

Tracing Influence in Small Steps: Richard Kirwan's Quantified Affinity Theory*

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This paper presents an attempt to negotiate the familiar historiographical difficulties of tracing influence in science without fear of accusations of whiggishness. Through a close reading of three papers presented to the Royal Society by Richard Kirwan in the early 1780s on specific gravity, proportions and affinity, it seeks to show that the search for the role of influence in the history of science need not be based on a present-centred value judgement of past science. Prevailing historiography tends to link Kirwan's work to notions of definite combining proportions, settling him firmly on the Proust side of the Berthollet–Proust debate and regarding his work as vaguely precursory to Dalton's atomic theory. My reading suggests, however, that these papers may well have had a surprising level of influence on Berthollet's *Chemical Statics* and should perhaps be viewed through a somewhat different historical lens. I hope to show that the tracing of historical influence can offer valuable insights to historians of science and that when influence is tracked in small steps only, and forwards rather than backwards, we can legitimately follow it without fear of present-centredness clouding our vision.

Introduction

The tracing of influence in the history of science involves a perpetual struggle against whiggishness. When we read a historical text we must be cautious when a voice in our head pipes up: “that is really a bit like . . .,” or “that seems to be an early recognition of . . .” The voice is particularly clamorous when we think that we spot hints of a precociously early appreciation of certain key concepts in our science. As historians, we are trained that we heed it at our peril. And yet, in spite our awareness of the dangers of allowing our knowledge of the way in which scientific thinking

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progressed to colour our assessments of historical texts, we also have the legitimate task of searching for and tracing that nebulous diffusion of ideas that we call “influence.” Indeed, only the historian can track influence, as such an endeavour requires the benefit of hindsight. The context of discovery is still sufficiently mysterious that the operations and workings of influence remain elusive, and yet we cannot deny its role in the history of science. In practice, however, difficulties arise when we search for influence, largely because we tend to work backwards chronologically, seeking to show how one of the canonical discoveries of science came to be formulated. Perhaps this is because influence is usually only of historical interest where successful ideas or practices provide the endpoint of our search. It can also be difficult for the historian to point to evidence that definitively proves that an early scientific paper was influential on other historical actors, as this is rarely admitted by the actors concerned. So, we have a dilemma. On the one hand, we must beware of whiggish tendencies, while on the other, influence, and its cohorts inspiration, stimulation and cause, must be admitted to be among the legitimate concerns of the historian of science. Whiggishness would seem, then, to be firmly embedded in our endeavour; but does it have to be? In this paper I hope to show that the search for the role of influence in the history of science need not be based on a present-centred value judgement of past science. When influence is tracked in small steps only, and forwards rather than backwards, we can follow it without fear of present-centredness clouding our vision.

What follows is a close reading of three papers presented to the Royal Society by Richard Kirwan in the early 1780s on specific gravity, proportions, and affinity. These papers offer something of a paradox to the historian. Their concern with combining proportions and with accurate quantitative measurement immediately suggests that they might have influenced the chemistry of the next century. Indeed, Mi Gyung Kim has argued that Kirwan’s “focus on the saturation capacity of acids and bases as the true measure of affinities opened a new frontier of analytic chemistry which developed into nineteenth century stoichiometry.”¹ Henry Guerlac, too, has included Kirwan’s work among that of other affinity theorists in a series of precursors to Daltonian atomism.² The claim that Kirwan’s attempt to develop a quantitative basis for the doctrine of affinity influenced a number of important developments in chemistry, viewed purely in the light of nineteenth-century atomic chemistry, appears to be almost indisputable. Kirwan’s papers were published in the *Philosophical Transactions* and translated into French and German, so the first question crucial to the assigning of influence — availability — would appear to be answered. And we know, too, that he was awarded the Copley medal for these papers in 1782, so we can reasonably argue that some aspect of his work was regarded as important at the

¹ Mi Gyung Kim, *Affinity, That Elusive Dream: A Genealogy of the Chemical Revolution* (Cambridge, Mass.: MIT Press, 2003), 269.

² Henry Guerlac, “The Background to Dalton’s Atomic Theory,” in *John Dalton and the Progress of Science*, ed. D. S. Cardwell (New York: Manchester University Press, 1968), 57–91. Kirwan’s latest biographer, E. L. Scott, also regarded the chief importance of his work on affinity as lying in its contribution to the theory of reciprocal proportions. See E. L. Scott, “Life and Work of Richard Kirwan (1733–1812) with Particular Reference to His Influence on the Chemistry, Geology and Meteorology of His Time” (Ph.D. Thesis, London University, 1979), 210.

time.³ This is not, however, the same as being influential. Although the views of the period concerned are clearly important — unless a work was deemed valuable when originally produced, it would be unlikely to be much read — they tell us little about its influence. Moreover, the calculation of combining proportions was presented by Kirwan largely as a means to accomplish the important task of quantifying affinities. The feature of his papers that we wish to select as important was not, it seems, regarded by him as such. Perhaps more ominously, it does not appear that Kirwan was remembered particularly kindly by his later contemporaries. Shortly after his death in 1812, one such wrote:

Through some fatality, attempting almost every subject, he did not thoroughly succeed in any. Scarcely ever did he advocate a theory, which was not almost immediately discovered to be unfounded: he took great pains to refute authors who have never been read, and evinced his learning more than his judgement, in quoting others that will never be believed.⁴

This writer, at least, does not seem to have regarded Kirwan's works as anything other than a series of unfortunate mistakes; indeed, most of those chemists who explicitly made reference to the papers that form the subject of this study were critical. So, we are left wondering, how should we, as historians, regard Kirwan's papers? Were they important either in their own right or through their influence on others? Must we accept the unpalatable fact that the merits we sometimes want to ascribe to scientific texts of the past are justified only by an indefatigable present-centredness? How, in short, can we accurately assess the historical importance of those texts that do not themselves contain any canonical discovery, but that nevertheless seem to contain the germs of ideas yet to come?

I argue that by subjecting the texts to the same kind of close reading that they were accorded by contemporaries, we can determine certain concepts, ideas or methods that were accepted or implemented by others. Thus, we can trace the workings of influence, not striding from great discovery backwards over time, but in smaller and more manageable steps forwards from text to text. In this way, we can demonstrate that Kirwan's work was indeed influential, although not in the direction that is usually maintained.

Richard Kirwan and affinity

Richard Kirwan was an independently wealthy Irish “gentleman chemist” born in 1733 and schooled in France,⁵ where he attended Rouelle's lectures.⁶ He was elected

³ It is not, however, particularly clear *which* aspect, as the award seems only to have specified “for the merits of his labours in the science of chemistry.” Royal Society Journal Book, quoted in M. Yakup Bektas and Maurice Crosland, “The Copley Medal: The Establishment of a Reward System in the Royal Society, 1731–1839,” *Notes and Records of the Royal Society of London* 46 (1992): 43–76, on 57.

⁴ R. Ryan, “Biographica Hibernica” (1821), quoted in Scott, “Life and Work of Richard Kirwan (1733–1812),” 122.

⁵ Scott, “Life and Work of Richard Kirwan (1733–1812),” 13. Scott's thesis is the most recent and comprehensive survey of Kirwan's life and work.

⁶ Kim, *Affinity, That Elusive Dream*, 269.

a Fellow of the Royal Society in 1780, only a couple of years before being awarded the Copley Medal for three papers that set out his novel system for quantifying affinity.⁷ Among other works, he also published a book on mineralogy, which was translated into French, German, Spanish and Russian,⁸ and a work on manures, which ran to seven British editions and one American edition as well as being translated into French and German.⁹ His work on the analysis of mineral waters was particularly praised, and his analytical methods were adopted by a number of other chemists for inclusion in textbooks.¹⁰ Victor Boantzsa has recently shown that Kirwan was regarded by both his British contemporaries and Lavoisier and his collaborators as “the most dominant authority on phlogistic matters.”¹¹ It appears, then, that Kirwan was rather more successful in his scientific endeavours than the rather harsh assessment quoted above might imply.

Nevertheless, this stance, or something quite similar, has tended to be adopted by the majority of historians of science since the mid-nineteenth century.¹² Kirwan’s role as one of the most determined defenders of phlogiston, and his Neptunist attack on the geological theories of Hutton, are, indeed, well remembered. Although scholars are now beginning to reassess Kirwan’s phlogiston theory, focusing on his role as systematiser that made him such a worthy foe, for the most part his *Essay on Phlogiston* has been something of a historiographical millstone around the neck of his reputation.¹³ This essay was the 1787 work that Lavoisier and his colleagues used as the foundation of their rebuttal of phlogiston theory, but by this date Kirwan already had a history of revitalising phlogiston. He had, in 1782, sought to confirm Cavendish’s tentative suggestion that inflammable air might be the elusive phlogiston, and had formulated his complex phlogiston theory to integrate this interpretation with the latest pneumatic discoveries, and the latest views of a material heat.¹⁴

⁷ Richard Kirwan, “Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances,” *Philosophical Transactions of the Royal Society of London* 71 (1781): 7–41; Richard Kirwan, “Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of Various Saline Substances,” *Philosophical Transactions of the Royal Society of London* 72 (1782): 179–xxxv; Richard Kirwan, “Conclusion of the Experiments and Observations Concerning the Attractive Powers of the Mineral Acids,” *Philosophical Transactions of the Royal Society of London* 73 (1783): 15–84.

⁸ Richard Kirwan, *Elements of Mineralogy* (London: Printed for P. Elmsly, 1784). See Bibliography of Kirwan’s works in Scott, “Life and Work of Richard Kirwan (1733–1812),” 432.

⁹ Richard Kirwan, *The Manures Most Advantageously Applicable to the Various Sorts of Soils, and the Causes of Their Beneficial Effect in Each Particular Instance* (Dublin: 1794). For further editions, see Scott, “Life and Work of Richard Kirwan (1733–1812),” 432–33.

¹⁰ For example: Thomas Thomson, *A System of Chemistry*, 5th ed., 4 vols. (London: Baldwin, Cradock, and Joy, 1817), vol. 3; and William Henry, *The Elements of Experimental Chemistry*, 9th ed., 2 vols. (London: Baldwin, Cradock, and Joy, 1823).

¹¹ Victor Boantzsa, “The Phlogistic Role of Heat in the Chemical Revolution and the Origins of Kirwan’s ‘Ingenious Modifications . . . Into the Theory of Phlogiston,’” *Annals of Science*, 65 (2008): 309–38.

¹² Although this attitude appears to be changing, with Boantzsa’s work being worthy of particular note. See, for example, Boantzsa, “The Phlogistic Role of Heat in the Chemical Revolution.”

¹³ Richard Kirwan, *An Essay on Phlogiston and the Constitution of Acids* (London: Frank Cass & Co. Limited, 1968).

¹⁴ Cavendish made the initial suggestion in 1766, in Henry Cavendish, “Three Papers, Containing Experiments on Factitious Airs,” *Philosophical Transactions of the Royal Society of London* 56 (1766): 141–84. Kirwan’s confirmation is set out in Kirwan, “Continuation of the Experiments and Observations,” and his mature phlogiston theory forms the basis of Kirwan, *An Essay on Phlogiston*.

It is not, therefore, particularly surprising that Kirwan's reputation is so intimately linked to phlogiston in the historical imagination, although it is doubtful whether any modern historian would share the views of the anonymous gentleman above. Nevertheless, in the tracing of influence, it is important to bear in mind contemporary views, and although Kirwan's work on phlogiston was well known, other aspects of his chemistry were also regarded as deserving of attention. Furthermore, history is often greatly enriched by the historian taking "the road less travelled," and hence I have chosen to focus here on his complex and novel affinity theory. What follows seeks to show that this theory, so far largely unappreciated by historians of science, ought to be incorporated into the canon of ideas that influenced the work of later chemists, and through them, the development of the science.

Affinity loomed large throughout Kirwan's scientific endeavours. Many of his publications, even those in fields only tangentially chemical, granted a key role to his theory of chemical affinity.¹⁵ This theory was first set out in the *Philosophical Transactions* from 1781 to 1783,¹⁶ and thereafter in further papers published in the *Transactions of the Royal Irish Academy*.¹⁷ His 1782 paper claimed unambiguously that chemistry was founded on the doctrine of affinity,¹⁸ and the 1787 *Essay on Phlogiston* similarly demonstrated the importance of affinity in his chemistry. Indeed, we might well argue that affinity held a higher place in his chemical cosmos than did phlogiston. The *Essay on Phlogiston* drew on ideas of chemical affinity to point out the inconsistencies of Antoine Lavoisier's anti-phlogistic claims, arguing that they did not accord with what he had presented as the affinities of the oxygenous principle.¹⁹ Kirwan's polemic seems to have backfired upon him, however, as the French chemists saw his publication as an opportunity to set out their arguments in detail, and to rebuff the arguments of the phlogistonists point by point. In 1788, they republished the French translation together with their refutations of Kirwan's arguments. As a matter of some interest, it is in these refutations of Kirwan's affinity arguments that we find perhaps the clearest expression of Lavoisier's own views on the doctrine. Finally, in 1789, Kirwan republished his original *Essay on Phlogiston*, together with the English translation of the French refutations, accompanied by yet further rebuttals by Kirwan. In both the French and the English contexts, though, affinities were regarded as axiomatic; if a theory contradicted the observed affinities, then the theory would seem to be at fault; the argument between Kirwan and the French chemists emphasises that this point of view was shared by both sides of the debate.²⁰

¹⁵ See Scott, "Life and Work of Richard Kirwan (1733–1812)," which explores all of Kirwan's publications, and gives many examples of how he drew on his affinity theory to substantiate his views in geology, mineralogy and even meteorology.

¹⁶ Kirwan, "Experiments and Observations"; Kirwan, "Continuation of the Experiments and Observations"; Kirwan, "Conclusion of the Experiments and Observations."

¹⁷ Richard Kirwan, "Of the Strength of Acids, and the Proportion of Ingredients in Neutral Salts," *Transactions of the Royal Irish Academy* 4 (1790): 3–73.

¹⁸ Kirwan, "Conclusion of the Experiments and Observations," 34.

¹⁹ See, in particular, Kirwan, *An Essay on Phlogiston*, 38–55.

²⁰ M. Beretta, "Lavoisier and His Last Printed Work: The *Mémoires De Physique Et De Chimie* (1805)," *Annals of Science* 58 (2001): 327–56; this shows that Lavoisier too worked on affinity, relating it to universal gravitation and linking it to his caloric theory. See Antoine Laurent Lavoisier, *Mémoires De Physique Et De Chimie* (Bristol: Thoemmes Continuum, 2004), vol. I, 1–28.

Some years later, Thomas Thomson was still describing chemical affinity as “confessedly the basis of the science,”²¹ and in fact the *Encyclopaedia Britannica* of 1823 still devoted ten pages to the subject.²² It is clear that when Kirwan published his papers, affinity was indeed considered, by phlogistic and anti-phlogistic chemists alike, as fundamental to chemistry. Kirwan’s papers on the subject were thus likely to be of great interest to most of his contemporaries.

The 1781–1783 papers: Saturation and proportions

In his 1766 chemistry course at Edinburgh, William Cullen pointed out a contradiction between saturation proportions and affinity. Explaining the “history” of volatile vitriolic acid, he explained that:

The volatile goes further in saturating alkalis than the fixed; for the fumes of a pound of burning sulphur, applied to a cloth impregnated with alkali, as in the case mentioned above, will convert more of this alkali into a neutral than will 16 ounces of the fixed [vitriolic acid]. It has a very weak adhesion, less than any acid, to alkalis; therefore may be dislodged by either of the four we have mentioned.²³

There was no correlation here, it seems, between the quantity of an acid required to saturate an alkali and the strength of affinity. Less volatile vitriolic acid was required to saturate the alkali than vitriolic acid, but the fact that the volatile acid could be “dislodged” by either vitriolic (fixed), nitrous, muriatic or vegetable acids showed that its affinity was weaker. Cullen’s observation exhibits an interesting attitude to quantity and measurement. He compared the very vague amount of volatile vitriolic acid (the result of burning a pound of sulfur) required to combine with an (unmentioned) amount of alkali with the quantity of alkali that united with 16 ounces (another pound) of vitriolic acid. This rather confusing comparison perhaps serves to illustrate the distinction between observation and experiment. While Cullen did quote some measurements, his language, mixing figures with relations, suggests that this is a phenomenon that he had noticed in the course of performing other operations rather than experiments carried out specifically in order to ascertain the quantities that combine together. Such a lack of interest in quantification perhaps places Cullen very firmly in his time; to all but those despised persons engaged in trade, such details were merely incidental. We must also, of course, remember the pedagogical context — statements of exact quantities would probably be both inappropriate and unnecessary in a lecture environment. Nevertheless, we can see that Cullen’s discipline was primarily qualitative; the chemist manipulated the natural inclinations of bodies to produce new substances with particular properties or qualities.

It cannot be said, though, that from this perspective there was no clear use for measurement. Cullen taught all his students to use diagrams that, in some cases, might be used to predict what would happen when compound substances were mixed

²¹ Thomas Thomson, *The History of Chemistry* (London: Henry Colburn and Richard Bentley, 1830), vol. II, 157.

²² *Encyclopaedia Britannica*, 6th ed. (Edinburgh: Archibald Constable and Company, 1823), vol. V, 439–49.

²³ William Cullen, “Notes Taken by Charles Blagden from Lectures on Chemistry 1765–6,” MS 1922, Blagden Papers, Wellcome Library for the History and Understanding of Medicine, London, Lecture 51.

together.²⁴ However, as is made tediously clear in correspondence exchanged between Cullen and his erstwhile student George Fordyce in 1759, although chemists could use affinity tables to ascertain whether the attraction between one pair of substances would be stronger than between another, such comparisons could only be made between pairs of substances one of which remained the same.²⁵ So, the affinity between A and B could be compared with that between A and C, and the chemist could state that one was stronger than the other, but the affinity between A and B and could not be compared a priori with that between C and D (indeed, there was no obvious methodology to enable such a comparison to be made experimentally either). Accordingly, when pairs of substances were mixed together, in most cases it was impossible to tell a priori whether decomposition would occur, as the affinities could not be compared directly. Cullen's "equations" show this problem quite clearly (Figure 1).

The table of affinities can tell us that $X > Y$ and $Z > W$, and that $W > Y$ and $Z > X$, but that does not actually enable us to predict what might occur if vitriolated tartar was mixed with silver dissolved in nitrous acid. Are $Y + Z > W + X$, or vice versa? This kind of question could only be answered by observation, and became an enduring problem for all those chemists who espoused the doctrine of affinities. The difficulty derived from the peculiar structure of the affinity tables on which they relied.²⁶ As Stephen Weininger has noted, affinity tables are topologically one-dimensional: "Each column is to be read vertically and independently of the others. There is no coherent horizontal reading of the table."²⁷ As each affinity series was essentially a separate one, comparison of the affinities shown in different columns was dogged by

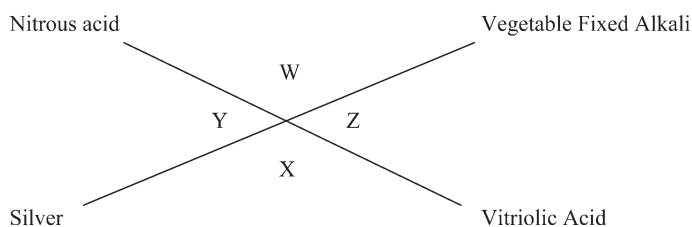


FIGURE 1

²⁴ Maurice Crosland, "The Use of Diagrams as Chemical 'Equations' in the Lecture Notes of William Cullen and Joseph Black," *Annals of Science* 15 (1959): 75–90.

²⁵ George Fordyce, "On Compound Elective Attractions," 1759, MS 89, Cullen Papers, Glasgow University Library, Glasgow; George Fordyce, "Five Letters to William Cullen," 1759–1774, MS 180, Cullen Papers, Glasgow University Library, Glasgow; William Cullen, "Draft Letter to George Fordyce," 1759, MS 90, Cullen Papers, Glasgow University Library, Glasgow.

²⁶ For a detailed exposition of the source of this difficulty, see: Georgette Taylor, "Variations on a Theme: Patterns of Congruence and Divergence among 18th Century Chemical Affinity Theories" (Ph.D. Thesis, University of London, 2006), chap. 5.

²⁷ Stephen J. Weininger, "Contemplating the Finger: Visuality and the Semiotics of Chemistry," *Hyle — International Journal for the Philosophy of Chemistry* 4, no. 1 (1998): 3–27.

problems. Quantification of affinities was the only way in which a solution might be found to these kinds of problems.²⁸ Some chemists did adopt a sort of algebraic approach, assigning conjectural integral numbers to familiar affinities, but this tactic was more often used a posteriori to illustrate the results of complex mixtures rather than to predict them.²⁹ A system of determining affinities through the *measurement* of some sensible effect of their action was clearly a desideratum towards the end of the eighteenth century. As Alistair Duncan has shown, Kirwan was not the only chemist to attempt to formulate such a system, although it seems that he was the first to try to measure affinities by focusing on the quantities of substances that combined together.³⁰

By 1783, when he presented the third paper in this series, Kirwan regarded combining or saturation proportions as providing the measures of affinities, but he had not always taken this view. Two years earlier, when he began his investigations, his aim had been to measure the specific gravities of two substances and compare them with the specific gravity of their compound. He had noticed that in most cases there was a difference between the specific gravity expected for the compound substance, which he called the “mathematical specific gravity,” and the specific gravity of the compound as found by “actual experiment.”³¹ Often, he argued, the specific gravity of the compound “is greater without any diminution of the lighter ingredient.”³² According to his original way of thinking:

This increase of density must then arise from a closer union of the component parts to each other than either had separately with its own integrant parts; and this more intimate union must proceed from the attraction or affinity of these parts to each other.³³

The idea that one of the actions of affinity was to increase the density of the compound substance was not in itself particularly novel. In 1765, the same notion had formed an important part of Cullen’s speculative theory of heat, fire and phlogiston.³⁴

²⁸ George Fordyce composed a lengthy treatise, intended for the Royal Society, in which he sought to solve this problem algebraically, but his efforts were disparaged at some length by Cullen, to whom he sent the first draft. See: Fordyce, “On Compound Elective Attractions”; Cullen, “Draft Letter to George Fordyce”; and Taylor, “Variations on a Theme,” Appendix 1.

²⁹ Duncan mentions, in particular, Joseph Black, John Elliot and Antoine François de Fourcroy; see Alistair Duncan, *Laus and Order in Eighteenth-Century Chemistry* (Oxford: Clarendon Press, 1996), 198–99. To this list, could also be added George Fordyce; see Taylor, “Variations on a Theme,” 167–68.

³⁰ Duncan lists a number of attempts to measure affinity by mechanical means, such as those by Guyton de Morveau and Carl Friedrich Wenzel. He distinguishes these endeavours from those that focused on the saturating proportions of combining substances, of which Kirwan’s was the earliest. Duncan, *Laus and Order*, 206–8.

³¹ Kirwan, “Experiments and Observations,” 8. Most of Kirwan’s theorising on specific gravities, and indeed the rules on which he relied for these various calculations, were taken from Roger Cotes, *Hydrostatical and Pneumatical Lectures . . . With Notes by Robert Smith*, 3rd ed. (London: J. Nourse, 1775), 81–107.

³² Kirwan, “Experiments and Observations,” 8–9.

³³ Kirwan, “Experiments and Observations,” 9.

³⁴ William Cullen, “Notes Taken by Will Falconer from Chemistry Lectures,” 1765, MS 1919–1921, Wellcome Library for the History and Understanding of Medicine, London, MS 1920. See Georgette 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. 4 (2006): 477–501.

Cullen had produced tables showing the combinations of substances that produced heat and cold.³⁵ From these, he argued that heat was produced only in cases of “proper mixture,” when substances combined by the action of affinity and their total bulk was reduced (in Cullen’s terms, a “condensation”). There is no indication in Cullen’s account of his hypothesis that he saw this phenomenon as a potential means to measure affinity; indeed, Cullen appeared to be uninterested in attempting to measure either the heat produced or the condensation of the mixture.

Kirwan, though, looked to this same condensation, the difference between the mathematical specific gravity and the experimentally determined specific gravity, to provide a measure of affinity. His initial assumption seems to have been largely intuitive, but he sought to prove it by experiment. Making use of Priestley’s recent discovery of “marine acid air” (regarded as spirit of salt entirely stripped of its water content), Kirwan first ascertained the quantity of pure or “real” acid present in spirit of salt of various specific gravities — in this case, he showed that the specific gravity of the acid matched its mathematical value, and that therefore there was little or no attraction between the acid and the water. From this, and from the amount of such pure or “real” acid that combined with fixed alkali, he hoped to be able to extrapolate his findings to determine the quantity of real acid contained in any of the common acids.³⁶ His hypothesis depended on the presupposition that:

The same quantity of all the acids was requisite for the saturation of a given quantity of fixed alkali; for if such given quantity of fixed alkali might be saturated by a smaller quantity of one acid than of another, the conclusion fell to the ground.³⁷

He produced a table showing the specific gravities of various concentrations of spirit of salt, and then proceeded to work out the quantity of spirit of salt (of known specific gravity) that would saturate a known amount of vegetable fixed alkali. Adding acid solution to his alkali solution drop by drop, Kirwan monitored the progress of his experiment by regularly applying drops of the mixture onto paper stained blue with radish juice; as soon as the faintest tinge of redness appeared, he considered the solution to be saturated, although with a small excess of acid (for which he made allowance in his calculations). With a little further calculation, he was able to assign proportions to the quantities of acid, fixed vegetable alkali and water in 100 grams of the resulting salt. Assuming that this amount of alkali would be saturated by a similar quantity of “real acid” in other acid solutions, he applied these figures to combinations of the same alkali with nitrous and vitriolic acids. Thus, he was able to ascertain the amount of “pure” acid in various concentrations of spirit of nitre and spirit of vitriol, and from this, the specific gravity of each “pure” acid. From this, in

³⁵ Some of his observations were published in William Cullen, “Of the Cold Produced by Evaporating Fluids, and of Some Other Means of Producing Cold,” *Essays and Observations, Physical and Literary* 2 (1756): 145–56.

³⁶ This methodology harks back to the belief in a universal or primeval acid, which is perhaps connected to the belief of Van Helmont, among others, in a universal solvent. Somewhat more recently, Stahl had claimed that all acids are modifications of a single universal acid, which he argued was the vitriolic acid, and Cullen in 1766 was still speculating along similar lines. See: J. R. Partington, *A Short History of Chemistry* (New York: Dover Publications, 1989), 46 and 88; and Cullen, “Notes Taken by Charles Blagden, Lecture 57.

³⁷ Kirwan, “Experiments and Observations,” 10.

turn he could calculate the mathematical specific gravities of the various concentrations of acids, which he compared with their actual specific gravities. By subtracting the former from the latter, he produced a figure for “accrued specific gravity,” that is, the increase in density of the dilute acid. These tables are, according to Partington, the first tables of specific gravities of acids to be produced.³⁸

In a later return to this subject in a paper published in 1790, Kirwan referred to what he then called “mere” acids, of which all acid solutions were dilutions, and whose specific gravities he had discovered, as “standards” for muriatic acid (1.5), vitriolic acid (2.0) and nitrous acid (1.5543).³⁹ Kim has drawn attention to this as the first use of standard solutions of acids, and as such the paper in which it appears certainly has a claim to be important in the history of chemistry.⁴⁰ “Firsts” are not necessarily influential, as we know from more notorious cases, such as Scheele’s chronological first discovery of oxygen, which remained unpublished until after Priestley’s subsequent rediscovery. Nevertheless, the use of standard solutions in chemistry has not, so far, been thoroughly explored by historians, and perhaps Kirwan’s role in this interesting development might be elucidated in the future.

It is at this point that we come to the first hint of one of the perceived difficulties of Kirwan’s theory, later to be highlighted by William Nicholson.⁴¹ After all these experiments and calculations, it seems as though Kirwan had got his conclusions mixed up with his premises, explaining that from all these experiments it followed that:

Fixed vegetable alkalis take up an equal quantity of the three mineral acids, and probably of all pure acids . . . it should therefore seem, that alkalis have a certain determinate capacity of uniting to acids, that is, to a given weight of acids; and that this capacity is equally satiated by that given weight of any pure acid indiscriminately. This weight is about 2.35 of the weight of the vegetable alkali.⁴²

This “conclusion” is not entirely surprising when it is borne in mind that it was a fundamental preliminary assumption of Kirwan’s calculations that the same amount of alkali united with the same amount of “pure” acid, whichever particular acid was being used. This presentation of his initial assumption as a demonstrated conclusion certainly seems to be methodologically suspect, but recall here that Kirwan was at this point in his work still proceeding on the basis that the affinity between substances was proportional to the difference between the mathematical and actual specific gravities (the “accrued density”). He had, in fact, sought to submit his measurements to “synthetical proof,” in which he tested his figures for accrued density by comparing calculated values for the actual specific gravity with the observed value. He also tested his figures against the data of other chemists, including Lavoisier. All these tests and comparisons had, he believed, served to prove that his assumption was

³⁸ J. R. Partington, *History of Chemistry* (London: Macmillan, 1961), vol. 3, 665.

³⁹ Richard Kirwan, “Of the Strength of Acids, and the Proportion of Ingredients in Neutral Salts,” *Transactions of the Royal Irish Academy* 4 [1791 (read 1790)]: 3–73, on 5.

⁴⁰ Kim, *Affinity, That Elusive Dream*, 269–70.

⁴¹ William Nicholson, *A Dictionary of Chemistry*, 2 vols. (London: G. G. and J. Robinson, 1795), vol. I, 163.

⁴² Kirwan, “Experiments and Observations,” 33.

justified. Methodologically speaking, he had set forth his hypothesis, tested it by experiment and measurement, and found it proven. It might perhaps be argued that his “proof” was insufficient, but the criticisms that were to come were not focused on his methodology in this first paper but on the way in which he built on this initial work.

Note that in this first paper Kirwan talks only of the “capacity” of alkalis to unite with acids rather than of affinity, and indeed he implies here that all alkalis and all acids have the same capacity to unite together. “Capacity” remains an indeterminate concept, but it seems most likely that he envisaged something similar to heat capacity, a concept that interested Kirwan enormously.⁴³ It was not, at this point in his investigations, directly equated with affinity or attraction. However, by the time he came to publish the third paper in his series, Kirwan had changed tack, and was explicitly linking the saturating proportions of two substances in combination with their affinities. Thus, the original assumption, which was at least upheld to some degree by observation, had almost imperceptibly become an assumption that the *affinities* of all three acids for fixed alkali were the same. It was this metamorphosed assumption, which was indeed presented as a conclusion in the third paper, that Nicholson later singled out for criticism.

Returning to the 1781 paper, Kirwan’s calculations of the accrued densities of the various acid solutions also led him to conclude that:

The density accruing to compound substances from the union of their component parts, and exceeding its mathematical ratio, increases from a *minimum*, when the quantity of one of them is very small in proportion to that of the other, to a *maximum*, when their quantities differ less; but that the attraction, on the contrary of that part which is in the smallest quantity to that which is in the greater, is at its *maximum* when the accrued density is at its *minimum*, but not reciprocally; and hence the point of saturation is probably the *maximum* of density and the *minimum* of sensible attraction of one of the parts.⁴⁴

It is difficult to know how Kirwan came to his assumption about the change in attraction between the substances. He did include columns in his tables showing the accrued densities of vitriolic and nitrous acids that purported to show the “Attract. of the acid to water” and “Attract. of water to the acid,” and there is a clear relationship between the attractions he lists against each particular solution and the accrued density. In the case of the nitrous acid, it seems that he took the maximum and minimum accrued densities and assumed that the minimum figure corresponded to the attraction between the acid and the water when the quantity of acid was at its maximum in relation to the water, while the attraction of the water to the acid was at its maximum when the quantity of water was at its minimum. At the point where the accrued density reached its maximum (before beginning to decrease slowly as

⁴³ He is credited with having produced the very first table of specific heats [D. McKie and Niels H. de V. Heathcote, *The Discovery of Specific and Latent Heats* (London: Edward Arnold, 1935), 43 and 109], which he inserted in Jean Hyacinthe de Magellan, *Essai Sur La Nouvelle Théorie Du Feu Élémentaire, Et De La Chaleur Des Corps* (London: 1780), and with having coined the term. See E. L. Scott, “Richard Kirwan, J H De Magellan, and the Early History of Specific Heat,” *Annals of Science* 38 (1981): 141–53.

⁴⁴ Kirwan, “Experiments and Observations,” 33–34.

more water was added), Kirwan assigned the maximum density figure to the attraction of the acid for the water, and the minimum density figure to the attraction of the water to the acid. In between, the series proceeded by regular gradations. Conveniently in this case, the measurements of the accrued densities as the amount of water increased appear to have increased in a linear mathematical series, so the total attraction (i.e. the sum of the figures given for the attraction of the acid to the water and the water to the acid) remained the same in all cases. In the case of the table produced for vitriolic acid, although the same methodology was apparently followed, it was much harder to see a pattern in the accrued densities, and the total attraction increased to a maximum in mid-series, and then decreased again. But there is no indication in the text of what prompted Kirwan to assign figures in this way, although he does comment slightly mysteriously that “the first two series were only found by analogy.”⁴⁵

It appears, then, that Kirwan held some speculative notions about how affinities were operating in the dilute acids, and that these led him to make apparently arbitrary assumptions about the relationship between accrued density and the attractions between substances. He still regarded accrued density as directly related to the attraction in the case of the attraction of the acid (up to saturation point, anyway), but the attraction of the water reversed the acid series. The affinities between acid and water were not quantitatively reciprocal, and the substance in excess at any one dilution had less affinity for the other substance. Some notion of a relationship between proportional quantity and affinity was undoubtedly present in Kirwan’s thinking, as he concluded in the first paper:

Hence no decomposition operated by means of a substance that has a greater affinity with one part of a compound than with the other, and than these parts have to each other, can be complete, unless the *minimum* affinity of this third substance be greater than the *maximum* affinity of the parts already united. Hence few decompositions are complete without a double affinity intervenes; and hence the last portion of the separated substance adheres so obstinately to that to which it was first united, as all chemists have observed.⁴⁶

He seems to have been saying here that as there was a maximum accrued density, there was a maximum affinity between two substances. If a third substance was added to an acid solution, with sufficient attraction for the acid, say, to combine with it, as the acid was removed from combination with the water, and the proportion remaining in combination with the water decreased, the affinity between the acid and the water would increase to a point where eventually the decomposition would stop, reaching a sort of equilibrium of affinities. This probably reflects his observations that when combined substances are separated by affinity, the operation rarely proceeded to completion.

⁴⁵ Unfortunately, it is not even clear which “two series” he is referring to. The two columns for attractions are actually the last two in the table. Nevertheless, it seems most likely that these are the series meant, as the other columns contain figures that were ascertained either experimentally by observation or mathematically by calculation. Only the figures for attraction can have been ascertained by analogy. See Kirwan, “Experiments and Observations,” 29.

⁴⁶ Kirwan, “Experiments and Observations,” 34.

In searching for those aspects of Kirwan's theory that had influence on his immediate successors, this particular observation is of some interest. It was made, it should be noted, some twenty years before Claude Louis Berthollet began to formulate his radical new theory of affinities moderated by the proportions.⁴⁷ As we know, much of the burden of Berthollet's later song was the role of proportions by weight in increasing or decreasing affinities. He specifically argued that as the proportions of substances present in a mixture/compound became more asymmetrical, so the affinity between the substance in excess and that being removed increased, until it would be almost impossible to remove the last adhering fraction of one ingredient of a compound by chemical means alone. Here we might justifiably be able to argue in favour of the "influence" of Kirwan's papers on Berthollet. This is just the first of a number of parallels between Kirwan's work and Berthollet's, and it is perhaps worth noting that these ideas remained embedded in Kirwan's theory throughout the series of papers and into his second version of his theory.

Kirwan's second paper, read to the Royal Society nearly a year and a half after his first, followed similar methods to ascertain the specific gravities of the common alkalis through their combining proportions with real acids.⁴⁸ It is worth noting, however, that although he revisited his work on the specific gravities of nitrous acid solutions (with a view to correcting a mistake), including a new table showing the accrued density in each case, he did not include any columns showing attractions.⁴⁹ It also set out at length Kirwan's conjectures concerning phlogiston, including his assertion that phlogiston in its free and uncombined state was in fact inflammable air.⁵⁰ As this paper was primarily concerned to set out his new phlogiston theory and incidentally to rebut the claims of Lavoisier, there is little reference to affinities, and I shall therefore pass over much of its content here.

As I have already indicated, Kirwan did not pursue his approach to the measurement of affinities through accrued density much beyond his tables showing his calculations of the affinities of nitrous and vitriolic acids for water. He stated in the introduction to his first paper that he had been "undeceived" about the relationship between accrued density and affinity.⁵¹ It is not clear at what point he decided that this idea was erroneous. It seems most likely that it was the results of these tables that had led to his rejection of the idea; certainly, they did lead him to modify it, as we have seen. His third paper claimed, perhaps as something of a rhetorical flourish, that he had been led "unexpectedly" to his new theory, which postulated a direct relationship between affinities and combining proportions.⁵² In any event, he moved apparently seamlessly into his new method of quantifying affinities. The third paper, read to the Royal Society later that same year, was avowedly concerned with the

⁴⁷ C. L. Berthollet, *Researches into the Laws of Chemical Affinity*, trans. M. Farrell (New York: Da Capo Press, 1966); C. L. Berthollet, *An Essay on Chemical Statics; with Copious Explanatory Notes, and an Appendix on Vegetable and Animal Substances*, trans. B. Lambert, 2 vols. (London: J. Mawman, 1804).

⁴⁸ Kirwan, "Continuation of the Experiments and Observations."

⁴⁹ Kirwan, "Continuation of the Experiments and Observations," 182–83.

⁵⁰ Kirwan, "Continuation of the Experiments and Observations," 195–96.

⁵¹ Kirwan, "Experiments and Observations," 9.

⁵² Kirwan, "Conclusion of the Experiments and Observations," 38.

quantification of affinities through the comparison of the proportions of substances uniting in combination.⁵³ This did not require any change in methodology. When determining the specific gravities of the alkalis and earths in the second paper, Kirwan had already ascertained the proportions that combined with acids, following the same procedure as he had used in the first paper, that is, adding acid to a solution of a known amount of base drop by drop and checking the results of the mixture using an indicator. In the third paper, Kirwan distinguished between saturation and neutralisation; the latter, in fact, was the point he sought to determine:

A body is said to be *saturated* with another, when it is so intimately combined with that other as to lose some peculiar characteristic property, which it possesses when free from that other . . . if both bodies are saturated, the compound is said to be *neutralized*.⁵⁴

It is perhaps of some interest to note here that in those cases, for example that of magnesia, the earth could not be dissolved in any acid without the addition of heat, which also drove off a proportion of the acid, making it impossible to know how much acid had entered into the combination. Kirwan solved this problem by “precipitating the solutions by another substance, whose capacity for taking up the acids was known.”⁵⁵ Thus he used “a tolerably caustic” fixed alkali to precipitate the magnesia — knowing the quantity of magnesia precipitated, the amount of fixed alkali required to precipitate it, and the amount of fixed alkali that normally combined with each acid, he was able to determine the proportion of acid that combined with a given quantity of magnesia. This kind of reasoning gives us perhaps the clearest indication of why historians of science have tended to link Kirwan’s work to Dalton’s atomic theory as part of discussions of the development of chemical equivalents or combining weights.⁵⁶

Following similar procedures in the third paper (although giving less and less experimental detail), he calculated the quantities of the various acids that were required to “take up” a given weight of each of the metals [including iron, copper, tin, lead, silver, gold (in aqua regia alone), mercury, zinc, bismuth, nickel, cobalt, regulus of antimony and regulus of arsenic]. He pointed out the practical uses that were likely to accrue from a more precise knowledge of the combining proportions of metals and alkalis and acids in this way, and continued:

The end which of late I had principally in view, was to ascertain and measure the degrees of affinity or attraction that subsist betwixt the mineral acids, and the various bases with which they may be combined, a subject of the greatest importance, as it is upon this foundation that chymistry, considered as a science, must finally rest.⁵⁷

Kirwan still saw the doctrine of affinity as the basis of the discipline, but he nevertheless acknowledged that problematic anomalies were coming to light. In many cases,

⁵³ Kirwan, “Conclusion of the Experiments and Observations.”

⁵⁴ Kirwan, “Conclusion of the Experiments and Observations,” 39.

⁵⁵ Richard Kirwan, “Continuation of the Experiments and Observations,” 193.

⁵⁶ See, for example, Henry Guerlac, “The Background to Dalton’s Atomic Theory,” in *John Dalton and the Progress of Science*, ed. D. S. Cardwell (New York: Manchester University Press, 1968), 57–91.

⁵⁷ Kirwan, “Conclusion of the Experiments and Observations,” 34.

such anomalies were due to the operation of double decompositions where only single attractions were expected.⁵⁸ He offered an example:

Vitriolic acid unites to a mild fixed alkali, and expels the fixed air from it, yet it does not necessarily follow, that the vitriolic acid attracts, or is attracted, by the alkali more strongly than the aerial acid; for though there appears here only a single decomposition, yet in reality a sort of double decomposition takes place, the vitriolic acid giving out its fire to the aerial, while the aerial resigns the alkali to the vitriolic; . . . therefore, to ascertain the quantity and force in this matter, it is necessary to ascertain the quantity and force of each of the attractive powers, and denote it by numbers.⁵⁹

Kirwan's introduction of "fire" into these combinations reminds us that, while he believed that free phlogiston could be collected and its affinities ascertained (recall that he believed that inflammable air was free phlogiston), less tangible substances such as the material heat that he called "fire" disturbed the action of affinities in ways that were harder to understand. He drew strongly on Adair Crawford's ideas of specific heat to distinguish between heat held in combination in a body and free, uncombined heat. Combinations and decompositions often required this combined heat to be transferred between substances in quantities determined by their specific heat capacities.⁶⁰ Any resolution of this kind of complex interplay of affinities would have to begin with their quantification. He acknowledged the recent efforts of Guyton and Wenzel in this direction, but complained that Guyton's method could not be "generalized."⁶¹ Anticipating Nicholson's criticism of Wenzel's method (which sought to assign numbers to affinities on the basis of the length of time each acid took to dissolve a particular amount of each substance), Kirwan pointed out that his results contradicted certain "well-known" affinities:

⁵⁸ Kirwan, "Conclusion of the Experiments and Observations," 36. The second paper in the three had, of course, demonstrated that, as metals were compound substances of an earthy calx and phlogiston, so many operations involving metals had now to be regarded as involving more affinities. Indeed, the traditional precipitation of metals from acid solutions by other metals had been shown by Torbern Bergman in 1780 to be largely dependent upon the various affinities of acid and calx for phlogiston. See Torbern Bergman, "Of Metallic Precipitates," in *Physical and Chemical Essays*, trans. Edmund Cullen (London: J. Murray, 1788), vol. II, 354–411.

⁵⁹ Kirwan, "Conclusion of the Experiments and Observations," 36.

⁶⁰ Although it might seem from this that Kirwan believed in some sense that this material heat or fire had affinities of its own and that specific heat capacities were a measure of such affinities, this is not the case. A later paper makes it clear that he appreciated that *all* substances attracted heat, which distributed itself among all substances according to specific heat capacities. But where chemical affinity was elective, heat affinities were equilibrical; the type of displacement that had always epitomised chemical affinity was not an appropriate model for the transfer of heat. See: Richard Kirwan, "Experiments on Hepatic Air," *Philosophical Transactions of the Royal Society of London* 76 (1786): 118–54; and Taylor, "Variations on a Theme," 235–37. See also Boantz, "The Phlogistic Role of Heat in the Chemical Revolution," which discusses Kirwan's use of Crawford's ideas in his phlogiston theory.

⁶¹ C. F. Wenzel, *Lehre Von Der Verwandtschaft Der Körper* (Dresden: 1777); Louis-Bernard Guyton de Morveau, "Affinité," in *Supplément à l'Encyclopédie*, ed. D. Diderot (Amsterdam: 1776–1777).

Tin and regulus of antimony are most rapidly attacked by this acid [spirit of nitre], lead and copper much more slowly; yet it is well known, that its affinity to lead is much stronger than its affinity to tin, and its affinity to copper greater than to regulus of antimony.⁶²

The “well-known” affinities in this case were the affinities of the metals for spirit of nitre based on displacements. Berthollet, too, was to adopt the well-worn tactic of contrasting prediction with observation in his early criticisms of Kirwan’s papers.⁶³

The key to Kirwan’s theory were his new laws of affinity, which related the saturating proportions that he had painstakingly determined to affinities:

First, That the quantity of real acid, necessary to saturate a given weight of each basis, is inversely as the affinity of each basis to such acid.

Secondly, That the quantity of each basis, requisite to saturate a given quantity of each acid, is directly as the affinity of such acid to each basis.⁶⁴

These two laws were intended to fit two different experimental scenarios, the first when the comparison was between quantities of acid and the quantity of base remained constant, and the second when the quantity of base varied while the quantity of acid was constant. Kirwan habitually thought in ratios, about relationships and proportions, rather than absolute quantities, and this facility enabled him to convert affinities into apparently quantified and quantifiable ratios. His two laws can also be expressed as two proportional equations, thus:

$$\begin{aligned} 1. \quad & \frac{\text{Quantity acid}}{\text{Quantity basis}} \approx \frac{1}{\text{affinity basis to acid}} \\ 2. \quad & \frac{\text{Quantity basis}}{\text{Quantity acid}} \approx \text{affinity acid to basis} \end{aligned}$$

It is clear that the two affinities, base for acid and vice versa, would be the same. However, Kirwan’s separation of the affinities in his laws suggests that the distinction was important to him. This perhaps implies that he envisaged the affinity as arising in consequence of the acid’s activity rather than that of the base. His two laws entailed an asymmetry between acid and base: assuming a fixed amount of base, the more acid required for saturation, the smaller the affinity of the base for the acid; on the other hand, assuming a fixed amount of acid, the more base required for saturation, the greater the affinity of the acid for the base. In more general terms, more acid meant less affinity, and more base meant more affinity. The acid is implicitly characterised as more active or aggressive than the base. There is a suggestion that if the acid had a great affinity for a base, it had a greater capacity to “imbibe” it. One of Nicholson’s biting criticisms of Kirwan’s theory was of his unexplained decision to embed this apparently arbitrary inequality therein:

⁶² Kirwan, “Conclusion of the Experiments and Observations,” 37.

⁶³ C. L. Berthollet, “Observations Sur L’eau Régale et Sur Quelques Affinités De L’acide Marin,” *Mémoires de L’Academie Royale des Sciences* (1788): 296–307, on 305.

⁶⁴ Kirwan, “Conclusion of the Experiments and Observations,” 38.

The fundamental assertion, that the attraction of an acid to its basis is proportionate to the quantity it demands for saturation, is so far from being founded upon any argument, that it is evidently nugatory.⁶⁵

As Nicholson pointed out, if the relation of the ratios to the affinities were reversed, so too would be the affinities. Kirwan presumably chose the particular combination that he did because it provided a closer fit with the “well-known” relations of affinities as shown in conventional affinity tables.

It is relevant here to note that Berthollet later adopted the same tactic of explicitly equating proportions with affinities in his *Chemical Statics*, although he inverted Kirwan’s relation. He claimed that the strength of the affinity between a base and a given weight of acid was inversely proportional to the quantity of base required for saturation (i.e. more acid, greater affinity, more base, less affinity).⁶⁶ Thomas Thomson, reviewing this some years later, maintained that considering the question metaphysically, one would be inclined towards Berthollet’s point of view, but that Kirwan’s was more in accordance with observation of the traditional displacement phenomena.⁶⁷ Once again, we have cause to note a feature of Kirwan’s theory that was to resurface in Berthollet’s later hypothesis. Although Berthollet inverted Kirwan’s formulae, the link that Kirwan had forged between combining proportions and chemical affinity was crucial to Berthollet’s later hypothesis, and indeed, in perusing *Chemical Statics*, we find an acknowledgement that Kirwan’s work had “the greatest analogy” with his own.⁶⁸

That this is something of an understatement becomes apparent later in the paper, when Kirwan expanded his quantitative rules, restating his conclusion drawn from his earlier investigations into specific gravity as:

If an acid be united to less of any basis than is requisite for its saturation, its affinity to the deficient part of its basis is as the ratio which that deficient part bears to the whole of what the acid can saturate.⁶⁹

As a particular quantity of an acid’s affinity for a base is satisfied by the addition of more and more base, so its affinity for the remainder of the base necessary for its saturation would decrease. At the same time, however Kirwan noted that “its affinity to the retained part is as its whole affinity.”⁷⁰ This notion is familiar from the first paper and also, although in a less mathematically formal statement, from Kirwan’s notes to Scheele’s *Chemical Observations*, in which he argued that as phlogiston was removed from combination with nitrous acid, changing nitrous air into nitrous vapour, the smaller proportion of phlogiston remaining was attracted more strongly by the acid.⁷¹ Quantitative proportion was clearly inextricable from affinity in

⁶⁵ Nicholson, *A Dictionary of Chemistry*, vol. I, 164.

⁶⁶ Berthollet, *Chemical Statics*, vol. I, 90–92.

⁶⁷ Thomas Thomson, *The History of Chemistry* (London: Henry Colburn and Richard Bentley, 1830), vol. II, 157.

⁶⁸ Berthollet, *Chemical Statics*, vol. I, 90.

⁶⁹ Kirwan, “Conclusion of the Experiments and Observations,” 39.

⁷⁰ Kirwan, “Conclusion of the Experiments and Observations,” 40.

⁷¹ Carl Wilhelm Scheele, *Chemical Observations and Experiments on Air and Fire*, trans. Johann Reinhold Forster (London: J. Johnson, 1780), 211.

Kirwan's theory, as indeed it was for Berthollet twenty years later, and once again, we must suspect that Kirwan's influence was at work on Berthollet.

Kirwan intended his empirically determined figures for affinity to be applied to complex mixtures of substances. Accordingly, he opposed those affinities that would tend to resist decomposition, which he called *quiescent affinities*, to those that would promote decomposition, which he called *divellent affinities*. So, to take his own example:

If the solutions of tartar vitriolate and nitrous selenite be mixed, a double decomposition will take place, a true selenite and nitre being the result of such mixture.

Quiescent Affinities		Divellent Affinities	
Vitriolic Acid to Fixed veget alkali	215	Vitriolic acid to calcareous earth	110
Nitrous acid to calcareous earth	96	Nitrous acid to vegetable alkali	215
Sum of the Quiescent Affinities	311	Sum of the Divellent	325

Hence a double decomposition must necessarily happen.⁷²

Cross-diagrams like Cullen's were no longer needed in this system; they were replaced with simple mathematical comparisons. More emphasis was placed on the quantified affinities of each body in a mixture than on the dynamics of chemical combination. Although each set of affinities competed in a single stage, there was also scope for two-stage processes. Kirwan used the distinction between single affinities and double affinities to draw conclusions about the relative affinities between substances. Referring to an experiment carried out by Antoine Grimauld Monnet, in which a solution of silver in nitrous acid added to a mixture of fixed alkali and common salt produced horn silver (a combination of silver and marine acid), he argued:⁷³

If the nitrous acid had a greater affinity to the free alkali than to the silver, it is evident, that the decomposition would be wrought by the free alkali, and then the silver would be precipitated pure, and not in the state of horn silver.⁷⁴

The diagram in Figure 2 helps to explain his reasoning.

If the fixed alkali that was mixed with the common salt (i.e. "free") had a stronger affinity for nitrous acid than did silver, it would have decomposed the combination between the silver and the nitrous acid (often known as lunar nitre) by single affinity, precipitating pure silver. The common salt would not have been decomposed. As the silver was precipitated in the form of horn silver, a double affinity must have been required to decompose the lunar nitre. In this case, the diagram would be as shown in Figure 3.

⁷² Kirwan, "Conclusion of the Experiments and Observations," 40.

⁷³ Antoine Grimoald Monnet, *Traité De La Dissolution Des Métaux* (Amsterdam: Didot, 1775).

⁷⁴ Kirwan, "Conclusion of the Experiments and Observations," 54.

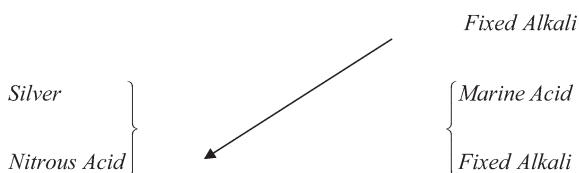


FIGURE 2

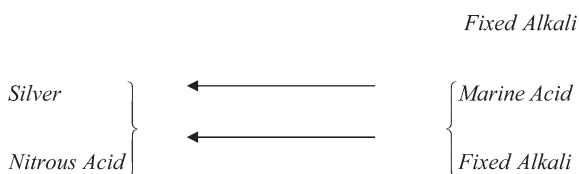


FIGURE 3

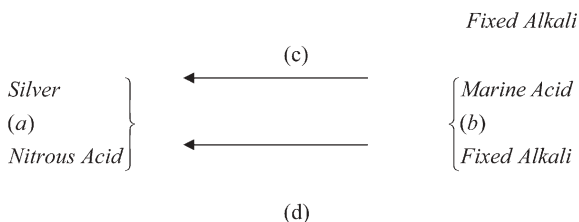


FIGURE 4

Kirwan's claim that the affinity of nitrous acid for silver was greater than its affinity for fixed alkali contradicted most of the affinity tables produced up to this point, from Geoffroy's to Bergman's. He also claimed that the marine acid had a greater affinity for silver than the nitrous acid had for fixed alkali. This claim, which compares affinities that would have appeared in entirely different columns of a traditional affinity table, requires some explanation (Figure 4).

As we know that the double decomposition took place, (c) + (d) (the divellent affinities) must be greater than (a) + (b) (the quiescent affinities). But we also know from the ingenious experiment above that (d) is less than (a). To reach his conclusion, it seems that Kirwan also made use of his knowledge that the affinities of all the acids for vegetable fixed alkali were the same, (d) therefore being equal to (b). On this basis, then, (c) must be greater than (a) and, as (d) is less than (a), (c), the affinity between the marine acid and silver, must be greater than (d).

Kirwan used his notion of the mechanism of combinations to clarify doubts about the orders of his affinities, and incidentally, in this case, solved the problem of comparing entirely different affinities. That this experiment was cited to justify his laboriously quantified affinities does not detract from the importance of the mechanism itself. Although Kirwan did not offer the diagrammatic rationale that I have used, similar assumptions presumably underpinned his thinking. In Kirwan's interpretation of the experiment, he assumed, like many other chemists, that only two

substances could combine at a time, and that where a single affinity was insufficient to decompose a compound, another carefully chosen compound might be successful by double affinity. The postulation of competing double and single affinities in the same mixture of substances was entirely in accordance with his concern throughout to ensure that *all* the various forces present in a mixture were properly accounted for in any explanation of chemical action. This concern enabled him to explain anomalous results by reference to factors such as the excess of one substance, previously unconsidered affinities or the states of aggregation (with particular reference to the role of “fire” in rarefying substances). Similar concerns and, of course, explanations featured in Berthollet’s later thinking.

Reception and influence

Kirwan’s figures for affinities were not received with immediate acclaim. They were included in the second edition of John Elliot’s *Elements*, and George Pearson also included them in his *Translation of the Table of Chemical Nomenclature*⁷⁵ alongside more conventional affinity tables. He admitted that the tables did “not exhibit *numerically*, as was once supposed, the precise forces of chemical attractions,” but argued nevertheless that they were of great assistance in his pedagogical efforts.⁷⁶ Kirwan’s terminology of quiescent and divellent affinities fared rather better. A number of people seem to have adopted these, even if they rejected Kirwan’s methodology and his quantifications.⁷⁷ Nicholson preferred to include Guyton’s conjectural figures in his *Dictionary*, and it would appear that for him, as for many, the figures were unacceptable because Kirwan’s methodology was regarded with disfavour. In particular, the measurements of “real acid” were criticised, with regard to both the concept and its execution. Fordyce was positively scathing in his lectures on the very notion of real acid, calling it a “vulgar prejudice.”⁷⁸ James Keir doubted many of the premises on which Kirwan based his reasoning, writing to Priestley in 1788:

You will find . . . my strictures on Mr KIRWAN’s investigation of the quantity and density of real acid in acid liquors, which, I think, is founded on false principles, but from which he has drawn numberless conclusions, and others have also reasoned from them as admitted truths, and consequently abundance of false reasoning introduced.⁷⁹

⁷⁵ [George Pearson], *A Translation of the Table of Chemical Nomenclature Proposed by De Guyton, Formerly De Morveau, Lavoisier, Bertholet, and De Fourcroy with Explanations, Additions, and Alterations to Which Are Subjoined Tables of Single Elective Attraction, Tables of Chemical Symbols, Tables of the Precise Forces of Chemical Attractions’ and Schemes and Explanations of Cases of Single and Double Elective Attractions* (London: J. Johnson, 1799).

⁷⁶ [Pearson], *A Translation of the Table of Chemical Nomenclature*, 122.

⁷⁷ For example: James Parkinson, *A Chemical Pocketbook* (London: 1800), 217–29; and Jane Marcet, *Conversations on Chemistry, in Which the Elements of That Science Are Familiarly Explained and Illustrated by Experiments* (London: Longman, Hurst, Rees, Orme and Brown, 1806), 12–13.

⁷⁸ George Fordyce, “Notes Taken by Richard Whitfield from Chemistry Lectures,” 1788, MS 58–MS 60, St. Thomas’s Collection, King’s College Library, London, vol. 2, Lecture 36, 24 November 1788.

⁷⁹ A. Moilliet, *Sketch of the Life of James Keir Esq. Frs, with a Selection of His Correspondence* (London: Private Printing, 1768), 83.

Nicholson appears to have included Kirwan's ideas in his *Dictionary* mainly in order to refute them point by point. Nevertheless, he remained hopeful that with greater methodological care and experimental corroboration, future endeavours along similar lines might meet with greater success:

It might perhaps have appeared unnecessary to enter into any discussion of . . . [Kirwan's] attempt . . . if it did not seem highly probable that the numerical expressions of the powers of chemical attraction, whenever they shall be obtained, will be derived from some method dependent on the general facts he then undertook to explain.⁸⁰

It is important to note that most criticism of Kirwan's endeavour was directed not at his implied assumption that the careful measurement of combining proportions might provide access to the hidden explanations of chemical phenomena, but at his hypothesis that these figures could be used to quantify affinities.⁸¹ Berthollet's 1785 critique is the most interesting of these in the light of the striking parallels that I have noted between Kirwan's ideas and his own later thinking in *Chemical Statics*. Like Nicholson, he objected to Kirwan's conclusion that all three acids had the same affinity for fixed vegetable alkali, pointing out that this did not accord with the observations of most chemists on the action of affinities.⁸² As we have seen, though, Kirwan's concept of "real acid" meant that he was endeavouring to explore the hidden reality behind unreliable appearances; to solve what Guerlac called "the problem of transdiction."⁸³ His papers make it explicitly clear that the quantified affinities that he postulated were often hidden or moderated by other factors. He had clarified this distinction between observed and measured affinities by suggesting that the apparently anomalous ability of some acids to decompose the vegetable alkali salts arose from their different capacities for heat, which he sometimes referred to as "elementary fire."⁸⁴ To give one example, he examined a mixture of vitriolated tartar and nitrous acid. Although no change was apparent to the naked eye, a small amount of the salt was found to have decomposed. Kirwan repeated the experiment using nitrous acid of a higher specific gravity, which, according to his theory, contained a higher proportion of "real acid." In this case, the result was more obvious as the temperature of the mixture rose, and the vitriolated tartar was dissolved quickly. From this, he argued:

The nitrous acid having the same affinity to the alkaline basis as the vitriolic, but giving out, during the solution, more fire than was necessary to perform the solution, the vitriolic receiving this fire was disengaged; for as it cannot unite to alkalies without giving out fire, so when it receives back that fire it must quit them. The reason why the nitrous acid, which specifically contains less fire than the vitriolic, gives out so much, is, that its quantity in both these experiments is far greater than that of the vitriolic.⁸⁵

Although the measured affinities between the mineral acids and the fixed vegetable alkali were exactly the same, in this particular experimental situation one acid took

⁸⁰ Nicholson, *A Dictionary of Chemistry*, vol. 1, 164.

⁸¹ Duncan, *Laws and Order*, 209–10.

⁸² Berthollet, "Observations Sur L'eau Régale," 305.

⁸³ Guerlac, "The Background to Dalton's Atomic Theory."

⁸⁴ Kirwan, "Conclusion of the Experiments and Observations."

⁸⁵ Kirwan, "Conclusion of the Experiments and Observations," 46–47.

priority over another; its *observed* affinity for the alkali was stronger. Where the nitrous acid was vastly in excess of the vitriolic acid, the amount of fire that it held outweighed the amount required to restore the vitriolic acid to its uncombined state. Kirwan also showed that when equal proportions were present, the vitriolic acid gave out more specific fire than either of the other acids. This would rarefy either of the other acids sufficiently to expel them from combination and ensure that, in the majority of situations, the vitriolic acid would have a greater “effective” affinity for fixed alkali than the other acids.⁸⁶ This accumulation of forces, and chemical influences within a particular system, formed one of the most fundamental tenets of *Chemical Statics*. Berthollet routinely sought to explain chemical behaviour by recourse to a whole battery of hidden and competing forces, of which affinity was only one, that produced the sensible effects that were observed. In this, too, the influence of Kirwan’s work is clearly present.

As I have indicated above, in spite of his 1785 criticism of Kirwan’s idea that combining proportions were proportional to affinities, Berthollet later adopted the very same hypothesis in his own work. Kirwan’s claim that changes in the proportions of substances present in a mixture led to a variation in the affinities was also notably espoused. But perhaps even more significantly, Kirwan’s explanatory tactic of including a variety of possible moderating or competing forces in his explanations of chemical action can be seen replicated a hundred-fold in *Chemical Statics*. Somewhere between 1785 and the first years of the nineteenth century, Berthollet began to make use of all of these facets of Kirwan’s affinity theory. In particular, in contradiction to his own early criticisms, *Chemical Statics* aped much of Kirwan’s earlier strategy, as it sought to unravel the complexities of chemical action by positing a variety of hidden forces to explain observational anomalies.

Conclusion

I referred above to Guerlac’s brief inclusion of Kirwan’s work in his list of Daltonian precursor theories.⁸⁷ Guerlac includes both Kirwan’s and Higgins’s ideas in his list, although he glosses both to argue, against tradition and a number of his contemporary historians, that Dalton was influenced by the work of the German chemist J. B. Richter.⁸⁸ Guerlac had first mooted this claim in a paper published in *Isis* in 1961, specifically against the arguments of Dalton’s early biographers, and had set off a debate that was still ongoing in 1968. In ascribing influence, Guerlac sought to show little more than that Dalton might have seen Richter’s table of equivalents. He seems to have taken the relevance of Richter’s table to Dalton’s atomic theory for granted.

⁸⁶ Kirwan, “Conclusion of the Experiments and Observations,” 44–45.

⁸⁷ Guerlac argues that observation of the action of chemical affinity offered the best opportunity to solve the problem of transduction, and it was after a long history of attempts to link the unobservable entities postulated with the observable behaviour of different substances that Dalton eventually arrived at his New System. See Guerlac, “The Background to Dalton’s Atomic Theory.”

⁸⁸ Henry Guerlac, “Some Daltonian Doubts,” *Isis* 52 (1961): 544–54; Henry Guerlac, “Quantification in Chemistry,” *Isis* 52, no. 2 (1961): 194–214; R. Siegfried, “Further Daltonian Doubts,” *Isis* 54 (1963): 480–81; Arnold Thackray, “The Origin of Dalton’s Chemical Atomic Theory: Daltonian Doubts Resolved,” *Isis* 57, no. 1 (1966): 35–55; Arnold Thackray, “The Emergence of Dalton’s Chemical Atomic Theory: 1801–1808,” *British Journal for the History of Science* 3 (1966): 1–23; Siegfried, “Further Daltonian Doubts.”

Among the responses offered, however, Arnold Thackray argued that Dalton could not have been influenced by Richter, whether or not he had seen his work before he formulated his theory, because they were in fact doing different things.⁸⁹

This perhaps emphasises just how complex our notion of influence is. It is not just a matter of showing that one actor had reason to be aware of the work of an earlier one that *we* might consider to have been similar. There is also the vexed question of whether or not the actors themselves would have considered the earlier work to be relevant to their own. Prevailing historiography would tend to link Kirwan's work to notions of definite combining proportions, settling him on the Proust side of the Berthollet–Proust debate. Although it is not unreasonable for historians of today to see Kirwan's affinity theory as a precursor of the theories of chemical equivalents or atoms of the next century, we do not find that these aspects of his theory were celebrated at the time, and nor did Kirwan present his theory in this guise. Only a few aspects of the theory set out therein were adopted by his contemporary chemists, and many aspects of his quantifying methods were roundly criticised. The question of Kirwan's influence on atomic theory is therefore a difficult claim to particularise. As I have shown, though, we can point to clear and distinct evidence that Kirwan's work had a deep influence on Berthollet's great work on chemical affinity. To answer my earlier question, then, yes, Kirwan's work on affinity was important in the history of chemistry through its undoubted influence on Berthollet's *Chemical Statics*. The next question, of course, concerns the influence of *Chemical Statics* on nineteenth-century chemistry. That question can only be answered, as I have answered this one, by taking small steps.

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⁸⁹ Siegfried, "Further Daltonian Doubts"; Thackray, "The Origin of Dalton's Chemical Atomic Theory."