making the Duke one of the richest men in the kingdom.[184]

The wealth and power of the Dukes of Argyll make them somewhat atypical of the great Scottish lords of the first half of the eighteenth-century. The Argylls achieved such economic success and independence that they no longer needed to borrow from their tacksmen. Few other lords held such economic freedom, nor did they enjoy the political power of the Argylls. The third Duke of Argyll used his wealth and political power to become one of the single most powerful patrons in Scotland. Contemporary diarist Thomas Somerville said of Argyll's role in Scottish patronage,

> All power was deposited in the hands of one individual, understood to be the minister for Scotland; and all the subaltern stations and executive offices were dealt out in conformity with his advice and recommendation. The list of the sixteen Scots' peers at the general election was dictated by him, and the majority of the representatives of counties and burghs were chosen, either in obedience to his instructions, or with consent and approbation. He stood interposed, as a sort of middle man, between the government and the people. All public measures of importance originated with him. He was the sole

[184] Creegen, "The Changing Role of the House of Argyll in the Scottish Highlands," 9-13.

> channel of solicitation to ministers, and all favours passed through his hands. Nor was his influence restricted to the disposal of places in the nomination of Government.[185]

This power, concentrated in the hands of one man and his clan, drew the ire of his peers. Recognizing their own economic and political decline, both in absolute terms and more stark relative terms in comparison to Argyll, many lords threw their lot in with the Squadrone hoping the restoration of the Jacobites "would wipe out both their debts and the Argyll empire to which so many of these were owed."[186] The failure of the '45 signaled the end of feudal lords in Scotland and the launching of a more widespread attempt at a commercial society based around agricultural improvement. In his three part Marxist history of the Scottish agricultural revolution, Neil Davidson argues,

> The Scottish lords inadvertently provided the prototype for the transitions that would follow in mainland Europe during the nineteenth century. It was the first transition to agrarian capitalism to be carried out almost entirely by an existing class of feudal landowners who realized that the only way to reverse their decline was to adopt the very methods of the capitalist agriculture that they had hitherto resisted. In this way they could at least remain members of a dominant

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[185] Thomas Somerville, *My Own Life and Times, 1741-1814*, ed. Richard Sher (Bristol, England: Thoemmes Press, 1996), 379.

[186] Davidson, "The Scottish Path to Capitalist Agriculture 1," 254.

> class, albeit within a new set of social relations, using new methods of exploitation.[187]

Stripped of their feudal armies, the labor services of their tenants, and their clan based territorial power, the Scottish lords had little choice but to emulate Argyll in transitioning to rent collecting land lords. As such, it was in their best interest to embrace the agricultural improvements that might increase the rent value of their lands, despite the concurrent growth of a bourgeois yeomanry.

While much of his attention was devoted to the political management of Scotland, Argyll also used his power to fill scientific and medical chairs with men who shared his interests in agriculture and botany. Argyll was widely read in medicine, chemistry, botany, and mathematics. His London library of over twelve thousand volumes included twelve-hundred eighty four volumes on medicine. Although he studied law in Utrecht, he received an honorary degree in medicine from the University and King's College of Aberdeen in 1708 and was made an Honorary Fellow of the Royal College of Physicians of Edinburgh in 1758. These honors were unusual for a lawyer and indicate the public recognition of Argyll's interest in medicine as well as his role as a patron of medicine in Edinburgh and the rest of Scotland.

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[187] Davidson, "The Scottish Path to Capitalist Agriculture 2," 420.

Argyll himself worked on invisible inks, medicines, smelting, and other chemical practices.[188] His house in London along with his estates at Whitton and Peeblesshire were equipped with chemical laboratories. Beginning in 1740, Argyll had a chemical laboratory built at his Scottish estate called Whim. Construction and repair records spanning the period 1740 to 1750 suggest a building with about two-hundred sixty square feet. The laboratory had two stills and seven furnaces including one that was likely use for iron ore smelting. Argyll also had an iron press installed and hired one James Gray from the Dalkeith iron mill to help with maintenance of his equipment. It appears from this partial inventory that the chemical laboratory at Whim was used primarily for mineralogy and metallurgy.[189] This idea is further supported by Argyll's experiments at the Whim with the abundance of peat cleared from the lands as a possible fuel for iron smelting. Emerson notes that, as the least used of his residences, Whim may have been the least stocked of his laboratories. Emerson also suggests that Argyll and his friends did more of their medical chemistry at his estates in the south. Argyll equipped his labs with thermometers, barometers, and weathervanes along with glass work including phials, tubing, vessels, and swan's necks. His collection of mathematical and astronomical instruments along with his

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[188] Emerson notes that Argyll's interest in medical recipes may have been part of a larger family tradition. His father and his cousin, also called Archibald Campbell, were also interested in medicine. A large collection of his cousin's medical recipes are held by the National Library and have been mistakenly attributed to Argyll by the National Library. See Emerson, "The Scientific Interests of Archibald Campbell, 1st Earl of Ilay and 3rd Duke of Argyll (1682-1761)," 28-29.

[189] For more on the laboratory at Whim see Emerson, "The Scientific Interests of Archibald Campbell, 1st Earl of Ilay and 3rd Duke of Argyll (1682-1761)," 40-42.

extensive work in botany further contribute to the image of Argyll as an active participant in the sciences.

4.4 Agricultural Improvement Societies

The Duke of Argyll was also a member of several agricultural societies. As Earl of Islay, he was a charter member of the first Scottish agricultural society, The Honourable Society of Improvers, founded in 1723. As one early study of the society notes, the Improvers were primarily members of the aristocracy and gentry,

> The names include those of three dukes, two marquises, nineteen earls, twenty-five lords, forty baronets and knights, sixteen judges, sixty or more lawyers (mainly advocates), six doctors and a professor of anatomy, a professor of mathematics and two other mathematicians, five merchants (one of whom styled "seedsman to the Society"), two booksellers, one engineer, three ex-Lord Provosts of the City of Edinburgh, and many landowners designated from their estates in all parts of the country.[190]

Like Argyll, these gentlemen saw agricultural improvement as a means of personal economic gain and also a patriotic step towards economic and social modernization of

[190] Alex MCallum, "The Society of Improvers," *The Scottish Journal of Agriculture* 18 (1935); p. 41. The membership roll is available in the Honourable the Society of Improvers in the Knowledge of Agriculture in Scotland, *Select Transactions of the Hounourable the Society of Improvers in the Knowledge of Agriculture in Scotland. Directing the Husbandry of the Different Soils for the Most Profitable Purposes* (Edinburgh: Printed by Sands, Brymer, Murray and Cochran. Sold by Mess. Paton, Symmer & Gordon, 1743), xviii-xxiii.

Scotland. Lord Kames said, “Every gentleman farmer must of course be a patriot; for patriotism, like other virtues, is improved and fortified by exercise. In fact, if there be any remaining patriotism in a nation, it is found in that class of men.”[191] The Scottish poet, Allan Ramsay marked the foundation of the Society of Improvers with a poem entitled “The Pleasures of Improv[e]ments in Agriculture.” Ramsay closes the fifty-nine line poem by praising the club and and wishing for their success in improving the economy of Scotland:

> Hope hear the sang which thy unwearied mind
> for Publick good me thus to sing inclind
> continou Best of Clubs Long to Improve
> your native Plains and gain your nations Love
> Rowse evry Lazy Laird of each wide feild
> that unmanurd not half their Product yeild
> shew them the proper season soils and art
> how they may Plenty to their Lands impart
> Treeple their Rents encrease the farmers store
> without the Purches of one Acre more.[192]

Ramsay optimistically predicts the tripling of rent and at the same time the increase of the “farmer’s store” in a cornucopian utopia brought about through agricultural

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[191] Kames, *The Gentleman Farmer*, xvii.

[192] Allan Ramsay, "The Pleasures of Improvments in Agriculture," in *The Works of Allan Ramsay. Miscellaneous and Uncollected Vol. 3, Poems*, ed. A. M. Kinghorn and Alexander Law (Edinburgh: Scottish Text Society, 1961), 172.

reform. Rather than blaming the lower classes for their penury, Ramsay places responsibility for the economic backwardness of Scotland with the "Lazy Lairds" who do not provide manure for the fields. Those progressive members of this "Best of Clubs" are acting patriotically in advancing their nation's economy and thus deserve their "nation's love."

The Society of Improvers, though intent on improving agriculture, was a social club exclusive to the gentlemanly classes. M'Callum highlights this exclusivity noting, "Two gardeners are specified, but it is significant that not one of the members is called a farmer, although doubtless a great many of the landowners themselves farmed portions of their family estates."[193] Though established in the midst of a transition from a feudal system to a more capitalistic one, the Society upheld the distinctions of class and rank and was not, in any significant way, a democratizing social institution.

Despite the social boundaries erected at the Society's formation, the Improvers did seek to interact with farmers in several ways. A council was formed to correspond with farmers throughout the nation to collect and study best practices and a report was written in "a familiar Stile [sic] such as Country Farmers might easily understand."[194] Farmers were also encouraged to write to the Society for advice or

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[193] MCallum, "The Society of Improvers," 41.

[194] Honourable the Society of Improvers in the Knowledge of Agriculture in Scotland, *Select Transactions of the Hounourable the Society of Improvers in the Knowledge of Agriculture in Scotland. Directing the Husbandry of the Different Soils for the Most Profitable Purposes*, 8.

with suggestions, and many of these letters were included in the Society's *Select Transactions*. The volume includes discussion of draining and clearing land, crops and crop-rotation, manures, and battling weeds and other pests. The Society also encouraged farmers to start smaller, regional societies for agricultural improvement. From the formation of the "Small Society of Farmers in Buchan" near Aberdeen in 1730 through 1835, more than one-hundred thirty agricultural societies were formed throughout the lowlands.[195]

Because of the death of many of its founding members and the political tumult of the period, the Society of Improvers had declined in significance by 1745. However, it was succeeded by two spin-off societies, the Board of Fisheries and The Board of Trustees for the Encouragement of the Fisheries, Arts, and Manufactures, both of which had been founded in 1727 following the suggestions of the Society of Improvers. The similar but separate Edinburgh Society for Encouraging Art, Science, Manufactures and Agriculture (founded in 1754) and the Philosophical Society of Edinburgh also treated agricultural issues. The Society of Improvers had also, from its start, been interested in the advancement of flax husbandry and the linen industry in Scotland going so far as to adopt a resolution at one meeting that no members should

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[195] A partial list along with geographic plotting of these societies can be found in R. C. Boud, "Scottish Agricultural Improvement Societies, 1723-1835," *Review of Scottish Culture* 1 (1984); pp. 74-77.

buy linen for any purpose that was not made in Great Britain.[196] Many members of the Society were involved in the founding of the British Linen Company.

4.5 Henry Home, Lord Kames

As a member of several improving societies and an investor in the British Linen Company, Henry Home, Lord Kames, was an active patron in the improvement of agriculture. Born into the gentry, Henry Home rose to prominence as an author and an advocate in the Scottish legal system. With the support of the Duke of Argyll, Home was named to the bench in 1751, and took the name Lord Kames after his family home. In 1766, Kames anonymously published a pamphlet entitled *Progress of Flax-Husbandry in Scotland*. Noting the importance of the linen industry to Scotland, Kames identified the 110,000 pounds spent annually importing flax as an economic and political weakness in need of improvement.[197] After acknowledging the past failures of flax cultivation in Scotland due to the difficulty of processing flax seed and the lack of a ready market, Kames assured his readers that technological advances along with a fifteen shilling per acre-seeded premium from the board of the Linen company would make flax a profitable crop. Kames' early work on flax demonstrates his economic and industrial motivations for agricultural improvement.

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[196] Alexander Ramsay, *History of the Highland and Agricultural Society of Scotland, with Notices of Antierior Societies for the Promotion of Agriculture in Scotland* (Edinburgh: Published for the author by W. Blackwood & sons, 1879), 22.

[197] Henry Home, Lord Kames, *Progress of Flax-Husbandry in Scotland* (Edinburgh, 1766), 8.

Early in his career, Henry Home acted as a go-between for Argyll identifying individuals with scientific and medical talents and introducing them to the Duke. Home entered into correspondence with the doctor and lecturer William Cullen in 1748 after Cullen critiqued the draft of an essay by Home on evaporation. Cullen had been lecturing extramurally in Glasgow since 1744 and had begun in 1746 to take over the lectures for John Johnstoun, who held the chair of medicine at Glasgow but was in declining health. In 1748, Cullen began to integrate agriculture into his chemistry course, giving nine lectures on the subject.[198] In 1749 Home nominated Cullen for membership in the Philosophical Society of Edinburgh. In the same letter that he tells Cullen of his nomination, Home admitted, "My sedate purpose is, that your name shall be carried down to posterity by a treatise on agriculture, better than the world ever yet saw."[199] In the same year, Home also arranged a meeting between Cullen and the Duke of Argyll. Argyll agreed to support Cullen for the chair of medicine at Glasgow. Although they had to wait for Johnstoun to retire, Argyll's support secured the position for Cullen in 1750.[200]

A letter from William Cullen to another of Argyll's clients, Robert Simson, shows that Argyll had full control over appointments at Glasgow. Cullen says, "The folkes here who have solicited the D. of Argyle about our new professorship have as

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[198] Withers, "William Cullen's Agricultural Lectures and Writings and the Development of Agricultural Science in Eighteenth-Century Scotland."

[199] John Thomson, *An Account of the Life, Lectures, and Writings of William Cullen, M.D* (Edinburgh: William Blackwood, 1859), 62-63.

[200] Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, 67-70.

yet received no other answer but that he must consult the College before he gives opinion."[201] In 1751, Argyll appointed another of Kames' proteges, Hercules Lindsay, to the chair of law. Among the long list of Argyll's appointments are Frances Hutcheson, Adam Ferguson, Joseph Black, Robert Dicks I and II, John Anderson, and Alexander Wilson.[202] Argyll was also active at the University of Edinburgh. In his memoirs, Thomas Somerville said of Argyll,

> I know it to be a fact, that Provost Drummond, the most meritorious benefactor of the community over which he presided, did not find himself at liberty to promise any preferment at the disposal of the Town-Council of Edinburgh, without the previous consent of Lord Milton, the delegate and political agent of Archibald Duke of Argyle. To such an extreme was this scheme of universal patronage stretched, that it was always deemed prudent to obtain Lord Milton's goodwill before making any application, even for places of the most inconsiderable emolument and importance. It was fortunate for the public that, in the enlightened scheme for filling the chairs in the University with the ablest candidates, the Duke of Argyle concurred with Provost Drummond.[203]

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[201] William Cullen, *Letter to Robert Simson* (GUA 26223) (February 8, 1752).; cited in Emerson, *Academic Patronage in the Scottish Enlightenment: Glasgow, Edinburgh and St Andrews Universities*, 122-123.

[202] Emerson and Wood, "Science and Enlightenment in Glasgow, 1690-1802," 86.

[203] Somerville, *My Own Life and Times, 1741-1814*, 379.

Through his chief agent, Andrew Fletcher, Lord Milton, Argyll collected clients and filled the universities with people who would support both his academic and political interests. In the hotly contested battle for the chair of chemistry in 1754-5, Joseph Black, William Cullen, and Francis Home all competed for the position. Francis Home was a relative of Lord Milton, but could not gain the approval of Argyll and ultimately withdrew his candidacy. Cullen was opposed by faculty members who preferred Black and felt that Cullen was being pushed on them by politicians like Kames. One observer noted, "At this critical juncture of affairs, the duke of Argyle arrived in Edinburgh, and employed the whole weight of his interest in favour of Dr. Cullen."[204] While Argyll could not act unilaterally, in either Glasgow or Edinburgh, he was one of the single most powerful academic patrons in Scotland from the 1720 up until the time of his death, and even after through his political successors, the 3rd Earl of Bute and James Stuart Mackenzie.

Kames remained an important figure in agriculture and academic patronage after Argyll's death in 1761. In addition to his political role in the judiciary, Kames also held power as a commissioner of forfeited estates. Those lords who rebelled against the crown in 1745 forfeited their estates. While most of these lands were sold off (often back to the lords who had forfeited them), the state retained control of thirteen estates and their proceeds used to promote "the Protestant Religion, good government, industry and manufactures, and the principle of duty and loyalty to his

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[204] Emerson, *Academic Patronage in the Scottish Enlightenment: Glasgow, Edinburgh and St Andrews Universities*, 301.

Majesty."[205] Kames and his fellow commissioners were responsible for administrating these estates and using them to promote agricultural improvement. In 1773, he commissioned Andrew Wight to survey the forfeited estates, eventually resulting in the publication of the multi-volume *Present State of Husbandry in Scotland* (1778-1784). Kames also commissioned Rev Dr John Walker to survey the highlands, resulting in the publication of Walker's *An economical history of the Hebrides and Highlands of Scotland* (1808). On his literary influence through the Select Society of Edinburgh, Kames biographer, Alexander Fraser Tytler said,

> The situation which Lord Kames now filled, while it extended his opportunities of promoting every species of improvement, gave the greater weight and efficacy to his patronage; and his example and encouragement were more particularly beneficial in exciting a literary spirit, which now began to prevail among his countrymen, and which was destined to shine forth in his own times with no common lustre. It was but a just tribute to his merit, when many years afterwards, Adam Smith, then in the height of his literary reputation, said, in reference to a remark on the great number of eminent writers which Scotland had

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[205] *An Act for annexing certain forfeited estates in Scotland to the Crown unalienably and for making satisfaction to the lawful creditors thereupon; and to establish a method of managing the same; and applying the rents and profits thereof, for the better civilizing and improving the Highlands of Scotland; and preventing disorders there for the future*, (London: Printed by Thomas Baskett; and by the assigns of Robert Baskett, 1752).

of late years produced, "We must every one of us acknowledge Kames for our master."[206]

He helped Francis Home to the *materia medica* chair in Edinburgh, and Kames was influential in the appointment Thomas Reid in 1764.

In 1766, Lord Kames' wife, Agatha Home née Drummond, inherited an estate in Perthshire worth 2000 pounds a year. Kames used this estate to experiment with his ideas on agricultural improvement. Based on his years of correspondence and his own experiences, he published an agricultural text in 1776 entitled the *Gentleman Farmer*. This book was divided into two parts: "Practical Agriculture" and the "Theory of Agriculture." The former is by far the larger section, comprising about three hundred fifteen of the book's four hundred sixty-six pages. Sections on the instruments of farming, cattle, cropping, and various plant cultures provided a general overview of the common practices of agriculture. In the opening pages of the theoretical section, Kames admitted that theoretical knowledge of agriculture was woefully imperfect, but "fortunately, agriculture depends not much on theory." Kames continued, "But admitting experience to be our only true guide, theory however ought not to be rejected, even by a practical farmer. Man is made for knowledge; and he has

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[206] Alexander Fraser Tytler, *Memoirs of the Life and Writings of the Honourable Henry Home of Kames: Containing Sketches of Literature and General Improvement in Scotland During the Greater Part of the Eighteenth Century; In Two Volumes* (Edinburgh, 1807), 159. Iris Fleßenkämper, *Considerations, Encouragements, Improvements. Die Select Society in Edinburgh 1754-1764: Soziale Zusammensetzung Und Kommunikative Praxis* (Berlin: Akademie Verlag Berlin, 2010), 195.

a natural curiosity to learn the reason of every thing."[207] Both in the structure and the language of his book, Kames presents theory as a supplement to practical experience. Kames downplayed the necessity of natural philosophy for the practical farmer, appealing instead to curiosity and reason as sufficient motivation to pursue self-education. Kames divided the theoretical part of the book into three sections: 1) Preliminary Observations; 2) The Food of Plants; and 3) the Means of Fertilizing Soils.

Most of the Preliminary Observations section is devoted to an overview of chemical agriculture. Kames said,

> To be an expert farmer, it is not necessary that a gentleman be a profound chymist. There are however certain chymical principles relative to agriculture, that no farmer of education ought to be ignorant of. Such as appear the most necessary shall be here stated, beginning with elective attraction and repulsion, which make a capital article in the science of agriculture as well as of chymistry.[208]

Kames then provided a twelve-page explanation of elective attraction and repulsion. Rather than presenting a table of affinities or rehashing the kind of encyclopedic description of chemical affinity that one would expect from Macquer or Diderot, Kames focused on the relative attractions between water and different kinds of soil. Drawing on common observation, Kames noted that clay attracts water more strongly

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[207] Kames, *The Gentleman Farmer*, 292.

[208] Kames, *The Gentleman Farmer*, 292.

than sand and that "even clays differ. Some clays attract water vigorously, others less."[209] He also noted that elective attraction only acts between individual particles. In order to maximize the beneficial water attracting qualities of clay, one should pulverize the clay to maximize surface volume. "The chief object of husbandry is, by ploughing and harrowing to pulverize clay, and every other soil that requires it."[210] Kames warned his readers that they should not plough wet clay. Doing so would expose an increased number of particles to the air, which has a higher affinity for water than does the clay. Thus ploughing wet clay only accelerates the dehydration of the soil.

Kames believed that plants drew no nutrition from the soil itself. "There is not the slightest evidence," according to Kames, "that plants attract any dry matter, however pulverized. Set the most healthy vegetable in dried earth, or in dust gathered from the highway: it dies, and the earth remains as weighty as before."[211] While Jethro Tull and his followers believed that earth was itself one nutrient of plants, Kames said that the only important factor in soil is how well it conveys water to the plant. "A plant can receive no nourishment but what is conveyed to it by air or water; and consequently that nothing can serve as its nourishment but what is soluble in these elements."[212] For Kames, plant nutrition was a chemical process in which plants

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[209] Kames, *The Gentleman Farmer*, 296.

[210] Kames, *The Gentleman Farmer*, 297.

[211] Kames, *The Gentleman Farmer*, 297.

[212] Kames, *The Gentleman Farmer*, 297-8.

attracted water and air and converted them into sap. As for the composition of the nutrients that the air and soil carry, Kames claimed that it is beyond the realm of human knowledge. He cautions farmers from subscribing to the latest theories on oil or salt based manures saying, "The province of agriculture is, to prepare the soil so as to furnish plenty of juices, leaving the rest to nature."[213]

4.6 Lord Dundonald

Archibald Cochrane, ninth earl of Dundonald, was, like the Duke of Argyll and Lord Kames, a member of the aristocracy concerned with the scientific advancement of agriculture.[214] Upon succeeding his father to the title of Earl of Dundonald, Archibald was saddled with an impoverished estate. His extensive experiments on soda production[215] and coal-tar never proved profitable, and Dundonald ultimately died in poverty. While he never enjoyed the financial success and patronal power of Argyll or Kames, Dundonald's primary contributions to science came from his pen. In addition to *The Quality and Uses of Coal Tar and Coal Varnish*

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[213] Kames, *The Gentleman Farmer*, 317.

[214] Dundonald's work on agricultural chemistry is addressed in David Knight, "Agriculture and Chemistry in Britain Around 1800," *Annals of Science* 33, no. 2 (1976): 187-196.

[215] Dundonald's factory on the Tyne at Walker was one of the first in England to adopt the Lablanc process. Developed by Nicolas Lablanc, this process made possible industrial scale production of soda, a necessary ingredient in textile bleaching, and the production of soap, glass, and paper. The Lablanc process was widely adopted until it was superseded by the Solvay process.

(1784), Dundonald published a *Treatise Showing the Intimate Connection between Agriculture and Chemistry* in 1795.

In the opening pages of his treatise, Dundonald addresses his two audiences, farmers and agricultural writers. According to Dundonald,

> The slow progress which Agriculture has hitherto made as a science, is to be ascribed to a want of education on the part of the cultivators of the soil, and the want of knowledge, in such Authors as have written on Agriculture, of the intimate connection that subsists between this science and that of Chemistry. Indeed there is no operation or process, not merely mechanical, that does not depend on Chemistry, which is defined to be a knowledge of the properties of bodies, and of the effects resulting from their different combinations.[216]

The first third of Dundonald's treatise addresses this gap with an experimental history.[217] Combining the encyclopedic lists of natural history's bestiaries and herbals with the experimental analysis of Joseph Priestley and Henry Cavendish, Dundonald's experimental history lists off the many varieties of earths, acids, alkalies, and salts common to British soil and provides the chemical characteristics of each. In one representative entry, Dundonald says,

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[216] Archibald Cochrane Dundonald, *A Treatise Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry* (London: Printed for the author and sold by R. Edwards, 1795), 1-2.

[217] For more on the term "experimental history" see Ursula Klein and Wolfgang Lefèvre, *Materials in Eighteenth-Century Science: A Historical Ontology* (Cambridge, Mass.: MIT Press, 2007).

> Magnesia, considered as a manure, is contained in steatities or soap rock, and in a variety of other earths and stones. It combines with acids, forming neutral salts, all of which are very soluble, and the greater of them promote, in a very considerable degree, the growth of plants. Magnesian earths may be applied with peculiar advantage to soils generally, and not improperly called sour soils, containing green vitriol, arising from the decomposition of pyrites. It will decompose the metallic salt by superior affinity, and form with the acid, Epsom salt, known in a high degree to promote vegetation; while the earth of iron will be separated in the state of an ochre, or iron combined with fixable air.[218]

This entry is rich in chemical information. Dundonald advocates the use of magnesia as a chemical manure for two reasons: 1) it neutralizes acids forming salts that are nutritious for plants; 2) it decomposes green vitriol, which is poisonous for plants forming the nutritious Epsom salt and the non-soluble and therefore biochemically impotent ochre. Both of these characteristics are derived from magnesia's high affinity for acid. In the first case it combines with the acids which are found uncompounded in the soil. In the second case the magnesia causes a displacement, drawing the acid away from the iron due to its "superior affinity." Throughout the first third of Dundonald's text, similar entries on the various acids, bases, salts, and

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[218] Dundonald, *A Treatise Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry*, 51.

earths draw on affinity based chemistry to explain the subterranean reactions that define a particular soil's fertility.

While the second section of the book focuses on the physical construction and placement of dung heaps, the third section focuses on soils. Again Dundonald includes in the introduction, a guide for the analysis and identification of the soils through chemical methods. Dundonald says,

> Cultivators of the soil should be able to distinguish by chemical tests, the proportion of the following substances in different soils, viz. Clay, Chalk, Sand, Magnesia, Earth of iron, and Vegetable Matter … in order that he may, from such information, be enabled to administer to each part those particular substances that it may require to constitute it rich and fertile mould.[219]

Dundonald then suggests the chemical apparatus needed for such experimentation including scales, porcelain or stone vessels, muriatic acid, and mineral alkaline salts. He outlines the precipitation reactions involved for isolating calcareous earths and magnesia and notes that sand, clay, and vegetable matter can all be identified by sight or touch. To distinguish between magnesia and calcareous materials, Dundonald suggests precipitation with mineral alkaline salts followed by washing with vitriolic acid. The calcareous materials will form gypsum through this process while the magnesia will form Epsom salt. Dundonald provides tables compiled by Torbern

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[219] Dundonald, *A Treatise Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry*, 151-152.

Bergman and Richard Kirwan showing the chemical composition of both gypsum and Epsom salt in parts per hundred so that the farmer will be able to derive a quantitative estimate as to the composition of his soil.

Dundonald's book was well received. *The Critical Review*, in agreement with the author's goals of explaining the chemical bases for agriculture, said,

> Chemistry, in its present state of improvement and extension, comprehends perhaps all the science with which it is requisite for the farmer to make himself acquainted; but the connexion of agriculture with chemistry is so close, that, without a competent knowledge of the latter, it is scarcely possible for the speculative farmer to avoid the grossest and most pernicious mistakes.[220]

The *Treatise* was excerpted in three issues of the 1795 volume of the *English Review of Literature, Science, Discoveries, Inventions, and Practical Controversies and Contests*. A third journal, the *Analytical Review* said of the Treatise,

> It abounds with new and interesting facts; that the deductions are clear, simple, and masterly; and that the continual reference to a large fund of experimental knowledge creates confidence in the reader, and is most honourable to the talents and judgement of the author. Every cultivator may receive instruction from this work; but a considerable

[220] "Rev: A Treatise Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry," *The Critical Review, or, Annals of Literature* , no. Jun (1795); p. 191.

> number, we apprehend, will find it necessary to have recourse to some popular treatise on general chemistry at the same time.[221]

The one dissenting review that could be found disagrees with several of Dundonald's conclusions, particularly his rejection of fallowing, yet it praises Dundonald as a "man of rank bending his attention towards his country's welfare, and anxious to fix its prosperity on a firm and lasting basis," which the review notes, "must be pleasing to every reflecting and patriotic mind."[222]

The most serious critique of Dundonald's *Treatise* focused on its price. For a text purportedly targeted at the cultivators of the earth, the price of one guinea was seen by several reviewers as too high. In the words of one reviewer, "A work so generally useful should have been adapted to general circulation; and although the price of paper, print, and advertising, have of late been greatly enhanced, the book should not have exceeded ten or twelve shillings."[223] The *Monthly Review* hoped, "Lord Dundonald will favour the public with an octavo edition, at a moderate price, of this truly interesting tract."[224] Dundonald admitted his limited means referring to

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[221] "Rev: A Treatise, Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry," *The Analytical Review: or, History of Literature* , no. July (1795); p. 39.

[222] "Rev: A Treatise, Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry," *The Monthly Review* , no. September (1795); p. 69.

[223] "Rev: A Treatise, Shewing the Intimate Connexion That Subsists Between Agriculture and Chemistry. By the Earl of Dundonald," *English review of literature, science, discoveries, inventions, and practical controversies and contests* , no. June (1795); p. 430.

[224] "Rev: A Treatise, Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry," 74.

his "*res angusti domi*" on the opening page of his "Prefatory Address,"[225] and he likely hoped to recoup some of the expense of his agricultural experiments through sales of his book. Nonetheless, the price of his *Treatise* did limit its accessibility for farmers.

The landed classes were a driving force in the improvement of eighteenth-century agriculture. As large land owners, they pressed for afforestation, enclosure, revisions in the concept of tenancy, and the adoption of new crops and new farming techniques. They assembled committees and societies to gather and disseminate information on the best practices in agriculture. As patrons, they hand-picked candidates for chairs in the universities who had similar interests in medicine, agriculture, and economic improvement. As writers, they identified areas for economic expansion and explained how science could be applied in the fields. In the next chapter, we will see how the university faculty, led by William Cullen, paid back the support of the landed classes in developing a chemical theory of plant nutrition, soil restoration, and manuring.

[225] Dundonald, *A Treatise Shewing the Intimate Connection That Subsists Between Agriculture and Chemistry*, 7.

Chapter 5. Chemical Agriculture and the Universities

5.1 Lecturing on Chemical Agriculture

Although a chair of agriculture had been proposed by James Maxwell, secretary of the Society of Improvers, as early as the 1720s,[226] the first lectures on agriculture in the Scottish universities were given by William Cullen in 1748. Cullen's course was particularly influential because of his popularity as a teacher. His classes expanded from between ten to twenty students a year when he began teaching at Glasgow in 1746 to approximately one-hundred forty paying students during his time at Edinburgh (1755-1790). He also helped his students by introducing them to his powerful patrons who in turn helped them to secure professorial appointments to Glasgow, Edinburgh, and Aberdeen. Many of his students, including Joseph Black, George Fordyce, and Rev. John Walker developed their own agricultural lectures. In documenting Cullen's agricultural work, Charles Withers used Cullen "to illuminate the links between agricultural improvement and scientific knowledge in eighteenth-century Scotland."[227] This chapter will take the next step by showing how his affinity based chemistry shaped the development of agricultural improvement. Cullen's students and his colleagues appropriated his teachings throughout the second half of the eighteenth century. Before 1750, efforts to improve soil focused on ploughing

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[226] Honourable the Society of Improvers in the Knowledge of Agriculture in Scotland, *Select Transactions of the Hounourable the Society of Improvers in the Knowledge of Agriculture in Scotland. Directing the Husbandry of the Different Soils for the Most Profitable Purposes*, xiii-xiv. MCallum, "The Society of Improvers," 45.

[227] Withers, "William Cullen's Agricultural Lectures and Writings and the Development of Agricultural Science in Eighteenth-Century Scotland," 148.

and pulverizing the soil. During the second half of the century, these chemical ideas of agriculture developed to a point where chemical reactions within the soil were a goal in and of themselves.

5.2 Affinity Based Agriculture

Beginning in 1746, Cullen taught courses on the practice of physic for the aging and infirm chair of medicine, John Johnstoun. In 1747 he added a separate course on botany and *materia medica* and also negotiated with the university for the establishment of a course on chemistry.[228] In 1748, Cullen inserted nine lectures on agriculture into his chemistry course of about one-hundred sixteen lectures. In the outline of his 1748 lectures, Cullen described the role of the natural philosopher in agriculture:

> The principal Means & Practices already found out & found by such Inductions as above but the foundations not transmitted or known to our Farmers therefore the Business of the Gentn Philos. to explain the foundations and thereby fix ascertain & properly diversify the common Methods the principle point.[229]

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[228] Withers, "William Cullen's Agricultural Lectures and Writings and the Development of Agricultural Science in Eighteenth-Century Scotland," 149.

[229] Cullen, *Abstract of Dr. Cullen's Lectures on Agriculture*. Quoted in Withers, "William Cullen's Agricultural Lectures and Writings and the Development of Agricultural Science in Eighteenth-Century Scotland," 152.

Cullen recognized the expertise of farmers and their inductive understanding of agriculture, but called on philosophers to provide the theoretical foundations for a more reasoned and methodic agriculture.

William Cullen was himself a gentleman farmer. He spent much of his childhood on his grandfather's farm and, as an adult, considered buying the farm for his brother Robert. William said of the farm, "the place where I spent so much of my infancy, I have always had a particular affection for."[230] However, because the farm had been subdivided to such an extent that it could no longer support a family, William bought a larger farm for his brother in 1752 at Parkhead, near Glasgow. Because Robert was a merchant in the West Indies, William took it upon himself to manage and improve the farm, and used the land to conduct agricultural experiments. William also managed his own farm in Ormiston, near Kirknewton, in West Lothian from 1756. Andrew Wight said of Cullen's Ormiston farm,

> I have reason to know that he is thoroughly acquainted with every branch of agriculture, both in theory and practice. Already during his short possession, his turnip and wheat make a figure. He will prove a blessing to the neighborhood, both by example and precept.[231]

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[230] Thomson, *An Account of the Life, Lectures and Writings of William Cullen*, 68. Quoted in Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, 4.

[231] Andrew Wight, *Present state of husbandry in Scotland*, Web (Edinburgh: Printed for W. Strahan, and T. Cadell, London, and W. Creech, Edinburgh, 1778), 469. Quoted in Withers, "William Cullen's Agricultural Lectures and Writings and the Development of Agricultural Science in Eighteenth-Century Scotland," 149.

Cullen was raised on a farm and continued to manage farms and conduct agricultural experiments throughout his life. This personal experience lent his agricultural lectures the authority of empiricism.

In his lectures, Cullen explained how chemistry can be useful both in farming and preserving crops:

> By attending to the chemical history of [putrefaction] we are directed how to avoid it & thereby to preserve most kinds of natural productions in their native perfection, the various advantages of which you can easily imagine. By the same chemical history of putrefaction we are also directed how to promote it, which is frequently required, as in furnishing the proper manures for the farmer.[232]

For Cullen, the chemical process of putrefaction was the key to improving agriculture for two reasons. First, slowing putrefaction was critical in preserving meat and crops that have already been harvested. Second, Cullen thought putrefaction was the key process in nature's production of plant food, saying:

> It appears to me probable that it is water impregnated with something that furnishes this pabulum, and not the pure element alone. If they should still go further, and inquire what this impregnating matter is; I would answer, probably animal or vegetable substances decomposed

[232] Cullen, *Abstract of Dr. Cullen's Lectures on Agriculture*.. Quoted in Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, 108.

> and subtilized by putrefaction, and in this state carried up by the water in the state of vapour.[233]

Like many other early eighteenth century natural philosophers, Cullen still believed that the primary nourishment for plants came from water. In the famous willow tree experiment, published in 1648, Jean Baptiste van Helmont grew a potted willow tree for five years adding only water to the pot. At the end of five years, Van Helmont weighed both the tree and the soil. While the tree had gone from a five pound sapling to a one hundred sixty-nine pound tree, only two ounces of the original two hundred pounds of soil had been consumed or were missing. Van Helmont concluded from this that water was the sole nutrient of plants.[234]

Unlike Van Helmont though, Cullen's water is "not the pure element alone" but rather rain water. Here Cullen appears to be drawing from J. J. Becher who had said, "Rainwater is the generative connatural humor of all plants. It is transmuted not only into their substance but even into their seeds. Plants are nothing else but coagulated rainwater."[235] However, Cullen went a step further than Becher by saying

[233] William Cullen, "The Substance of Nine Lectures, on Vegetation and Agriculture, Delivered to a Private Audience in the Year 1768," in *Additional Appendix to the Outlines of the Fifteenth Chapter of the Proposed General Report From the Board of Agriculture. On the Subject of Manures*, ed. Board of Agriculture (London: printed by W. Bulmer and Co., 1796), 6-7.

[234] Jan Baptista van Helmont, *Ortus Medicinæ. Id Est, Initia Physicæ Inaudita. Progressus Medicinæ Novus, in Morborum Ultionem, Ad Vitam Longau*, ed. Franciscus Mercurius van Helmont (Amsterodami: L. Elzevivium, 1648).

[235] Johann Joachim Becher and Georg Ernst Stahl, *Chymischer Glücks-Hafen: Oder, Grosse Chymische Concordantz Und Collection, Von Funffzehn Hundert Chymischen Processen* (Leipzig: J. P. Kraus, 1755), 77. As translated in Charles A Browne, *A Source Book of Agricultural Chemistry* (Waltham: Chronica Botanica, 1944), 97.

that rainwater was impregnated with putrefied plant and animal material. Cullen drew on the experiments of John Woodward which confirmed that "the waters which were most liable to putrescency were best adapted to nourishing vegetables."[236] While Cullen taught his theory of impregnated rainwater until at least 1768, the theory was not widely adopted. In the notes for Cullen's agricultural lectures published in 1796, Cullen's student George Pearson says,

> Our great Professor could not possibly have imputed the nutritive power of rain water to the solution of putrefied animal and vegetable substances, if he had either been acquainted with the experiments of Margraaf[237], or had evaporated to dryness pure rain water i.e. collected at a distance from towns and after the atmosphere had been washed by long-continued rain, for then he would have known that such water is almost as pure as distilled water, and does not contain an atom of animal or vegetable matter. Further, if impure rain water be nutritive from its impregnation, then other things are nutritive also, in so far as they contain water and animal or vegetable matter, which is

[236] Cullen, "The Substance of Nine Lectures, on Vegetation and Agriculture, Delivered to a Private Audience in the Year 1768," 7. Woodward had actually been arguing against Helmont's water thesis asserting instead that earths, in the form of putrid matter, were the nutritive material of plants. John Woodward, "Some Thoughts and Experiments Concerning Vegetation," *Philosophical Transactions of the Royal Society of London* 21 (1699): 193-227.

[237] Pearson is referring to Andreas Sigismund Marggraf, "Experiences Chymiques Faites Dans Le Dessein De Tirer Un Veritable Sucre De Diverses Plantes, Qui Croissent Dans Nos Contrees," *Histoire de l'Academie Royale des Sciences et des belles lettres de Berlin* 3 (1749): 79-90.

> inconsistent with our teacher's doctrine. Dr. Woodward's observation is nevertheless just; of course, water most disposed to putrefy, must contain the greatest proportion of animal or vegetable matter, and, hence, be most nutritive; but this militates against the doctrine of rain water containing the sole food of plants.[238]

Cullen's belief that "rain water is prepared by the Creator, and sent down upon us sufficient for all the purposes of the husbandman"[239] was abandoned by many of his students, but his recognition that water was impregnated with putrescent organic matter would prove far more influential.

Having argued that rain water was the pabulum of plants, Cullen lectured on the importance of mechanical and chemical improvements to the soil to insure that plants could readily obtain this putrid water. Mechanically, the soil must be porous enough that water can filter through it. It must also be pliable enough that a plants roots can grow and push through the soil. On this mechanical role of manures, Cullen says,

> Again, we can render soils fertile for a very long time, by the application of manures which we know are not the food of plants; as marl, which if laid upon the ground will impregnate it and render it fruitful for fifty years; and yet this marl, alone, is a poison to plants. It

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[238] Cullen, "The Substance of Nine Lectures, on Vegetation and Agriculture, Delivered to a Private Audience in the Year 1768," 7.

[239] Cullen, "The Substance of Nine Lectures, on Vegetation and Agriculture, Delivered to a Private Audience in the Year 1768," 6.

> would, therefore, seem natural to imagine, that those manures render the ground fertile, by altering its texture, and making it more proper for administering the water to the roots of plants. The horse-hoeing husbandry lately introduced by Mr. Tull, which consists wholly in breaking and dividing the soil, seems likewise to owe its effects to the same cause, and not, as Mr. Tull himself imagines, by reducing the earth itself into such small parts as to enter the roots itself.[240]

Cullen acknowledged the popular and widely discussed work of Jethro Tull, accepting the efficacy of tilling, but casually dismissed Tull's claims that the crushed particles of soil can be absorbed into plants roots. Cullen did not believe that soil was soluble, no matter how finely it had been ground, so it could not be involved in the water based nourishment of plants. Good soil allowed water to easily pass to a plant's roots and retained water without drowning a plant.

In addition to the mechanical functions of soil and manure, they also had a chemical role in promoting fermentation and putrefaction. To this end Cullen promoted using certain mineral manures:

> All acids are antiseptic; and therefore, when they are present, retard the formation of this mucilage. Acids are copiously present in every soil; and hence it is evident that whatever destroys them must promote the fermentation. Hence, therefore, calcareous earths, which absorb the

[240] Cullen, "The Substance of Nine Lectures, on Vegetation and Agriculture, Delivered to a Private Audience in the Year 1768," 6.

> acid and convert it to a neutral state, will promote the fermentation in the soil, and therefore be useful manures.[241]

In the eighteenth-century, Scottish soil was particularly acidic both from the natural composition of the soil and centuries of run-rig farming. Scottish farmers from this period often described their soil as cold and sour, based on the sour taste of acids within the soil. Beginning in the 1970s, a soil survey conduced by the Macaulay Institute of Soil Research in Aberdeen found that the natural acidity of the Brown Forest soil common to Scotland was approximately pH 5, but the pH of Scottish soil could have been as low as 3.5 during the eighteenth-century due to exhaustion. Pasture grasses and cultivated crops like wheat and oats typically need a pH closer to 6, so we can see in retrospect the importance of combatting the acidity of the soil.[242] While William Cullen did not measure or discuss the pH levels of his soil (the pH scale was established in 1909 by Søren Peder Lauritz Sørensen), he did recognize that "acids are copiously present in every soil." The chemical efficacy of manures was wholly dependent on their ability to promote fermentation and putrefaction by neutralizing acids. Thus, those substances like lime, marl, and other calcareous earths that had the highest affinity for acids, were the best chemical manures. Marl was particularly advantageous because it served both the chemical role of neutralizing acids and the mechanical role as a friable, moisture retaining soil.

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241 Cullen, "The Substance of Nine Lectures, on Vegetation and Agriculture, Delivered to a Private Audience in the Year 1768," 32.

242 For a discussion of eighteenth-century conditions see Richard Hindle Fowler, *Robert Burns* (London: Routledge, 1988), 121.

Cullen's correspondence with Lord Kames further illustrates his belief that manures should be based either on putrid organic matter or substances that will accelerate putrefaction. In a letter from the fourteenth of July, 1752, Kames asked whether moss could be used as a manure. While staying at Lord Argyle's estate, Whim, a boggy, moss covered tract of land, Kames had discussed the possible use of moss as a manure with Argyll and his other guests. In his letter, Kames relates the theory of a Mr. Lind[243] "to make moss a fit manure for land, he proposes to mix it in a dunghill, in order to putrefy it throughly, after which it will be a good manure."[244] Kames said that this scheme was particularly appealing, "For I have in my farm a good quantity of shell-marl covered two or three feet with moss. If I can turn all this moss into good manure by putrefaction, I shall have a store of dung, and my shell-marl laid open to be carried to my land, without trouble or expense."[245] Plentiful throughout Scotland, moss might have proven an abundant source of manure. However, Cullen responded, "The spongy friable moss that lies upon the surface, I take to be good for nothing. What lies deeper is more firm and unctuous, and you will find it very difficult to putrefy, or to be converted into manure."[246] Cullen believed that acids retarded fermentation and putrefaction, so peat moss was more of

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[243] Kames is referring to James Lind (1716-1794), most famous for his correlation of citrus fruits with preventing and curing scurvy.

[244] Henry Home, Lord Kames, *Letter from Home to Cullen* (MS Cullen 1185) (July 14, 1752).

[245] Kames, *Letter From Home to Cullen*.

[246] Cullen to Kames, July 1752, quoted in Thomson, *An Account of the Life, Lectures and Writings of William Cullen*, 600.

a poison to the soil than a viable manure. While disagreeing about the utility of moss, the correspondence does show that all three men defined manure as putrefied animal or plant matter. This correspondence illustrates the interest in agriculture and the growing understanding of the chemical properties of plants that was developing in the 1750s.

Cullen's interest in agriculture extended beyond its applications to chemistry and *materia medica*. He also wrote on the plow. The text for "On the Construction and Operation of the Plough" is still extant in three different manuscripts, with extensive annotations and corrections in Cullen's hand. The work, prepared for the Philosophical Society at Glasgow, lists the various parts of the plow and how they should be customized based on local physical geography and soil conditions. Cullen's work on the plow demonstrates his interest in the practice of farming and his understanding of the locally variable aspects of soil cultivation.

Despite the persistent urging of Lord Kames,[247] Cullen never published his agricultural theories. Surviving manuscripts suggest that he tried to gather his notes into a book. Both a thirty-three page, undated manuscript entitled "Reflexions on the Principles of Agriculture" and a nine page manuscript entitled "Agriculture" are divided into an initial, theoretical section on the nourishment of plants and a second, more practical section on providing this nourishment to plants. As with his medical theories, Cullen's agricultural research fed into his lectures. In 1755 Cullen collected

[247] From the first letters in 1749, through correspondence in 1752, 53, and 1759, Kames continued to urge Cullen to publish.

a set of his notes entitled “Lectures on the Chemical History of Vegetables,” which drew from both his *materia medica* course and his chemistry course. Ultimately though, Cullen’s chemical agriculture would not be published until 1796, well after his death, when his student George Pearson published an abridged version of his 1768 lectures.[248]

5.3 Francis Home’s *The Principles of Agriculture and Vegetation*

Francis Home’s *The Principles of Agriculture and Vegetation* (1756) was the first book that used chemical affinity to explain agricultural principles.[249] This textbook on agricultural technique was the extended form of an essay written in 1755 which had won a gold medal “For the best dissertation on vegetation and the principles of agriculture” from the Edinburgh Society for the Improvement of Arts and Manufactures.[250] At the time Home submitted his prize essay, he was also competing with William Cullen and Joseph Black for the chair of chemistry at the University of Edinburgh. Like Cullen and Black, Home was a successful doctor who had earned his medical degree from Edinburgh in 1750. Home likely hoped his *Principles of Agriculture* would impress Lord Argyll and other patrons who could

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[248] Cullen, "The Substance of Nine Lectures, on Vegetation and Agriculture, Delivered to a Private Audience in the Year 1768."

[249] There is no monograph-length biography of Francis Home (1719-1813). See Iain Milne, "Home, Francis (1719-1813)," in *Oxford Dictionary of National Biography* (Oxford: Oxford University Press, 2004), http://www.oxforddnb.com/view/article/13640 (accessed May 19, 2012). His agricultural work is discussed in Fussell, *Crop Nutrition: Science and Practice Before Liebig*. Browne, *A Source Book of Agricultural Chemistry*.

[250] Home, *The Principles of Agriculture and Vegetation*, iii.

bolster his chances at gaining the appointment. However, Argyll gave his support to Cullen. When Cullen moved on to the chair of medicine in 1766, Home again applied for the chair of chemistry but was again passed over, now in favor of Joseph Black. Home did eventually gain an appointment to the faculty of Edinburgh in 1768 as the first professor of *materia medica*.

Home's agricultural theory, like that of Cullen was predicated on understanding the nutrition of plants. Home denied that there was any single, elemental pabulum of plants arguing instead that plants were nourished by all four Aristotelian elements and the additional principles of salt and oil. "These six principles joined together together," Home says, "constitute the vegetable nourishment."[251] While acknowledging the omnipresence of fire, water, air and earth, Home placed particular emphasis on the role of oil and salt:

> It is observed of all soils, the moss and boggy ground excepted, that the blackest are the richest. This colour gives us a strong presumption, that these soils contain much fat and oleaginous matter; for all fossil and vegetable oils, when they have a great admixture of earth, are of this colour. It is owing likewise to these oils, that all vegetable or animal substances gain a black colour when in the road to putrefaction.[252]

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[251] Home, *The Principles of Agriculture and Vegetation*, 109.

[252] Home, *The Principles of Agriculture and Vegetation*, 13.

Home believed that oils within the soil would nourish plants if they were made soluble through combination with lime. However, Home cautioned against the danger of soil exhaustion from the overuse of lime and other calcareous earth manures:

> There is a very great attraction betwixt quick-lime and all oily bodies; it unites intimately with expressed oils. With this intention it is used in the manufacture of soap, to help the junction of the alkaline salts and oils. It must, therefore, attract the oils powerfully from the air and earth, dissolve them, and render them miscible with water: it must, from this reason, soon exhaust the soil of all its oleaginous particles, if the farmer does not take care to supply them by dung or animal substances.[253]

Because of the high level of affinity between quick-lime and oils, forcing manures, those that accelerated putrefaction, had to be used in tandem with dung or plant based manures that provided oil-rich mucilage.

Like Cullen, Home used affinity reactions to explain the neutralization of acids and the formation of salts:

> Experiments have shown that all fertile soils and all manures, except those already converted into mucilaginous nature, consist of particles, which in part, or all together, attract acids. Dung, the ashes of vegetables, burnt earth, contain such particles; lime, marl, animal shell, chalk, etc., are wholly of this nature. These then must attract and retain

[253] Home, *The Principles of Agriculture and Vegetation*, 55-56.

> all acids, when they come within the sphere of attraction. If the air, to which the soil is continually exposed, contains any acids, these bodies will draw it out and be converted to a neutral saline substance, enjoying the properties of salt, such as solubility in water, dissolving oils and rendering them miscible with water. Nothing then remains to be proved, in order to the conversion of these manures into a salt, but that the air contains an acid salt.[254]

Again we see a concern for neutralizing acids in the soil and the use of chemical affinity in explaining how this neutralization would occur. Unlike Cullen though, Home argues that the salts produced in the soil are nutritious for plants. He says salt is "the most active and therefore the most necessary principle of all."[255] Home argues that salts are produced in the soil. In his theory of nitrogen fixation, Home details how nitrous acid is chemically fixed by certain particles in the soil:

> All earths are not fit for this purpose; only such as are attracters of acids, or absorbent earths, viz. lime, marl and other absorbents; or putrefied vegetables and animals, which afford an absorbent earth, and likewise a volatile salt. Almost all earths have more or less of absorbent particles in their composition. These absorbent earths catch

[254] Home, *The Principles of Agriculture and Vegetation*, 111.

[255] Home, *The Principles of Agriculture and Vegetation*, 110.

> the nitrous acid, as it passes by them with the air, or fix and collect it as it arises from the inner parts of the earth.[256]

Citing the universally acknowledged beneficial qualities of nitrous salts, Home produces an affinity based ranking of the effectiveness of manures:

> If this reasoning is just, the effects of different manures on the ground should be visible, in proportion to their strength of attracting acids. This happens really so in fact, and is a strong confirmation of the truth of our reasoning: for ashes have the speediest effects of any manure; because the alkaline salts which they contain attract acids stronger than any body. Soot and dung come next, which are volatile alkalines, whose attraction comes next to the first; then the class of absorbent earths. The same observation is made of the marls: for according to their rank as attracters of acids, so they operate on the ground.[257]

The centrality of affinity theory in Home's explanation of manures' relative efficacies is striking. For Home, a manure is a chemical substance capable of fixing aerial acids into beneficial salts. In his description of the manure marl, Home says, "This quality which marl has of attracting and destroying acids, is one of its distinguishing properties, without which no substance can be called marl."[258]

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256 Home, *The Principles of Agriculture and Vegetation*, 122.

257 Home, *The Principles of Agriculture and Vegetation*, 127.

258 Home, *The Principles of Agriculture and Vegetation*, 45.

It is unclear where Home had acquired his understanding of chemical affinity. Home's ranking of manures matches Etienne Geoffroy's column for "esprits acides" in his *Table des rapports*,[259] but it is unlikely that Home would have encountered Geoffroy's work in any of his classes at Edinburgh. Home earned his MD in 1750, but affinity tables were not commonly taught until Cullen introduced them in his chemistry courses in 1755. Home studied briefly at the University of Leiden in 1749 while serving with the 6th Inniskilling regiment of Dragoons during the War of Austrian Succession, and it is likely that Home would have encountered the secondhand teachings of Hermann Boerhaave. While Home does not quote Boerhaave directly, his explanation of putrefaction is similar to Boerhaave's as expressed in *New Method of Chemistry,* which had been published in English by Peter Shaw in 1727 and in new editions in 1741 and 1753.[260] In essay on the mineral waters of Dunse-Spaw, published in 1751, Home mentions the works of Peter Shaw, so he was at least acquainted with Boerhaave and Shaw's ideas on chemical attraction. However, Home uses the word "affinity" in reference to displacement reactions, saying "The oils and salts having a natural affinity, will unite; and so the salts, by the natural volatility of oil, will become volatile themselves, from being

[259] Étienne François Geoffroy, "Table Des Différens Rapports Observés En Chymie Enter Différens Substances," *Mémoires de l'Acaémie royale des sciences* for 1718 (1719); pp. 202-212.

[260] Boerhaave, *A New Method of Chemistry; Including the Theory and Practice of That Art: Laid Down on Mechanical Principles, and Accomodated to the Uses of Life*.

fixed before."[261] Shaw uses "affinity" to mean similarity of characteristics between two substances. Shaw uses the term "attractions" to refer to both a Newtonian gravitation attraction and chemical attractions. Home's affinity theory is more mature than Shaw's and was likely influenced by his wide readings.

While little had been published in English on affinity before Home's own works, Home also read French and Latin as evidenced by his citations of Lemery[262] and Stahl.[263] Home references more than half-a-dozen essays from the *Memoires de l'Academie des Sciences,* so it is entirely possible that he read Geoffroy's work on the "Table des rapports" in the 1718 volume. It is also possible Home would have read P. J. Macquer's explanation of Geoffroy's affinity in his *Elemens de Chymie Practice* which was published in 1749. However, for someone so liberal with their citations, Home does not mention Geoffroy or Macquer. Home's operational conceptualization of affinity is much like Cullen's, but he did not take classes from Cullen or any of his students, nor does he mention Cullen or any of his students within the text. Home also expresses a vitalistic understanding of affinity reactions within living animals,[264] which is not mirrored in the works of Cullen or his students.

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[261] As an example Home says, "The oils and salts having a natural affinity, will unite; and so the salts, by the natural volatility of oil, will become volatile themselves, from being fixed before." Home, *The Principles of Agriculture and Vegetation*, 65.

[262] Home cites an essay by Lemery from the 1708 *Memoires Academie des Sciences*. Home, *The Principles of Agriculture and Vegetation*, 18-19.

[263] Home cites a Latin passage from Stahl's *Fundamenta Chymiae*. Home, *The Principles of Agriculture and Vegetation*, 72-73.

[264] Home, *The Principles of Agriculture and Vegetation*, 155.

Home's idea of manures was broader than that of Cullen. In addition to putrefying materials and manures that would force putrefaction, Home also suggested using manures to solve other chemical problems in the soil. Metallic salts were considered poisonous for plants, but Home had an affinity based cure:

> If this poison can admit of a cure, I imagine it is only to be found in lime or marle, which will attract the acids from the iron, and make it, at least in great measure indissolvable in water.[265]

Metallic salts were soluble and thus could be absorbed by the roots of a plant. However, if marl or lime was used to strip the metallic salt of its acid in a displacement reaction, the insoluble metal was left inert and impotent.

Francis Home's *Principles of Agriculture and Vegetation* was successful, both as a gold medal winning essay and as a popular book. After an initial print run of five hundred copies, *Principles* was reprinted in 1757 and republished in a second edition in 1759, a third in 1762 and a fourth in 1776.[266] It was also translated into French in 1761 and into German, first in 1762 and then again in 1779. In a survey of four hundred fifty book catalogues from late eighteenth- and early nineteenth-century libraries, Mark Towsey found that Home's *Principles of Agriculture and Vegetation* was held by eleven percent of the libraries. While not as popular as Hume's *History* (70%) or Burns' *Poems* (60%), *Principles of Agriculture and Vegetation* compared well with other scientific books like Robert Simson's *Elements of the Conic Sections*

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[265] Home, *The Principles of Agriculture and Vegetation*, 30.

[266] H Holmes, "The Circulation of Scottish Agricultural Books During the Eighteenth Century," *Agricultural History Review* 54 (2006); p. 56.

(14%), Colin MacLaurin's *Treatise on Algebra* (13%) and James Hutton's *Theory of the Earth* (6%).[267] Home proved influential amongst his peers garnering citations in the works of Andrew Dickson, James Anderson, Joseph Black, George Fordyce and many others.

5.4 Cullen's Students

Though rarely mentioned in studies on agricultural chemistry, Joseph Black included lectures on plants in his chemistry course. After Black's death, his friend, John Robison, edited his lectures to produce *Lectures on the Elements of Chemistry*, published in 1803. This is the most readily available and most often cited version of Black's lectures, but we need to be aware of Robison's influence as editor. Robison cleaned up Black's prose, often parsing the long oratorical sentences, into more grammatically correct sentences. Robison also drew from multiple versions of the lectures, with the result that some passages make use of both phlogiston based substances, like phlogisticated air, and Lavoisier's new nomenclature. One passage from Black's lectures on earths illustrates the impact of Robison's editing on possible understandings of Black's conceptualization of affinity. Robison's text on absorbent earths reads, "And further, these earths attract different acids with different degrees of force, and this is in much the same order as that in which they are attracted by

[267] Mark R. M. Towsey, "Reading the Scottish Enlightenment: Libraries, Readers and Intellectual Culture in Provincial Scotland c.1750-c.1820" (PhD diss., University of St. Andrews, 2007), 42-55.

alkalis."[268] Thomas Cochrane's notes from Black's 1767/68 lectures read, "These are in general very mild bearing the same relation to acids as the alkalis do."[269] A set of course notes likely from 1776[270] reads, "These earths attract the acids precisely in the same order as they are attracted by the alkalies, so that they resemble the alkalies in every particular almost without regard to the nature and mode of this attraction."[271] Black's 1767 and 1776 lectures emphasized the significance of affinities in comparing the absorbent earths to alkaline salts, while Robison's editing minimizes the similarity. Robison's text is valuable as a synthesis of Black's works, but in his attempts to present an up-to-date and coherent chemical textbook, Robison stripped many of the older theoretical concepts from Black's work. I will refer to Black's course notes whenever possible.[272]

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[268] Joseph Black, *Lectures on the Elements of Chemistry, Delivered in the University of Edinburgh*, ed. John Robison (Printed by Mundell and Son, for Longman and Rees, London, and W. Creech, Edinburgh, 1803), vol. 2, p. 22.

[269] Joseph Black and Thomas Cochrane, *Notes From Doctor Black's Lectures on Chemistry, 1767/8*, ed. Douglas McKie (Cheshire: I.C.I. Pharmaceuticals Division, 1966), 56.

[270] This undated set of notes is held by the Chemical Heritage Foundation as QD 14. B533 1828. The name Paul Panton appears on the first pages of volumes 1 and 5 of a 6 volume set of lecture notes. Panton was a student at the University of Edinburgh in 1776. There is a write-in on the first page of volume 1 that refers to John Robison's edited volume of Black's notes from 1803, but I believe this was added to the set by Panton or a book seller at a later date. I will refer to this set as Black, *Lectures on Chemistry*.

[271] Black, *Lectures on Chemistry*, vol. 3, p. 221.

[272] For more on Robison's role as editor, see J. R. R. Christie, "Joseph Black and John Robison," in *Joseph Black, 1728-1799: A Commemorative Symposium*, ed. A. D. C. Simpson, Royal Scottish Museum studies (Edinburgh: Royal Scottish Museum, 1982), 47-52.

In lecture 111 of his 1776 notes, Black acknowledges Home's theory of vegetable nutrition saying, "Those who have entered deeply into the subject have spoken of oily and saline parts, which they suppose the oil furnishes for their subsistence."[273] However, Black dismisses this theory returning instead to water as the primary nutrient of plants. Black says, "But as a great variety can be furnished by water alone, there is reason to believe that it is the principle and only probable food of the rest."[274] Black dismisses salts and oils in regards to plant nutrition, because he does not consider them elemental. Black maintained an Aristotelian matter theory arguing that salts and oils were further reducible to earth, water, fire and air.

Like Cullen, Black emphasizes the importance of putrefaction in the understanding the chemistry of vegetation. He says, "Every rich soil contains vegetable matters in their decayed state, and all rich manure either contains such vegetable substances or promote the decomposition of the vegetable matters, as the calcareous earth..."[275] Black maintains that putrefying plant and animal matter release the principle of inflammability which then combines with water or salt and then is absorbed by the plant. For Black, this theory is confirmed by the growth of plants in air infused with inflammable matter. He also thinks that plants absorb inflammable matter in the form of sunlight.

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[273] Black, *Lectures on Chemistry*, vol. 6, p. 163.

[274] Black, *Lectures on Chemistry*, vol. 6, p. 163.

[275] Black, *Lectures on Chemistry*, vol. 6, p. 164.

Affinity would have been fresh in the minds of his students having been the subject of lectures 105 through 108.[276] Since Black lectured daily, the lectures on vegetables would likely have occurred within a week of his affinity lectures. Implicit in his discussion of manures, Black used affinity explicitly in lecture 111 while analyzing the constituent parts of vegetables. Black found "a quantity of fixed air which is attracted by alkaline substances."[277] In his dissertation on magnesia alba, Black had established the affinity between fixed air and alkaline substances as a key characteristic of the gas. He returned to this quality in identifying fixed air as a byproduct of venous fermentation of vegetables in lecture 112. Black said, "I suspended an alkali over a quantity of fermenting beer, in a shallow vessel, it attracted a great quantity of fixed air, and was rendered milder."[278] Black's chemistry was based on analyzing chemical substances to find their constituent parts. Affinity theory provided the means for analysis via displacement reactions and proved a key tool in identifying the products of reactions.

George Fordyce (1736-1802) was another highly successful graduate of Edinburgh's medical school. Fordyce enjoyed an excellent string of tutors, working first with William Cullen before graduating MD in 1758, then attending John Hunter's lectures in London, and finally Bernard Albinus' lectures at Leiden in 1759. Beginning in 1759, Fordyce gave private lectures on chemistry in London, and in

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[276] Lectures 109 and 110 were on fixed air.

[277] Black, *Lectures on Chemistry*, vol. 6, p. 183.

[278] Black, *Lectures on Chemistry*, vol. 6, p. 217.

1764 he added courses on *materia medica* and physic. In addition to being a popular lecturer for thirty years, Fordyce became a licentiate to the Royal College of Physicians in 1765 and physician at St Thomas's Hospital in 1770. He was elected to the Literary Club in 1774, having been nominated by Oliver Goldsmith and Samuel Johnson, and he became a fellow of the Royal Society in 1776. Fordyce was elected a fellow of the Royal College of Physicians in 1787. Along with John Hunter, he founded the Society for the Improvement of Medical and Chirurgical Knowledge in 1793 attending meetings with the likes of Edward Jenner, Matthew Baillie, and Everard Home.[279]

Fordyce wrote several medical works including *Elements of the Practice of Physic* (1770), *A Treatise on Digestion and Food* (1791), *Dissertations on Fever* (1794-1802), and his many papers in the *Philosophical Transactions* and other academic journals. Of more interest here though is his *Elements of Agriculture and Vegetation*, first published in 1765. Part one of the book is entitled "Elements of Chemistry, Necessary to be understood for the explanation of the Principles of Agriculture." In this section, Fordyce provides a table of elective attractions listing in descending order the reactants for acids, alkalis, metals and air (see Figure 7).[280] In the first line, we can see Fordyce's acceptance of phlogiston as a chemical substance,

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[279] Coley, "George Fordyce M.D., F.R.S. (1736-1802): Physician-Chemist and Eccentric." Noel G. Coley, "Fordyce, George (1736-1802)," *Oxford Dictionary of National Biography*, Online Edn (Oxford University Press, 2004), http://www.oxforddnb.com/view/article/9878 (accessed July 13, 2011).

[280] Fordyce, *Elements of Agriculture and Vegetation*, 9-12.

differentiating him to some degree from both Cullen and Black who were more ambivalent about the reality of phlogiston. Unlike Cullen who reproduced Geoffroy's table, or Black who produced his own, Fordyce writes out the English names of chemical substances in a vertical list. This listing would have been accessible to a broader readership than the tables which relied on a prior knowledge of chemical symbols.

In part two of *Elements*, Fordyce presents an experimental history listing twenty-four common salts, earths, airs, and organic substances and the chemical characteristics of each. In figure 8, we see the entry on "fixt vegetable alkali." In the left column, Fordyce lists synonyms and common naturally occurring forms of the substance, including pot-ash and soap leys. The center column tells the reader how to produce the substance, and the right column lists the chemical properties of the substance. In the right column, Fordyce lists the other chemical substances with which fixt vegetable alkali is most likely to unite, in order of chemical affinity, and their chemical products. In this case, the order of affinity is vitriolic acid, nitrous acid, and then muriatic acid. This experimental history represents the foundation of Fordyce's agricultural theory. Like Cullen and Black, Fordyce began his courses with a set of observed facts on each topic and slowly built an inductive theory. In *Elements of Agriculture and Vegetation*, Fordyce provides the chemical characteristics of common agricultural substances as the introduction to his theories on plant anatomy, physiology, and nourishment.

Part four of *Elements* is Fordyce's theory "Of the nourishment of plants." While Fordyce agrees with Cullen that water is necessary to convey nutrients to a plant through its roots, he argues that nutrients held within the soil are dissolved by water and conveyed to the plant. Fordyce says, "A Plant may be nourished by pure Water and Air alone; but it will be more luxuriant, if it also absorbs, and digests, a Quantity of Gelatinous Mucilage."[281] Along with organic mucilage, Fordyce also lists nitrous ammoniac, nitrous selenites, common ammoniac, and fixt ammoniac as water soluble nutrients "found in all rich soils."[282] Adhering to the empirical epistemology so common to the Scottish Enlightenment, Fordyce does not provide a theory explaining the role of these nutrients, but rather leaves the reader with the empirical observation of their presence in rich soils.

Fordyce next turns to manures, focusing on the role of "forcing" manures like alkali and calcareous earths in putrefying organic substances into soluble mucilage.[283] Like Francis Home, Fordyce cautions that forcing manures cannot help soils that are poor in organic matter. Forcing manures also help to neutralize metallic salts and pyrites and other uncombined acids. For a poor soil, Fordyce suggests applying "enriching manures" like gelatinous mucilage. He also advocates using enriching manures rather than fallowing saying that "fallowing for several years would destroy a soil, as it would convert the whole putrescent substances into mucilage, and that

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[281] Fordyce, *Elements of Agriculture and Vegetation*, 59.

[282] Fordyce, *Elements of Agriculture and Vegetation*, 59.

[283] Fordyce, *Elements of Agriculture and Vegetation*, 60-61.

mucilage into salts, and these would be decomposed."[284] Because of the natural and ongoing chemical processes, soils are more depleted of plant matter and mucilage after fallowing than before. This became a common argument within chemical agriculture books and was appealing on a practical level, because fallowing is inherently expensive in terms of opportunity cost. However, Fordyce's advocacy of "enriching manures" could not be carried out universally because of the finite amount of organic dung and the expense of carting dung to the fields.

Fordyce also advises the farmer on how to chemically evaluate his soils. He suggests eight substances that the surveyor should have at hand, viz.: vitriolic acid, muriatic acid, fixt vegetable alkali, common caustic vegetable alkali, caustic volatile alkali, sal ammoniac, galls, and pure water. Fordyce explains how to use these substances to conduct simple precipitation reactions to determine whether the soil contains metallic salts, pyrites, magnesia, and neutral salts and to measure the amount of calcareous earth and mucilage in a given sample of soil. This guide draws from the information already provided in the experimental histories in part two of the book providing practical information on determining the chemical properties of his own soil. Fordyce, along with Cullen and many of his other students, advocated *in situ* experimentation, recognizing the variables in real world agriculture while maintaining the utility of affinity based chemistry.

Although *Elements of Agriculture and Vegetation* was intended to be a useful guide for practicing agriculturalists, Fordyce included a set of theoretical diagrams

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[284] Fordyce, *Elements of Agriculture and Vegetation*, 64.

depicting his matter theory at the end of the book. In the accompanying text for his first figure (my figure 9), Fordyce says,

> From Experiment it is found, that Bodies upon cooling contract and retain their Shape; therefore that they contract in every Direction. Suppose AAA BBB to represent the Section of a Sphere, the Diameters A B upon the Sphere's being cooled, become equally shorter in all their Parts; but if the Particles lying in the Direction of these Diameters touched, they could not come nearer, and the Diameters could not contract. As therefore they are actually found to contract, it is evident that the Particles do not touch.[285]

Fordyce references this diagram on the first page of the book saying, "The Particles of Bodies do not touch, but adhere by attraction."[286] Fordyce represents matter as spherical particles that interact through chemical, rather than mechanical forces. Fordyce makes this point again with his fifth figure (top right in my figure 10) saying,

> As the Particles of Bodies do not touch but adhere by Attractions, and Repulsions, they may be considered as acting at the Sphere, where their Attractions are in Equilibrio. If there be four Particles P P P P, they may be considered as producing their Effects at the Spheres A A A A.[287]

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[285] Fordyce, *Elements of Agriculture and Vegetation*, 76.

[286] Fordyce, *Elements of Agriculture and Vegetation*, 1.

[287] Fordyce, *Elements of Agriculture and Vegetation*, 78.

Particles are depicted as having material form and boundaries, but they find a position relative to other particles where their attractions and repulsions are balanced.

In figure six (top diagram in my figure 11), Fordyce depicts four sets of united particles - he does not have the word molecule yet. Each particle retains its own sphere of chemical activity (c), but the pairings create new spheres of mechanical action (m). In figure seven (bottom diagram in my figure 11), he provides further nuance depicting the union of copper with sal ammoniac (volatile alkali and any acid). In this reaction, the two particle salt acts as a single chemical substance with a strong affinity for copper and other metals. Chemical reactions did not necessarily involve two simple chemical substances, but rather compounds could consist of compounds. Fordyce considered this a principle of chemical theory, arguing that we can not know what the true chemical elements are.

In 1765, the same year that he published *Elements of Agriculture and Vegetation*, Fordyce gave a course on chemistry in which he further detailed his matter theory. He says,

> Physical Elements are form'd of ye ultimate division possible, & are to be consider'd as indefinitely small; whereas Chemical Elements are form'd of ye ultimate division as yet made; & tho they may be in ymselves compounds, yet as we can't decompose ym, we consider them as simple elements.[288]

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[288] Fordyce, *Elements of Agriculture and Vegetation*, figure 37.

In this lecture Fordyce posits the ontological reality of physical elements but cautions his students that they can only know about those substances which have been empirically identified. Georgette Taylor has noted that this “preempted Lavoisier’s historically lauded definition of simple substances.”[289]

Though an interesting example of chemical atomism that predates John Dalton by three decades, these diagrams have eluded notice in the historiography on chemistry and science more broadly. Fordyce’s novel representations of affinity relations and of atomic reactions may have been overlooked because of their publication in a work on agriculture.

5.6 Carbonic Acid as Pabulum of Plants

By the end of the eighteenth century, affinity had become a central theory for chemistry, and affinity based agriculture had spread through Great Britain. Jan Ingenhousz, known to his contemporaries for his *Essai sur la vegetaux*, developed a theory of plant nutrition that placed the emphasis on chemical reactions. Ingenhousz held that carbon and oxygen were the two key nutrients for plants. Having adopted the French nomenclature, he saw carbonic acid (formerly called fixed air and later known as CO2) as an ideal pabulum of plants. Ingenhousz said,

> As the carbonic acid is composed of the acidifying principle, the oxygen, and the carbon or coal, plants may derive from these two

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[289] Taylor contrasts Fordyce’s matter theory with those of his contemporaries including Cullen and Torbern Bergman. Taylor, “Variations on a Theme: Patterns of Congruence and Divergence Among 18th Century Chemical Affinity Theories,” 104.

> principles some of the most essential substances we find in them: their acids, their oils, their mucilage, &c. these ingredients, together with the azote absorbed also with the atmospheric air, being elaborated in their organs, variously modified and combined, in a manner somewhat analogous to the wonderful, though to the human understanding incomprehensible, elaborations and combinations which we observe in the bodies of animals.[290]

Ingenhousz viewed carbonic acid as an abundant, readily available material which was produced in many (perhaps the majority) of chemical reactions. Referring to any pair or set of chemical substances which have an affinity for one another, Ingenhousz said,

> Which substances brought in close contact by moisture, act on one another chemically; that is to say, by various combinations, attractions, or simple and double, or compound chemical affinities. Of all those species of synthesis, analysis, and attraction, an almost constant attendant is the disengagement of carbonic acid. Animal and vegetable substances probably act as manures only, when in the act of

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[290] Jan Ingenhousz, "An Essay on the Food of Plants and the Renovation of Soils," in *Additional Appendix to the Outlines of the Fifteenth Chapter of the Proposed General Report From the Board of Agriculture. On the Subject of Manures*, ed. Board of Agriculture (London: printed by W. Bulmer and Co., 1796), 4.

> decomposition by putrefaction, during which period a great quantity of carbonic acid is produced.[291]

As with Cullen and his students, Ingenhousz said that manures are efficacious when they promote putrefaction. However, unlike his predecessors, Ingenhousz was not concerned with the organic mucilage produced, but with the carbonic acid that was generated as a by-product. For Ingenhousz, almost any chemical reaction was beneficial for plants because carbonic acid would be produced. James Headrick, a follower of Ingenhousz, explained this phenomenon in affinity based language, saying, "Carbonic acid, or fixed air, which has but a weak attraction for most bodies, will be displaced, and assume its elastic form."[292] This theory explains the utility of lime (CaCO3) as a manure, because it is rich in carbonic acid. By the end of the eighteenth century limestone and other calcareous earths were thought to be composed of calcium, carbon, and oxygen (CaCO). Calcium, an alkaline substance, has a greater affinity for sulphuric acid and other strong acids than for carbonic acid. When applied to the fields, lime will attract acids, which were abundant in Scottish soil, and these acids will displace the carbonic acid. Because of the relatively low affinity of carbonic acid with lime, Headrick cautions that lime already tainted with strong acids, will not be a good manure:

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[291] Ingenhousz, "An Essay on the Food of Plants and the Renovation of Soils," 12.

[292] James Headrick, "Essay on Manures," in *Additional Appendix to the Outlines of the Fifteenth Chapter of the Proposed General Report From the Board of Agriculture. On the Subject of Manures*, ed. Board of Agriculture (London: printed by W. Bulmer and Co., 1796), 14.

> If lime, therefore, be already saturated with sulphuric acid, for which it has a stronger attraction than for most others, we cannot see how it should produce even so powerful an effect as when saturated with carbonic acid, or some other for which it has a weaker attraction.[293]

For Ingenhousz and Headrick, it was the affinity reactions themselves that should be stimulated in order to feed plants. Dung, which was rich in carbon was itself a good fertilizer, but forcing manures like lime greatly increased its effect by stimulating the production and release of carbonic acid. Even without dung or other mucilaginous (carbon-rich) substances, lime was an effective manure because it contained carbonic acid. While Fordyce and others had warned of the dangers of over-liming poor soils, Ingenhousz did not think this was possible.

5.7 Conclusion

Affinity was popularized in Great Britain through the university lectures of William Cullen and his students. In the same chemistry courses, sometimes in the same week, students were taught about the chemical characteristics of the various earths, salts, and vegetable substances. Because of the importance of *materia medica* to medicine and vegetable substances to chemistry, the medical students of Edinburgh and Glasgow gained an education in agricultural chemistry. The pervasiveness of the improvement movement in eighteenth-century Scotland provided a popular audience for these early agricultural lectures and fueled a boom in agricultural publications.

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[293] Headrick, "Essay on Manures," 28.

The historically contingent correlation between the constructions of affinity theory and agricultural theory allowed for the production of an agricultural chemistry steeped in affinity language and concepts. This new, utilitarian sub-discipline offered practical applications for farmers in the field. Novel understandings of the workings of manure generated a ranking of manure efficacies based on their affinities for acids. The idea that water was an active chemical substance with affinities of its own led to changes in plowing wet soils and dry soils. By the end of the century, Jan Ingenhousz had proposed that carbonic acid was the pabulum of plants, and that the sole job of manure was to spur the chemical reactions which produced it. During the second half of the eighteenth century, affinity became a central concept in understanding and predicting chemical reactions. As they constructed agricultural chemistry, the professors of the Scottish universities utilized and expanded the explanatory power of affinity theory.

Farmers, primarily from the tenant class, read the works of these lecturers and appropriated their theories into new knowledge systems. References in early farmers' magazines demonstrate an awareness and dialogue based off texts like Fordyce's *Elements of Agriculture and Vegetation*. One commonplace book has been found, which gives rare insight into how a tenant class farmer read Home's *Principles of Agriculture and Vegetation*.[294] The highly literate Scots farmers had access to

[294] Angus Local Studies Centre, MS 324, Pierson of Balmadies Farm Commonplace Book. This manuscript is discussed in Towsey, "Reading the Scottish Enlightenment: Libraries, Readers and Intellectual Culture in Provincial Scotland C.1750-C.1820," 217-219.

agricultural texts through libraries, reviews in popular magazines, a growing number of agricultural periodicals, and most often, word of mouth. In addition to published materials, changes in manuring practices and tenant contracts also indicate the utility of agricultural chemistry in the second half of the eighteenth century. Farmers did not however accept chemical agriculture, or academic agriculture more broadly, as an entirely authoritative, established truth. For many, farming by the book[295] smacked of speculative philosophy and elided empirically established variances in local geography and customs. William Amos[296] and others filtered academic theory through a sieve of first-hand experience to produce practical guides to agriculture for his fellow farmer. Farmer's appropriated those methodologies and techniques which suited their geographic and economic realities and asserted their own authority as to the proper implementation of new ideas. Though often confined by the economic limitations of their position in society, tenant farmers were the actual practitioners of agriculture, and it was through their participation that the theories of Cullen, Home, and Fordyce were effected in the fields of Scotland. Blurring any distinction between "elite" and "popular" science, chemical agriculture involved members of all strata of society.

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[295] Farming practices in America and the popular ambivalence towards academic texts on agriculture are studied in Benjamin R. Cohen, *Notes From the Ground: Science, Soil, and Society in the American Countryside* (New Haven: Yale University Press, 2009).

[296] William Amos, *The Theory and Practice of the Drill-Husbandry; Founded Upon Philosophical Principles, and Confirmed by Experiment* (London: G. G. and J. Robinson, 1794).

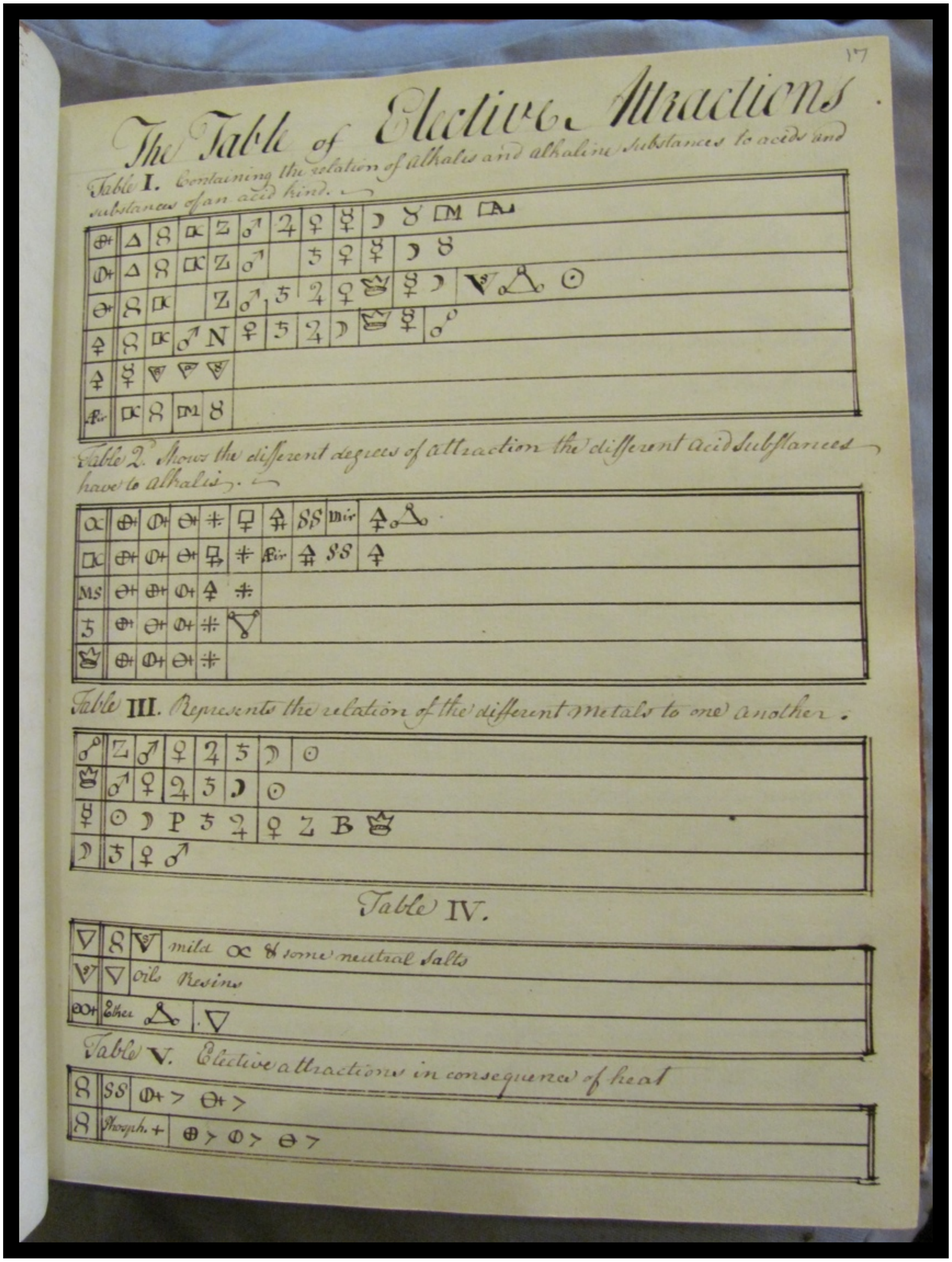
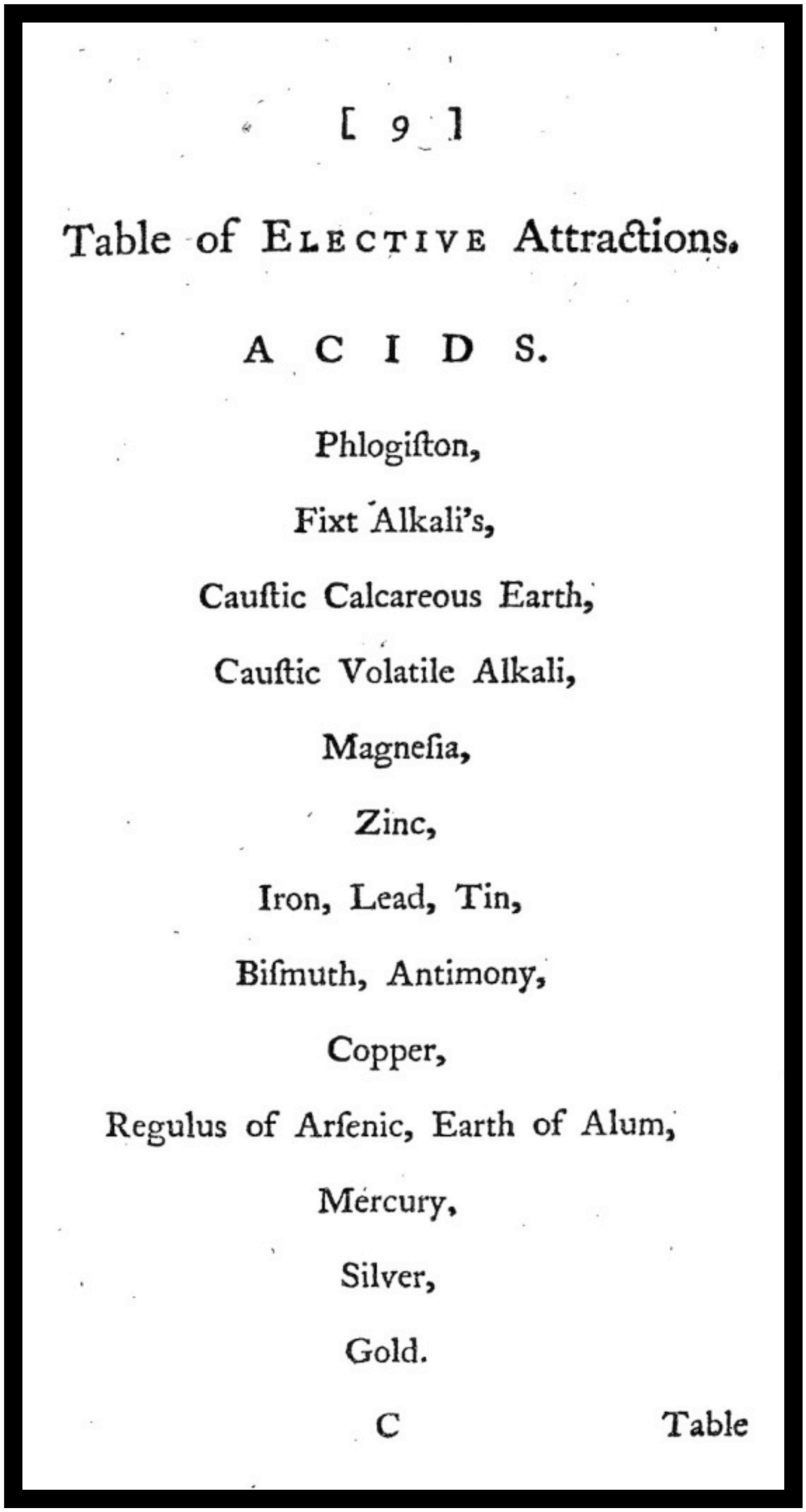


Figure 6: Joseph Black, Affinity Table, "Chemistry Lectures," 1777, vol. 6, ff. 17.



[9]

Table of ELECTIVE Attractions.

A C I D S.

Phlogiſton,

Fixt Alkali's,

Cauſtic Calcareous Earth,

Cauſtic Volatile Alkali,

Magneſia,

Zinc,

Iron, Lead, Tin,

Biſmuth, Antimony,

Copper,

Regulus of Arſenic, Earth of Alum,

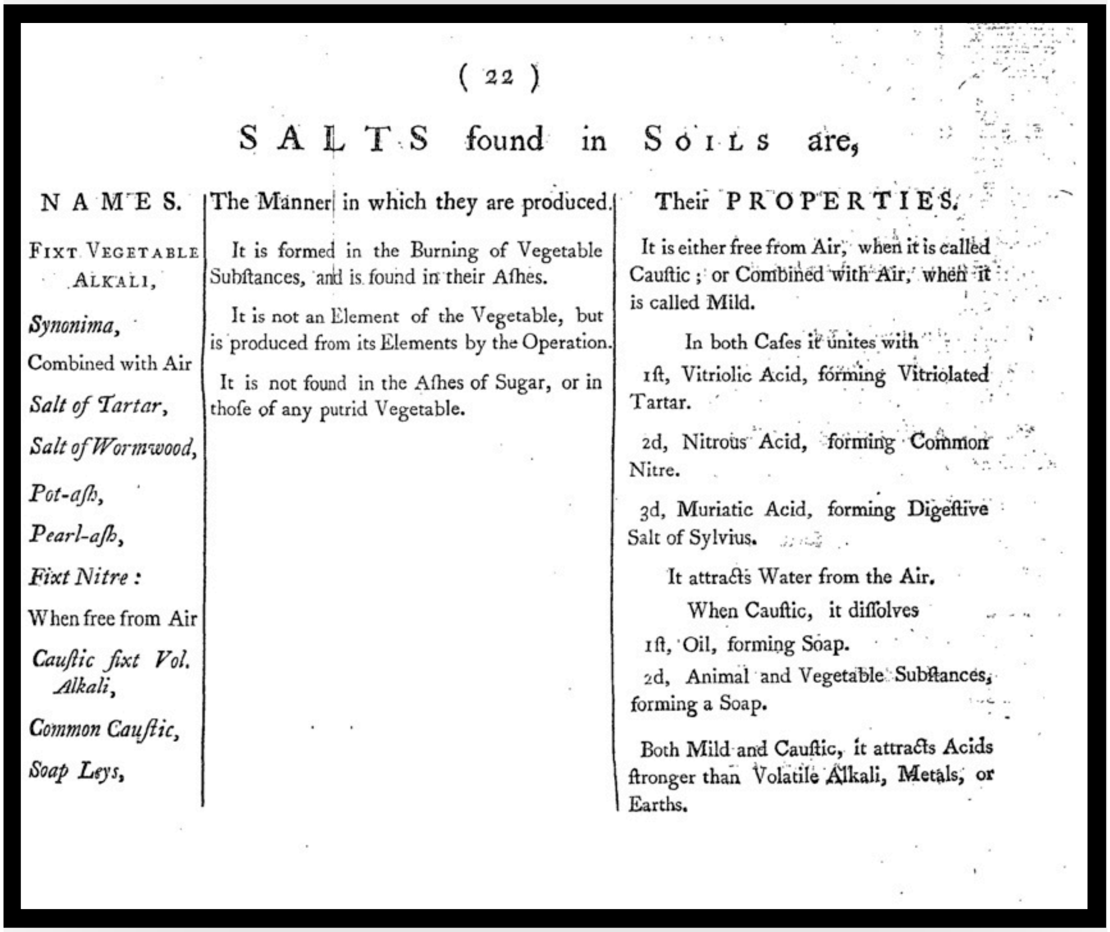
Mercury,

Silver,

Gold.

C Table

Figure 7: George Fordyce, "Affinity Table," in *Elements of Agriculture and Vegetation.* Edinburgh, 1765, 9.



(22)

SALTS found in SOILS are,

NAMES.	The Manner in which they are produced.	Their PROPERTIES.
FIXT VEGETABLE ALKALI, *Synonima,* Combined with Air *Salt of Tartar,* *Salt of Wormwood,* *Pot-aſh,* *Pearl-aſh,* *Fixt Nitre:* When free from Air *Cauſtic fixt Vol. Alkali,* *Common Cauſtic,* *Soap Leys,*	It is formed in the Burning of Vegetable Subſtances, and is found in their Aſhes. It is not an Element of the Vegetable, but is produced from its Elements by the Operation. It is not found in the Aſhes of Sugar, or in thoſe of any putrid Vegetable.	It is either free from Air, when it is called Cauſtic; or Combined with Air, when it is called Mild. In both Caſes it unites with 1ſt, Vitriolic Acid, forming Vitriolated Tartar. 2d, Nitrous Acid, forming Common Nitre. 3d, Muriatic Acid, forming Digeſtive Salt of Sylvius. It attracts Water from the Air. When Cauſtic, it diſſolves 1ſt, Oil, forming Soap. 2d, Animal and Vegetable Subſtances, forming a Soap. Both Mild and Cauſtic, it attracts Acids ſtronger than Volatile Alkali, Metals, or Earths.

Figure 8: George Fordyce, *Elements of Agriculture and Vegetation*, London: J. Johnson, 1765, 22.

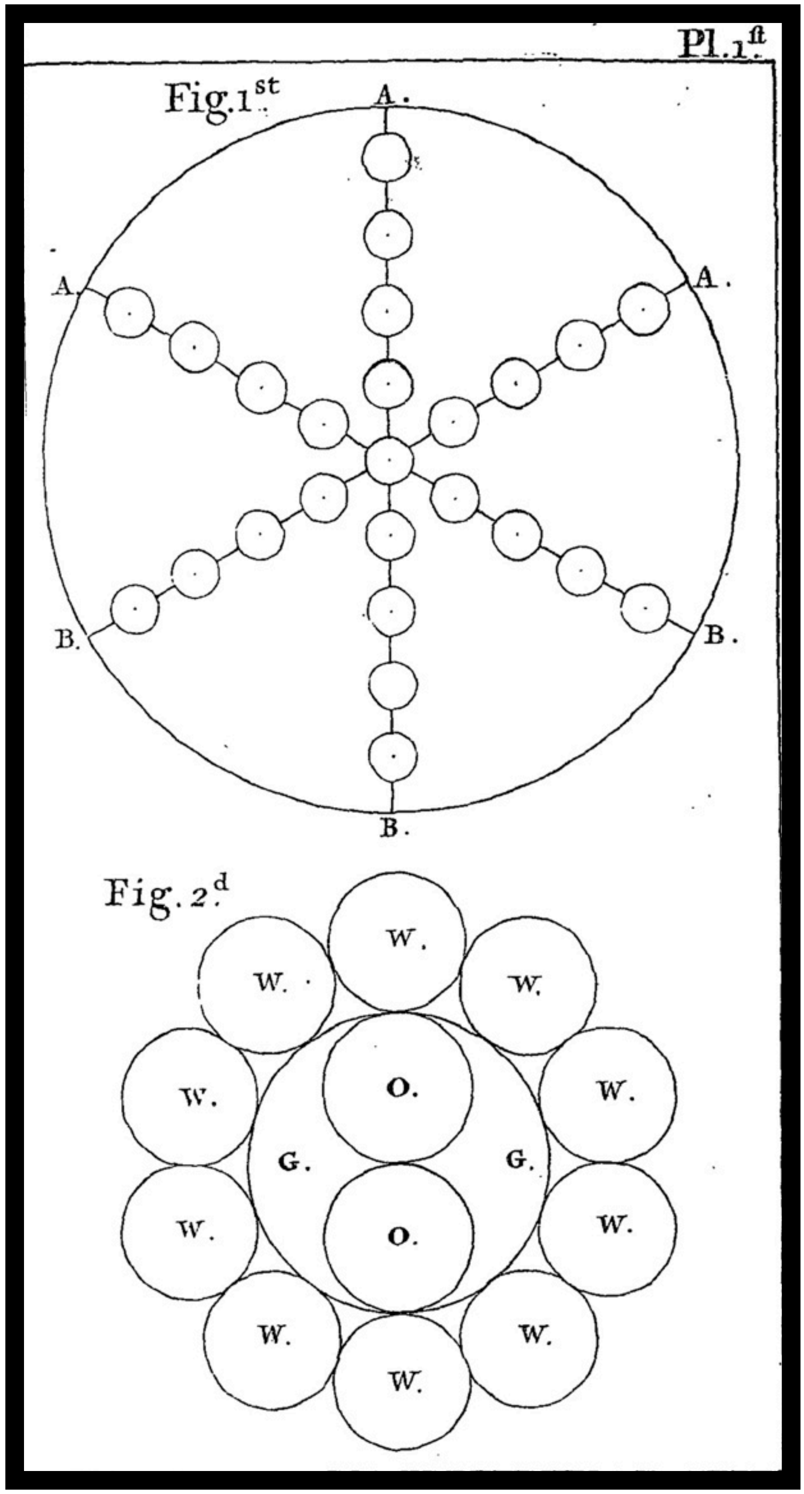


Figure 9: George Fordyce, *Elements of Agriculture and Vegetation*, London: J. Johnson, 1765, 77.

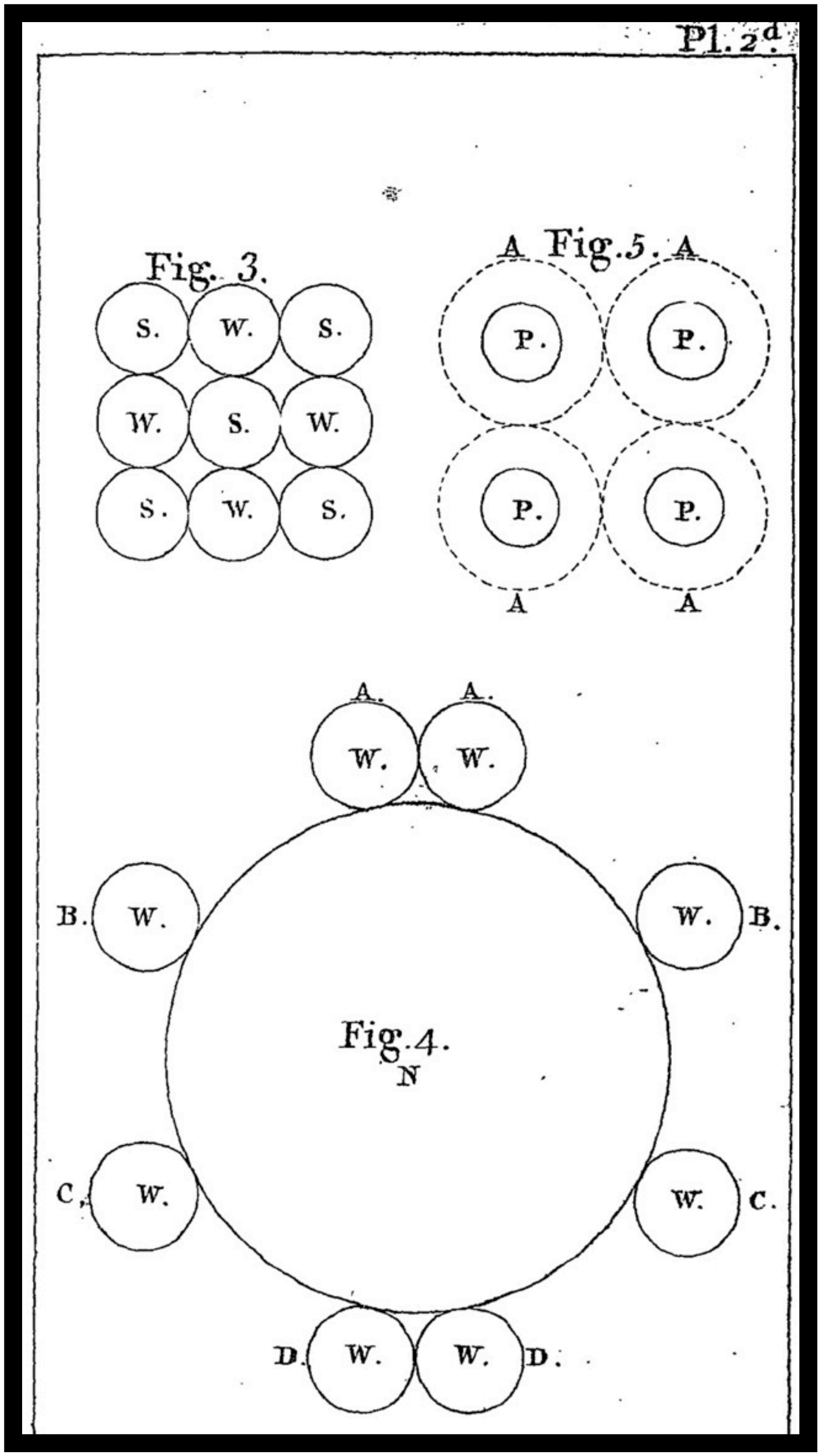


Figure 10: George Fordyce, *Elements of Agriculture and Vegetation*, London: J. Johnson, 1765, 79.

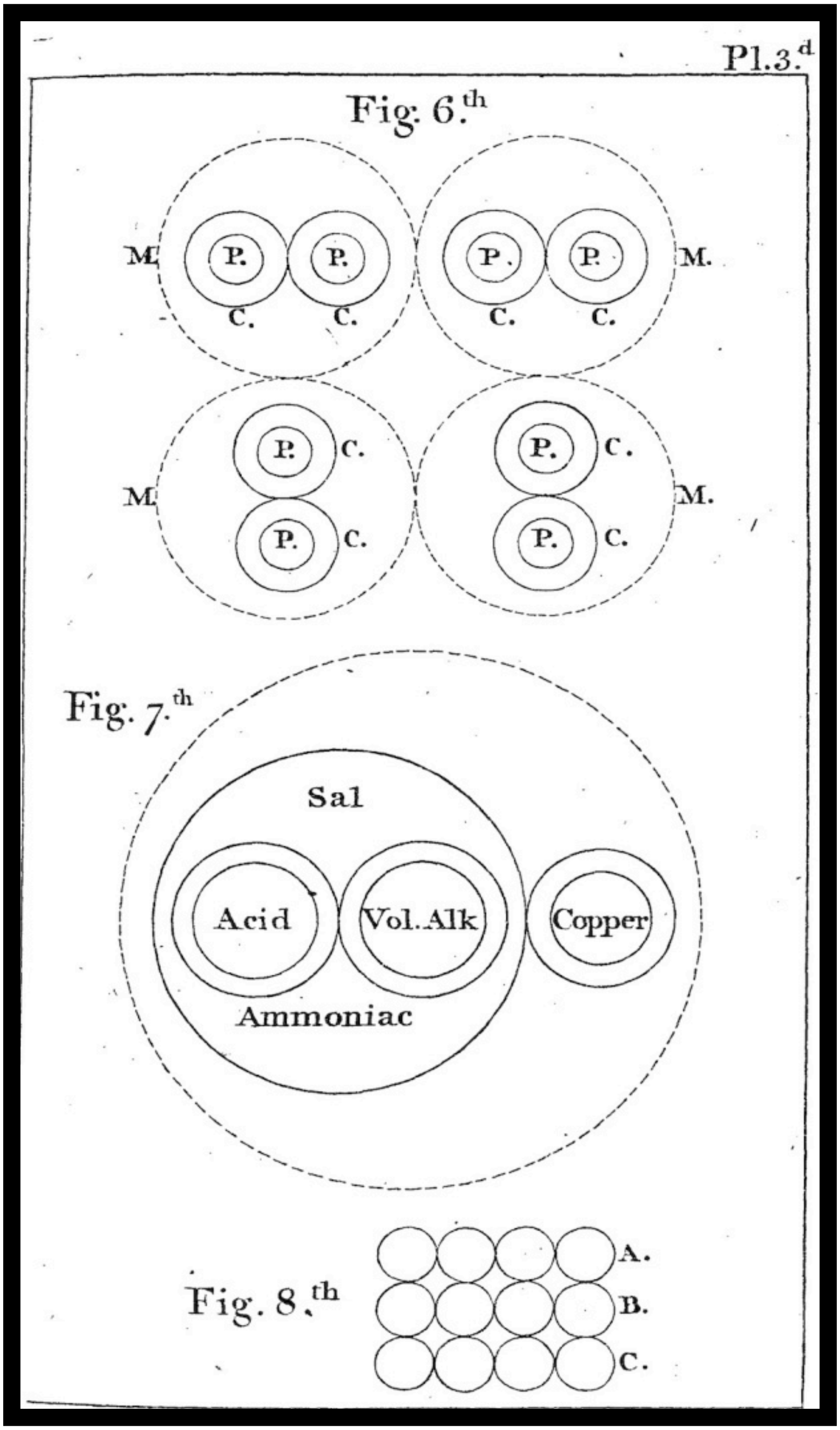


Figure11: George Fordyce, *Elements of Agriculture and Vegetation*, London: J. Johnson, 1765, 81.

Chapter 6. Conclusion

6.1 Chemical Affinity in the Scottish Enlightenment

Chemical affinity theory specified the elective attractions of the various chemical substances in forming compounds. Understanding affinities allowed chemists to better analyze solutions into their constituent parts and synthesize useful compounds. Introduced in Scotland through the chemistry lectures of William Cullen, chemical affinity became the central chemical tool for a generation of students in a broad range of society. Many of Cullen's students went on to be chemistry lecturers or lecturers in other related subjects like *materia medica*, medicine, and natural philosophy. As has been shown within this dissertation, Joseph Black, George Fordyce, Thomas Charles Hope, and many of Cullen's other students-turned-teachers continued to teach a chemistry based around chemical affinity. Thus far, the chemical historiography has focused on the development of the concept of affinity within the boundaries of theoretical chemistry focusing on historical figures who self-identified as chemists or professors of chemistry. However, this narrow focus misses a broad array of people who identified as doctors, farmers, politicians, and industrialists who used affinity in real world pursuits and helped to advance analytical techniques and theory. Because of the pedagogical ties between chemistry and medicine, affinity was also applied to the study of physiological processes and the treatment of disease. The rise of affinity theory coincided with the height of the Scottish Improvement movement, so affinity was also appropriated for the scientific rationalization of agriculture and various industrial processes including salt production. This dissertation has drawn on the lecture notes, correspondence, and publications of Cullen and his network of students to situate them within the milieu of the Scottish Enlightenment and argued that their interest in chemical affinity produced a unique disciplinary alignment, which was perpetuated well into the nineteenth century in Scotland, England, and America.

6.2 Original Results of the Dissertation

Foregrounding the role of affinity in understanding physiology draws our attention to a cluster of bodily processes and diseases and provides a new understanding of the eighteenth-century experience and treatment of these diseases. The chemical study of respiration has been studied as an important innovation of the late eighteenth century, but the understanding of asthma as a biochemical breakdown in the routines of the healthy lung has been overlooked. John Haygarth's contributions in preventing contagion have been studied, but it was affinity that helped him to recognize the sources of contagious miasmas and to conceptualize their chemical and mechanical behavior as airs. That liver obstructions and syphilis could both be treated with the same chemicals compounded for the most efficacious delivery of oxygen is not readily apparent, even within the medical framework of the eighteenth century. By studying the affinities of bile, Helenus Scott started a series of investigations into the uses of acids as a mechanism for the delivery of oxygen. These conceptualizations of these diseases and their treatments changed throughout the nineteenth and the twentieth centuries to the point where many of them seem nonsensical. However, the study of eighteenth-century physiology and pharmacy inform our understandings of the experience of disease and contemporary understandings of the interplay between compounds constructed in the laboratory and the vital processes of the body. That so many doctors were trained in the Cullen's affinity based chemistry and medical theory shaped a three-dimensional understanding of the human economy as a chemically composed system of bodily fluids and nervous sensations.

The connection between eighteenth-century mineralogy and chemistry has been recognized in the secondary literature, most notably in the works of David Oldroyd, Rachel Laudan, Matthew Eddy, and Evan Melhado.[297] The chemico-mineralogical classificatory systems of Johan Gottschalk Wallerius (1709-1785), Axel Fredrik Cronstedt (1722-1765), and Torbern Bergman (1735-1784) have drawn attention to a Swedish and German mineralogical community that was increasingly influential in the development of chemical nomenclature and analytical techniques in the second half of the eighteenth century. More recently, Eddy and others have

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[297] D. R. Oldroyd, "Some Phlogistic Mineralogical Schemes Illustrative of the Evolution of the Concept of "Earth" in the 17th and 18th Centuries," *Annals of Science* 31 (1974): 269-305. D. R. Oldroyd, "Mineralogy and the Chemical Revolution," *Centaurus* 14 (1975): 54-71. Rachel Laudan, *From Mineralogy to Geology: The Foundations of a Science, 1650-1830*, Science and its conceptual foundations (Chicago: University of Chicago Press, 1987). Evan M. Melhado, "Mineralogy and the Autonomy of Chemistry Around 1800," *Lychnos* 55 (1990): 229-262. Matthew D. Eddy, "Scottish Chemistry, Classification and the Early Mineralogical Career of the 'Ingenious' Rev. Dr. John Walker (1746 to 1779)," *British Journal for the History of Science* 35, no. 4 (2002): 411-438. Eddy, *The Language of Mineralogy John Walker, Chemistry and the Edinburgh Medical School, 1750-1800*.

shifted their attention to John Walker (1731-1803) and an Edinburgh community largely composed of William Cullen's students.

However, none of these works have addressed the trans-national network of Scottish trained doctors that commodified the mineral waters of Britain and America and then used affinity to produce and market imitation waters. Mineral water literature was a medium of advertising, for the water as a natural commodity, the spa as a medical resort, and the doctor as an authority. While advanced chemical analysis buttressed the legitimacy of the growing number of mineral spas, the precision required in isolating dilute salts drove the advancement of affinity theory and its analytical techniques. The recognition that gases and non-soluble earths contributed to the medical efficacy of mineral waters but could not be studied in samples that had been bottled and shipped also led to the rapid development of in situ experimentation. Yet without such an understanding, we are left with an inadequate description of the role played by chemists and chemistry in a key field of *materia medica*, urban water systems, and the beverage industry. The work of John Murray in 1815 and 1817 triggered an epistemic crisis, not only in the study of mineral waters, but for affinity theory more generally. If affinity based analysis could not be relied on to indicate the salts that were present in solution, then affinity theory lost its utility.

In the "Age of Improvement," agriculturalists used chemical affinity to develop new theories in plant nutrition and to develop new understandings of soil fertility. Agriculture became a standard part of undergraduate chemical lectures and became a subject of study for natural philosophers and for more practical farmers and politicians. The patronage of Lord Kames and the Duke of Argyll for Cullen and Black has been noted in the various biographies, but Kames' emphasis on the utility of affinity for the educated farmer demonstrates the economic importance of chemistry in a way that has been previously missed. The utilization of chemical agriculture in the large agricultural holdings of both Argyll and (through the Board of Trustees) Kames demonstrate that affinity was not merely a book theory but rather a principle in the manuring and cultivation practices of the Scots.

In demonstrating the utility of chemistry for agriculture in the eighteenth century, this dissertation challenges the historiography on agricultural chemistry and science and industry more broadly. Neither G. E. Fussell's oft-cited "Science and Practice in Eighteenth Century British Agriculture," nor David Knight's "Agriculture and Chemistry in Britain around 1800"[298] discuss affinity or any other chemical theory in detail. David Knight focuses on the rhetorical strategies of chemists like Humphrey Davy in appealing to agrarian readers. Fussell largely dismisses the idea that farmers benefitted from chemical agriculture texts, saying, "Neither by inclination nor education were they able to comprehend these profundities."[299]

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298 Knight, "Agriculture and Chemistry in Britain Around 1800."

299 G E Fussell, "Science and Practice in Eighteenth-Century British Agriculture," *Agricultural History* 43, no. 1 (1969): 7-18.

Chemical Agriculture is more often associated with the work of Justus von Liebig (1803-73).[300]

John Pickstone has pointed to Liebig's work as an example of a broader second scientific revolution in nineteenth-century Germany, from which the modern relationships between science and industry emerged.[301] My dissertation supports instead the work of Andrew Cunningham and Perry Williams. In a well-known article from 1993, Cunningham and Williams said,

> To sum up, historical scholarships over the last twenty years enables us to identify the Age of Revolutions as the period which saw the origin of pretty well every feature which is regarded as essential and definitional of the enterprise of science: its name, its aim (secular as distinct from godly knowledge of the natural world), its values (the 'liberal' values of free enquiry, meritocratic expert government and material progress), and its history.[302]

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[300] Justus Liebig and Lyon Playfair, *Organic Chemistry in Its Applications to Agriculture and Physiology* (London: Printed for Taylor and Walton, 1840). Pat Munday, "Liebig's Metamorphosis: From Organic Chemistry to the Chemistry of Agriculture," *Ambix* 38 (1991): 135-154.

[301] Pickstone said, "I would argue that the interests of governments, of academics and of commercial companies were still substantially distinguishable from each other in the mid-nineteenth century, at least in peace time. ... It was from c. 1870, I will argue that we begin to see the development of more intensive, intense and self-perpetuating synergies between the three sets of interests." John V Pickstone, *Ways of Knowing: A New History of Science, Technology, and Medicine* (Chicago: University of Chicago Press, 2001), 14.

[302] Andrew Cunningham and Perry Williams, "De-Centering the 'Big Picture': 'The Origins of Modern Science' and the Modern Origins of Science," *British Journal for the History of Science* 26, no. 4 (1993); p. 427.

This is a broad claim, but this dissertation provides evidence to support the idea that the second scientific revolution is better located in the second half of the eighteenth-century than the middle of the nineteenth. Both the chemical agriculture of the Scottish Enlightenment, the uses of affinity in isolating industrial chemicals like alkali salts for bleaching, and the commercial success of artificial mineral waters indicate the industrialization of chemistry.

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