VARIATIONS ON A THEME: PATTERNS OF CONGRUENCE AND DIVERGENCE AMONG 18TH CENTURY CHEMICAL AFFINITY THEORIES

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I, Georgette Nicola Lewis Taylor, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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Abstract

The doctrine of affinity deserves to be recognised by historians of chemistry as the foundational basis of the discipline of chemistry as it was practiced in Britain during the 18th century. It attained this status through its crucial structural role in the pedagogy of the discipline. The importance of pedagogy and training in the practice of science is currently being reassessed by a number of historians, and my research contributes to this historiographical endeavour. My analysis of the variety of theories sheltered under the umbrella term 'affinity theory' has emphasised the role of pedagogy in influencing both the structure and the content of knowledge. I have shown that there were wide ranging discrepancies between many of the components of individual affinity theories. Nevertheless, the scope of divergence was limited. This underlying organisation resulted from the unifying hub of affinity theory, the logical common ground. This was the essence of the doctrine of affinity, encompassing the law of affinity and the conceptualisation of the table that brought together the relations described in the law. The doctrine of affinity thus provided a disciplinary common ground between chemists, providing a mediating level of understanding and communication for all those who subscribed to the doctrine of affinity, in spite of their detailed differences.

1. 'Manufacturing a Theory': The Doctrine of Affinity in 18th Century Chemistry

1.1 Introduction

Historiography of 18th century chemical affinity has not been characterised by consensus. Historians have disagreed widely about the significance and role of affinity within 18th century chemistry and their controversies testify to a significant gap in our understanding of the subject. A clue taking us to the heart of the puzzle can be found in the fact that while historians commonly refer to 'affinity theory', philosophers of the time as often alluded to the 'doctrine of affinity'.[1] The word 'doctrine' might refer to a *system* or *complex* of theories, of laws, tenets or principles; it might even refer to a *whole science*. My research shows that affinity encompassed more than just a single theory; the primary sources point to a multiplicity of positions held. Nevertheless, secondary literature has generally assumed a single theory model of affinity to be appropriate. Historians have largely failed to explore this theoretical variety, and I suggest that it is this lack of appreciation of the theoretical diversity that is responsible for the lack of historiographical harmony.

The word 'doctrine' offers further clues for the alert historian. Etymology points towards a pedagogical, didactic link; to quote Samuel Johnson's *Dictionary* (published 1755), it referred to "the principles or positions of any sect or master, that which is taught".[2] My study confirms the close links between affinity theories and chemical pedagogy. Affinity theories came to prominence in Britain as pedagogical tools, were disseminated via a pedagogical pyramid and were subject to the vagaries that necessarily accompanied this type of context. In this sense, they were indeed doctrinal.

This study is intended to perform two distinct but related tasks. The first is to explore in detail the variations and conformities prevailing amongst British affinity theories. This is accomplished through a 'decomposition' of theories into their constituent components and a comparison of each component with others that performed similar functions. This analysis also serves to highlight

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[1] Elliot 1786, Lewis 1753, Alcock 1750.

[2] Johnson 2002, 142.

the predominantly tacit components that were consistent, that formed the logical common ground on which each individual theoretical edifice was built. The second task, accomplished in a more diffuse fashion, is to explore in general terms the way in which chemists used their theories and the roles allocated to them, to try to elucidate what made these theories valuable as part of the chemistry of the 18th century. This enables me to offer a more nuanced account of the use and development of the doctrine of affinity in Britain than has so far been available.

1.2 Some Preliminary notes about Language

1.2.1 'Affinity'

Etymological concerns have plagued chemical theories of affinity from their beginning. Individuals made their own choice of term to adopt: affinity, rapports, attractions, elective attractions, and so on. These decisions were, more often than not, based on negative associations; choices were made in preference to an alternative, disfavoured term rather than on the basis of inherent suitability. The choice of term was often perceived as conferring unwelcome metaphysical associations: those who referred to attraction were revolting against the use of the word 'affinity' and its connotations, while those who preferred 'affinity' in turn objected to the ontological implications of 'attraction'. Etienne François Geoffroy, who produced the first affinity table, adopted the term 'rapports', presumably in order to avoid any connotations at all,[3] but this line was not pursued by anyone else.

Historians have long been alert to this phenomenon and have tended to assume an identity of expression and philosophy. In many cases this simple equation may well be appropriate, but in others it is somewhat facile. Moreover, an over-zealous focus on the choice of term over-emphasises the role of metaphysics in affinity theories. My research shows that the doctrine of affinity was not tied to any particular matter theory, metaphysic or ontology. Affinity theories explained and guided macroscopic chemical operations and it is on this level of functionality that my study is focused. Whilst, like Geoffroy, I would wish to

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[3] Duncan 1996, 111.

avoid giving rise to tacit assumptions, the use of the word ‘rapports’ would be inappropriate in a study of British chemistry, and the alternatives ‘attraction’ or ‘elective attraction’ still resound with obvious metaphysical connotations. ‘Affinity’, on the other hand, suffers less in today’s English language from such associations. Accordingly, I have chosen to use the latter term, except when quoting from sources. I must emphasise, however, that my use of ‘affinity’ is on a purely nominal basis. I am fully aware that a number of my actors would not have described their theories so – although they would have recognised all the different terms as essentially signifying the differing tendencies of individual substances to combine together. But for the sake of clarity and brevity, such a measure is necessary. When speaking of an individual’s particular configuration of all their chosen components of affinity, I refer to their ‘affinity theory’.

1.2.2 **‘Chemists’**

Modern historiography teaches us to be uncomfortable with the use of the word ‘chemist’ to describe many of those 18th century natural philosophers who practised or taught chemistry. There is a general feeling that such usage is anachronistic as they would not have described themselves so.[4] On the other hand, it is not always clear how they would have described themselves, whether as physicians, lecturers, chemical philosophers or natural philosophers.[5] Many used the term ‘chemist’ somewhat pejoratively, referring to the ‘sooty empirics’, artisans who were socially, if not intellectually, beyond the pale. On the other hand, Johnson defined a ‘chymist’ as “a professor of chymistry; a philosopher by fire.”[6]

As he also defined a ‘professor’ *inter alia* as “one who publickly practices or teaches an art”,[7] to Johnson at least, most of my actors, public practitioners and teachers of chemistry as they were, would be quite reasonably described as ‘chemists’.

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[4] On anachronism see, Jardine 2000. The canonical text is Skinner 1969.

[5] Joseph Black’s Will described him as “physician in Edinburgh and professor of Chemistry in the University of Edinburgh” Black 1800.

[6] Johnson 2005 “Chymistry”, 129.

[7] Ibid, “Professor”, 455.2.

This is not to deny that there are undoubted historiographical difficulties with applying the term ‘chemist’ to many of my actors; these difficulties are fully admitted. However, it is only limitedly anachronistic, as the term itself would have been familiar, whether or not they would have so described themselves. My actors were all content to state that the discipline they practiced and often taught was ‘chemistry’. This term too is bound up with expectations and assumptions about disciplinary status and autonomy. Although it was taught as an adjunct to a medical training, William Cullen’s lectures accorded chemistry the status of a distinct discipline, with its own history and practices.[8] If disciplines are indeed “regimes of organized behaviour inculcated and appropriated in educational institutions”[9] then it was through the efforts of Cullen and his successors that chemistry attained disciplinary status. For this reason, as well as for the sake of simple readability, I have chosen to dub them ‘chemists’. This emphasises the fact that it is my actors’ chemical theories and beliefs that are the subject of my study, rather than their whole lives or works. Cullen, for example, could variously, and legitimately, be described as an apothecary, surgeon, physician, professor, philosophical chemist, and natural philosopher, as well as father, brother, rival, friend and colleague. So far as this thesis is concerned with Cullen, it is solely with his adventures in the chemical realm. The Cullen appearing in the following pages is Cullen the chemist, and Cullen the chemist alone. The same applies to my other actors. My chosen classification serves to emphasise this fact, as well as contributing substantially to the concision and intelligibility of what follows.

1.3 **The Historiography of Affinity**

It is something of a truism that there are as many different ways of ‘doing’ history as there are historians. Similarly, it is probably unnecessary to point out that the context dictates (at least in part) the history presented. The doctrine of affinity makes an appearance in almost every study of 18th century chemistry, whatever the focus, but it is rarely clear why it was so prevalent or what its role in the discipline actually was. It has taken the lead role in several narrowly

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[8] Christie 1994.

[9] Jardine 2000.

focused developmental studies, with a number of historians devoting themselves to 'two handers' exploring its nativity in particular.[10] It has also taken supporting roles in more general topic research into such matters as chemical tables, Newtonian chemistry or the chemical revolution. Finally, it has appeared in walk-on parts in even more general works on the history of chemistry.

Each of these contexts imposes different limitations on the historiography, and in many cases these limitations have resulted in a distortion of the picture. To begin with the last category, the 'sweep of history' approach has inevitable and well recognised shortcomings. In the case of affinity theory, as one of the 'two pillars'[11] of 18th century chemistry it is rarely omitted from general histories of the discipline, but it is most usually represented by Geoffroy's 1718 *Mémoire* alone, without regard for the array of theories that succeeded it. It is unclear what role affinity took in chemistry, and why (or indeed if) it was perceived to be important. Perhaps more importantly, the practical demands of such a panoramic view obscure detail and elide difference. My research indicates that affinity theories demonstrated complex patterns of convention and divergence, but these patterns are, perhaps inevitably, imperceptible when seen through the wide-angle lens necessary to produce this type of history. Most such commentary refers to an undifferentiated 'affinity theory'; this is what I term the single theory model.

That the single theory model is problematic is particularly apparent when we consider the fact that Geoffroy's *Mémoire* is commonly adopted as the single theory of the model. In general histories of chemistry, the 1718 paper appears as regularly as clockwork between Newton and Stahl and Lavoisier.[12] But Geoffroy's table, although the first, was by no means the only affinity table produced, and likewise his affinity theory was the first of many. Although it was only in the latter half of the 18th century that affinity became truly

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[10] Klein 1994, Klein 1995, Klein 1996, Holmes 1996.

[11] Eklund 1971, 96.

[12] See, for example, Partington 1989, Brock 1992, Levere 2001, all of which refer to the theory of affinity. The theory inevitably forms a far larger proportion of studies specifically devoted to 18th century chemistry.

ubiquitous, the historiography is clearly biased in the opposite direction: towards Geoffroy, and away from those later chemists who adopted and utilised the doctrine.

The inaccuracy of this model has been appreciated by many historians, including Levere, who describes affinity as adopting "protean shapes" throughout its history:

> "It was flexible enough to be useful in the most varied contexts, but its precise meaning was far from universally agreed."[13]

Perrin too has noted the lack of consensus with regard to affinity.[14] In spite of this appreciation of the problem, no solution has been proposed, and indeed it is questionable whether any solution is possible. My work adopts a new mode of theory analysis to delineate the variety within the doctrine of affinity and to distinguish the common components that characterised affinity theories as a class. This 'logical common ground', I would like to suggest, offers a new exemplar for describing in broad brushstrokes the doctrine of affinity, and perhaps a new solution to the familiar dilemma of the panoramic view.

Narrowing the historiographic focus complicates matters further. Contributing to the problem is the fact that 18th century chemistry is so often seen as transitional, lacking a unified character of its own. Falling as it does between two scientific revolutions, tales of Newtonian assimilation dominate studies of the first half of the century, while those of the latter half are concerned in the main with the great changes to come. These two paradigm shifts tend to be smeared like grease across the historical lens, resulting in a soft focus view of events that obscures detail and subordinates affinity to the overriding narrative. Hence the tendency to Newtonianise affinity evident in the works of Thackray, Cohen and Crosland,[15] and a similar over-emphasis on a monolithic phlogiston theory in many of the more popular accounts of the chemical revolution.[16]

Holmes has roundly criticised the historiography of affinity, arguing that a

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[13] Levere 1971, 1.

[14] Perrin 1988, 60.

[15] Crosland 1959, Crosland 1963, Thackray 1995, Thackray 1970, Cohen 1964.

[16] Affinity is notably absent from Hankins 1985 for reasons which are far from clear.

present-centred concentration on certain narrative themes has resulted in an unjustifiable emphasis on affinity to the detriment of more crucial aspects of 18th century practice.[17] He cites Crosland's 1963 paper "The Development of Chemistry in the Eighteenth Century" as the first to demonstrate such an unwarranted emphasis, ascribing historical importance to affinity as a precursor to the ordered and predictive sciences of later periods.[18] The theme of order emerging out of chaos through the quantifying of chemistry is indeed a popular one.[19] The implication that chemistry was not a science until it was quantified overwhelms the historiography of affinity, leading historians to canter from Geoffroy to Berthollet without stopping for breath.[20] But this results in little or no understanding of where affinity fitted into the practices of chemists. How were the theories used, if indeed they were used at all? Were affinity tables and theories useful, or simply decorative?

Crosland's 1963 paper also formulates an equation that has since become familiar, linking affinity and Newtonianism:

> "One might say that every chemist who spoke of chemical attraction was an atomist, since the theory of attraction presupposed elementary particles of matter between which the attraction took place."[21]

Thus Crosland subordinates affinity to the Newtonian influence, implying that a particulate view of matter was essential to such a theory. Schaffer has drawn attention to the fact that traditional historiography has taken as its basis the 'Newtonian' unity of 18th century natural philosophy, arguing that this is in fact a "profoundly unhistorical" practice.[22] He goes on:

> "Contrasting developments, … are pictured as so many deviations from a 'Newtonian' norm."[23]

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[17] Holmes 1989.

[18] Crosland 1963.

[19] Guerlac 1968 describes a historiographical trail from Newton to Dalton via affinity although Guerlac doubts Geoffroy's Newtonian credentials.

[20] See e.g. Partington 1989, 322-325 which identifies Geoffroy's affinity as directly precursory to Berthollet's mass action, and the physical chemistry of the next century.

[21] Crosland 1963, 377.

[22] Schaffer 1980, 56.

[23] Ibid.

As Kuhn has made clear, the identification of a ‘Newtonian’ chemistry is itself problematic. He argues that chemists resorted to a stratagem of inhering Newtonian forces in chemical substances, resulting in an ontology that was contrary to Newton’s own intentions:

> “Newton himself had denied the chemical specificity of the ultimate atoms which composed the mechanical universe. But the eighteenth century Newtonian chemists … emphasized instead the attractive and repulsive forces which he had hypothesized to govern the interactions and accretions of the *minima*. In spite of Newton's explicit disclaimer, these forces were, in the eighteenth century, usually taken to be inherent in the material corpuscles whose behaviour they governed. They became “occult” forces which determined the characteristic properties of the various chemical substances.”[24]

These affinities, in the form of distinctively chemical “forces” differentiated substances from each other. This is often interpreted by historians as the Newtonisation of chemistry, but Kuhn has rightly described it in terms that suggest instead the chemicalisation of Newton.

More generally, the assumption that affinity was only associated with a particulate metaphysic is open to question, as Eklund has pointed out:

> “Although affinity theory has often been associated with corpuscular ideas, it need not be. True, the idea of affinities or attractions between particles was occasionally used, but most eighteenth century discussions on affinity spoke simply of the attraction between substances or parts (components) of substances in a general, indeed, vague manner".[25]

In fact Crosland seems to have revised his viewpoint more recently, arguing that there were alternative spectacles through which to view affinity:

> "Indeed one did not have to be an avowed Newtonian in order to accept a vaguer but probably more useful concept of affinity which meant simply that if a reaction AB + C = AC + B took place, this was an indication that the affinity of A for C was greater than that for B."[26]

The purported link between affinity and Newtonianism is particularly prevalent

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[24] Kuhn 1952, 35.

[25] Eklund 1971, 137.

[26] Crosland 1980, 397.

in those works which explore the history and development of matter theories. These works tend to regard the doctrine of affinity as subordinate to the ontologies that are their primary investigative concern. Unfortunately they do not only make this assumption for themselves, but for the historical actors as well. Reductionism is superposed on the past, as it were.

Thackray's *Atoms and Powers* sought to counter what he saw as the excessive bias of 19th century historiography against Newtonian influence; he saw his work as:

> "a recovery of the dominating influence of Newtonianism in all its forms"[27]

However, the result of this approach has been a similarly unwarranted bias in favour of Newtonian influence. Thackray's study persists in the assumption that the use of affinity theory implied a Newtonian stance; as (according to him) the first table was a Newtonian artefact, so too must be all such tables and associated hypotheses. This contention results in an overcompensation, the assertion that affinity was initially and remained throughout the century a Newtonian phenomenon, a clear example of an erroneous single theory model. Klein has criticised Thackray's argument, and in particular his failure to prove his thesis by a detailed comparison of Geoffroy's table with Newton's Query. Her own meticulous research has demonstrated that Thackray's thesis is empirically under-determined.[28] I would add to this my own methodological criticism, that wherever Geoffroy's own philosophical allegiances might have lain, they cannot be simply assigned to the doctrine of affinity wholesale. While it is undoubtedly fair to say that many chemists would have perceived a link between Newton's natural philosophy and affinity,[29] any assertion that the association was fundamental to the doctrine is both unfounded and misleading. The variety of specific theories, practices and assumptions encompassed by the doctrine of affinity over its long life preclude any such facile judgements being made.

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[27] Thackray 1970, 3.

[28] Klein 1995, 81.

[29] Indeed, Cullen was one of those who saw such a connection, although his preferred version of Newton's ontology was aetherial. See below for further detail.

The very variety and malleability of affinity theories, the feature which enabled their persistence into the 19th century, might thus have proved their historiographic downfall. One or other affinity theory can be slotted into place in most of the favoured narratives, as indeed one or other matter theory can be incorporated into the doctrine. Thackray's single theory model leads him to label Geoffroy as a Newtonian, a label that has been challenged by both Schofield and Smeaton.[30] Schofield argued that:

> "Geoffroy had not spoken of attraction. The word he used was "rapports" and the context of his work was elementary and Stahlian, not mechanistic and Newtonian."[31]

Thackray's claims are not without precedent; Cohen also argued that Query 31 provided the impetus for the 1718 paper.[32] Klein has disposed of this argument too on empirical grounds but unfortunately, this type of historiography is self-replicating, as can be seen from Lundgren's recent discussion of quantification in 18th century chemistry.[33] Lundgren refers unquestioningly throughout to affinity as a Newtonian development, and Geoffroy as a Newtonian chemist.[34] Thackray, Cohen and Schofield are keen to brand Geoffroy himself, and by extension, his table (note that Schofield replaced 'Newtonian' with 'Stahlian'); to align the "seminally important"[35] affinity with one or other of the systems available to chemists of the time. But where Thackray argues that affinity was always and everywhere Newtonian, Schofield's *Mechanism and Materialism* demonstrates an implicit grasp of the diverse nature of affinity. He writes:

> "During much of the eighteenth century there were persistent attempts to relate affinities … to Newtonian forces of gravity, capillarity, or cohesion. Many of the most distinguished European natural philosopher chemists … were active in these efforts, but many more decried even the term "attraction" and retained the Stahlian aversion to mechanical assumptions. Most British chemists belonged to the latter group, agreeing with William Lewis that affinities were just those "laws of another

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[30] Schofield 1970, Smeaton 1971.

[31] Schofield 1970, 216.

[32] Cohen 1964.

[33] Klein 1995, 81-82.

[34] Lundgren 1990.

[35] Thackray 1970, 90.

> order" than mechanical which distinguished chemistry from the mechanical philosophy."[36]

Schofield accepts that the doctrine of affinity allowed for differing views of matter. As his interests lie elsewhere, Schofield does not explore the divergence any further, but his work does make clear that affinity, like Newtonianism itself, was not a single theory, but allowed for some differences of opinion within the framework of its doctrine. Nevertheless, Schofield's work implies that the only basis for a taxonomic classification of affinity theories lies in their philosophies. This historiographical stance has been criticised by Christie and Golinski who have pointed out that:

> "much historical work seems to assume that matter theory is in some uncomplicated way fundamental to chemistry, serving as the 'philosophical basis' for the thoughts and actions of any self-conscious chemist. Our historiographical approach is obviously not in sympathy with this position."[37]

Nor, as my work shows, is mine. My research has confirmed that this criticism is justified. The strength of affinity theories lay in the fact that they were able to guide and assist the chemist whatever his ontological commitments. While matter theories may not have been irrelevant to the way in which chemists understood their affinity theories, it is clear that the latter were intended to deal with the sensible macrophysical world that chemists inhabited and manipulated. My study approaches the doctrine of affinity from this point of view, and it results in a more accurate depiction of the role of affinity theories in the practice of chemistry than do those studies that seek to embed such theories in matter theoretical speculations.

Narrowing the focus of the historian's field of vision still further, we begin to find a focal distance at which the single theory model is appropriate. Some historians have touched on the affinity theories of particular chemists as part of biographical investigations.[38] Most notably Donovan, Golinski and Christie have all discussed Cullen's affinity theory to some degree, while Sivin has

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[36] Schofield 1970, 216.

[37] Christie and Golinski 1982, 246.

[38] See, for example, Donovan 1975 which briefly discusses Cullen's affinity theory, and Crosland 1959 which examines both Cullen and Black's development of their affinity theories to include diagrams which Crosland sees as early 'equations'.

examined that of William Lewis.[39] In terms of unpublished works, Eklund, Scott and Crellin have also touched on the affinity theories of particular British chemists as subsidiary elements to their primary theses.[40] A single theory model poses no significant problems when dealing with an individual's theory of affinity in this way, as, for example in Klein's excellent papers on the origins of Geoffroy's table.[41] Klein has carried out the most enlightening research on the development of Geoffroy's affinity table, examining the traditional craft knowledge from which the relations included in the table originated and why Geoffroy chose the particular array of substances that he inserted in his columns and rows.[42] Her analysis shows that Geoffroy's table articulates a novel concept of the chemical compound as composed of homogeneous, 'pure chemical substances', not necessarily elemental, but sufficiently simple for recovery from combination.[43] As I have already indicated, Klein argues strongly against the automatic coupling of the affinity table with the Newtonian research programme, stressing that while the experimental basis of the table was not new, the novelty lay instead in the abstraction from social and theoretical context to create new ideas of composition and combination. These ideas of composition and combination were essential to the concept of affinity and to the affinity table, which can thus be seen as a marker of chemistry's disciplinary development.

As I mentioned above, Holmes[44] argued that affinity tables should be seen as but one facet of the chemistry of salts which formed the chemical research programme of the Académie des Sciences in the first half of the 18th century. Like Klein, Holmes focused on Geoffroy's theory alone, adopting the single theory model. Nevertheless, controversy arose between Klein and Holmes concerning Geoffroy's theory of affinity. As Klein points out, the contents of Geoffroy's table were not restricted to neutral salts, covering also various

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[39] Golinski 1992, Christie 1993, Christie 1983, Donovan 1975, Donovan 1982, Sivin 1962.

[40] Crellin 1969, Scott 1979, Eklund 1971.

[41] Klein 1995, Klein 1996, Klein 1994.

[42] Klein 1996.

[43] Ibid, 268-274.

[44] Holmes 1989, Holmes 1996.

sulphides, alloys and amalgams. Klein and Holmes differ too in their evaluations of the novelty of Geoffroy's theory of affinity. It is clear that even in arguments where the single theory model is not inappropriate, its adoption does not necessarily result in harmony between historians. Nevertheless, both Klein's and Holmes's analyses are percipient. Although they differ in their details, there is an underlying correspondence as both essentially claim that the phenomena that Geoffroy tabulated were familiar, not to say commonplace, within his milieu.

Latterly, Klein's work has focused on the roles of 'paper tools' in chemistry (predominantly the formulae of Berzelius, but affinity tables too fall into this category).[45] Her analysis emphasises the correspondences between affinity tables and the actual practice of chemistry, an emphasis that is timely. Where she has led, others have quickly followed, and a number of more philosophical studies of the practices of visual representation epitomised in affinity tables have appeared in the past few years.[46] This approach seems to put the problems of the single theory model of affinity into abeyance, and might be termed the 'no theory model'. Lissa Roberts has adopted this model, arguing that the affinity table epitomised the pre-revolutionary state of chemistry as a practice that had yet to become a science.[47] Roberts has studied the affinity tables of Geoffroy, Guyton and Bergman which, she argues, functioned as "a theoretically neutral accrual of matters of fact".[48]

Following this evaluation, that affinity tables were simply synoptic collections of chemical facts, she contrasts them with Lavoisier's table of simple substances, and the table of chemical nomenclature which embodied:

> "highly specific categories based on processes, such as oxygenation, which spread out to organise the investigative understanding of nature through a set of predetermined research projects."[49]

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[45] Klein 2001a, Klein 2001b, Klein 2001.

[46] See e.g. Cohen 2004, Spector 2003b, Spector 2003a.

[47] Roberts 1991.

[48] Ibid, 131.

[49] Ibid, 102.

Roberts's assessment depends for its accuracy on the evaluation of affinity tables as being 'theoretically neutral', and this point is far from proven. Moreover, theoretical neutrality must not be confused with lack of theory. Whilst I would agree with the ascription of neutrality, as my research shows, affinity tables were far from atheoretical. The strength of affinity lay in its potential compatibility with a variety of ontologies and metaphysical systems while still providing a common ground on which chemists could meet. Affinity tables may have purported to represent empirical facts without theoretical bias, but their creation, expansion, pedagogy and use, as I show below, were guided and determined by theoretical assumptions. The conclusion that Roberts draws from her comparison of affinity tables with Lavoisier's table of simple substances suggests that her tacit definition of theory is perhaps a little narrow. Lavoisier himself presented his tables as theoretically neutral, and it requires a deeper probe to draw out the level of implicit theory proposed by Roberts.[50] This narrative of discontinuity is difficult to accept as it seems to accord certain assumptions embedded in Lavoisier's tables the status of theory, while similarly implicit assumptions inherent to the use and intentionality of affinity tables are denied the same status.

Finally in my taxonomy of affinity historiography, I reach perhaps the most important works. Affinity has taken the leading role in larger scale thematic studies by Duncan, Levere, Goupil, Tsukahara and more recently Kim.[51] While Levere's excellent work only picks up the story of affinity from 1800 onwards, his introductory chapter deals with earlier centuries. His comments, brief though they are, are insightful, and clearly appreciative of the multiple-theory nature of affinity (see above) and it is perhaps to be wished that he had extended his chronological scale to cover the 18th century in detail.

Tsukahara's analysis of the introduction of western chemistry into Japan allots affinity a defining role in the teaching of chemistry in 19th century Japan. My

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[50] See Lavoisier 1965, 177 and Duncan 1970, 34 where Duncan argues that Lavoisier's table of simple substances was in the same tradition as affinity tables, "avoiding the dilemma between the need to avoid speculation and the need to bring the facts of chemistry into order by producing an orderly system which emerges naturally from the facts themselves".

[51] Duncan 1988, Duncan 1962, Duncan 1981, Duncan 1970, Duncan 1996, Levere 1971, Goupil 1991, Tsukahara 1993, Kim 2003.

study, although focused on 18th century Britain, similarly highlights the fundamental role of affinity in chemical pedagogy.

The works of Duncan, Goupil and Kim cover a wider chronological span than the 18th century, in the case of Goupil tracing the origins of the concept of affinity back to the 16th century. All three are concerned with tracing the conceptual development of the concept of affinity in Europe.

Perhaps the most comprehensive study of affinity is provided by Duncan's 1996 work, which provides a detailed survey of affinity tables, discussing their prehistory and development across Europe over the 18th century and into the 19th.[52] He argues that affinity tables reflected changes in 18th century chemistry as tabulated synopses of empirical observations with little or no underlying theory, and that this theory-free status was their strength.[53] As chemical discoveries mounted, so too did the empirical observations that could be tabulated. His study concentrates on the science behind the affinity tables, the reasoning that led substances to be included or removed, the search for operational regularities. The affinity table is, in his view, a passive reflector of assumptions from outside the domain of affinity. This approach implies, of course, that a careful comparison of affinity tables will result in a progressive story of operational discovery and development in chemistry as a whole, and this is indeed what Duncan's work offers. This work can rightly be described as the bible of the researcher in affinity theory. Duncan's list of the affinity tables published is undoubtedly without equal, and his discussion of the specific differences between them is comprehensive. Nevertheless, the simultaneous breadth and narrowness of focus of his study, discussing both the general developments in chemical theory and the specific additions and subtractions to individual affinity tables leaves many questions of utility, context and practice unanswered. His assumption that affinity tables simply mirrored changes in the discipline leaves them somehow emasculated. As I show below, affinity theories and their tables provided the foundations upon which a coherent discipline of chemistry was built in Britain. They were both important and

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[52] Duncan 1996.

[53] See also Duncan 1988, Duncan 1962, Duncan 1981, Duncan 1970.

useful, enabling and driving chemical practice through their associated theories. While Duncan's treatment, in effectively denying the existence of any affinity theory avoids the trap of the single theory model, it also obscures such important factors as the role of pedagogy in establishing the doctrine of affinity as the basis of the discipline.

I am not seeking to argue that such historians as Thackray, Roberts and Duncan are or were absolutely wrong in their assertions. I do, however, share Schaffer's view that any historical representation of a unified natural philosophy is a mis-representation.[54] Any attempt to label or class the doctrine of affinity as a whole ignores the fact that individual chemists devised their own distinct varieties of affinity theory.

Most recently Mi Gyung Kim has discussed the role of affinity in French chemistry in detail, adopting a novel 'genealogical' historiography that has proved extremely successful.[55] Her study affords a clear indication of the breadth of influence and omnipresence of the doctrine of affinity in 18th century French chemistry. Kim draws out of key chemical texts the details of their authors' discourse on what she calls the theory domains of composition and affinity. She follows the articulation and formulation of the theory domains of affinity and composition in the early 18th century, their stabilization, fracture and rehabilitation. Kim delineates how chemists structured their discourse, managing the three layers of philosophy, theory and practice, often implicitly, to stabilise each domain. A picture emerges of a system rarely in equilibrium, with each layer compelling change in the others. Her tactic of examining texts emanating from each chemist separately serves to highlight the differences between their views on affinity as well as their correspondences. Her analysis demonstrates throughout an understanding of the necessity of adopting a multiple theory model of affinity. This understanding permeates the structure of her work and her research tactics, and the multiple theory model is allowed to guide the structure of the work, rather than being subordinated to narrative concerns.

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[54] Schaffer 1980, 70-71.

[55] Kim 2003.

One of the most notable facts about all these previous studies is that they have not dealt in detail with the British experience of affinity. Kim's survey admirably sets out the development of affinity theory in France, but apart from the inclusion of Richard Kirwan, (whose work was influential on French chemists), she does not venture across the English Channel. Similarly, those studies that have dealt with Geoffroy's formulation of his theory focused with the Parisian context in which it was produced. Affinity theories of certain British chemists have been discussed by those historians investigating their lives and works,[56] but no specific comparison has been made of the variety of British theories in circulation. The particular reason for this neglect is not clear, although there has long been an undoubted bias in historiography of 18th century chemistry towards French chemistry, which, perhaps basking in the reflected glory of Lavoisier, seems to have been regarded as more exciting and rewarding of study. Those chemical developments that originated in Britain (and in fact there were many) have tended to be viewed in contrast as anomalous, perhaps as lucky accidents. I would suggest that the problem lies in the concentration upon such 'developments', rather than on the conditions that made them possible.

Kuhn's contrast between normal and revolutionary science, while useful, has perhaps served to concentrate historians' minds on the 'revolutions' to the detriment of the 'normal science'. My study is intended to rectify this situation by exploring the details of hitherto neglected British affinity theories while at the same time setting out a new model for historical comparison that enables the diverse nature of the doctrine to be assimilated. As I show below, the doctrine of affinity formed a crucial part of the norm of British chemistry, a norm that remained impervious to the more 'revolutionary' developments that ordinarily receive 'top billing' in the received view of 18th century chemistry. Neither new airs nor new nomenclature deposed the doctrine of affinity which remained omnipresent in the teaching and the textbooks of the discipline from the 1750s well into the 19th century. Indeed, for Thomas Thomson, writing in 1830, affinity still constituted "confessedly the basis of the science" in spite of the fact

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[56] E.g. Scott 1979, Donovan 1975.

that “it had been almost completely overlooked by Lavoisier”.[57] It is clear that affinity theories provided sufficient continuity to the discipline to enable avoidance of the complete disjunction that seems to be implied by Kuhnian historiography. On the other hand, as my research shows, the doctrine of affinity was riddled with discontinuity and divergence. My intention here is to try to unpack the variety of affinity theories to try to reach some understanding of this dichotomy.

1.4 ‘Manufacturing’ a Theory: Methodology

It is apparent from the foregoing that a new view of British affinity theories is required. The failure of most prior historiography of affinity to tackle the variations within the doctrine requires correction. From the initial stages of this research, the evidence confirmed Perrin’s view that affinity should not be regarded as a single monolithic theory.[58] I have endeavoured to put forward a more accurate and practicable analysis, wherein each individual’s affinity theory is shown to consist of a complex bundle of assumptions and auxiliary theories, many of which provided rules for its practical use.

Many of the prior historiographical difficulties have arisen from too great a concern with an overriding developmental story of one type or another. Such narratives, concerned as they are with documenting and exploring changes in ideas can, of course, be helpful. However, the doctrine of affinity has not been well served by such treatments. Affinity theories are made to appear, as they do in Duncan’s work, as passive receptors (or reflectors) of invigorating ideas and discoveries from other areas of the science. Alternatively, the focus on chronological change or genealogical relations between theories and ideas has (possibly inevitably) tended to emphasise flaws in theories, simply by the fact that they almost always invoke a meta-narrative of progress or decline. Where a theory forms part of a progressive narrative, problems tend to be emphasised as the historian documents the additions and ‘improvements’ made to it during its useful life; stories of decline, by their very nature, stress defects. Such approaches obscure the questions of how and why affinity theories were

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[57] Thomson 1830, 157.

[58] Perrin 1988, 60.

adopted and used at all and these questions are important. Time and effort were consumed by natural philosophers throughout Western Europe in formulating and refining their affinity theories, and as Duncan has admitted:

> "Eighteenth-century chemists thought that affinity or attraction was important; and even if the concept had eventually to be discarded, they used it a great deal in the course of thinking which did have successful results in other directions."[59]

Duncan's focus on use here is perceptive. British chemists were generally more concerned with using their affinity theories to accomplish their specific chemical aims, than with exploring the nature of affinity as a force or power.[60] Any attempt to understand their role must thus focus in detail on the contents of each theory, not as a stage in a process of theoretical evolution, but as a tool, manufactured in order to perform a function. To this end my study has endeavoured to separate out the theoretical components of affinity theories in order to probe their intended practical and operational functions.

I have examined texts produced by a number of British chemists active between 1740 and 1800, extracting where possible details of each individual's affinity theory. My examination of these primary texts shows that each chemist formulated their own affinity theory, comprised of different theoretical components according to preference. Many of these components were tacit knowledge, which poses certain obvious problems for the historian seeking to pin them down.[61] Nevertheless, many of these components became explicit, and thus available for comparison in the pedagogical context. In spite of their differences, I found that components proved to be comparable inter-theoretically on criteria of intended function. Apparently different components of individuals' theories could thus be classed together into component-types that performed the same functional role within each theory. The patterns of divergence within the doctrine are traced by comparing components within each component-type.

My methodology is perhaps easier to explain with the use of an extended

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[59] Duncan 1996, 224.

[60] Schofield 1970, 216.

[61] Polanyi 1962, Polanyi 1967.

metaphor. A car, to take a simple example, is manufactured from many different components. Similarly, a theory of affinity was manufactured from theoretical components. Just as there are many different makes of car, so the doctrine of affinity consisted of an array of individual affinity theories manufactured by chemists.

Examining the notion of components a bit more closely; in the case of motor manufacture most component-types offer a certain amount of choice to the manufacturer. He can decide according to his own requirements what particular engine he will use, what sort of exhaust or gearbox, or what size wheels. Engines, for example, can be of different types or capacities, all offering advantages and disadvantages. But all these components are nevertheless types of ‘engine’ - although they might work in different ways, they perform a similar function as part of the vehicle. In the same way, for affinity, certain theoretical components can be classed together in types according to the function they performed in the specific context of their affinity theory. An example might be types of theories of combination. While an affinity theory may require a theory of combination as a component, the chemist had a certain freedom of choice as to which particular theory of combination he used. It was always possible for a chemist to invent his own hypothesis just as some motor manufacturers will invent and manufacture their own components if none of those available are appropriate. It is vital to realise here that while a theoretical component may have been needed for an affinity theory to be functional or useful, such a component need not have been precisely the same for all individuals.

In spite of all this divergence, there was a strong degree of conformity amongst affinity theories. My study has also sought to shed light on the bundle of theoretical components that formed this common ground. Of course, in spite of the huge potential range of cars/theories of affinity that can be imagined, there is still something that tells us in each case that each individual production is still a car/theory of affinity. In general, people are able to recognise a car whatever make or model it might be, although it might be difficult to explain precisely how they come to their recognition. There will inevitably be discussions about those models that seem to be on the margins of any definition, such as the Reliant Robin (which lacks the conventional number of wheels, but is still a car) or the BMW C1 (which has a roof, but would be classed as a motorbike). However, the majority of motor cars are easily identifiable as such. Similarly, historians of chemistry, like their subjects, can recognise a theory of affinity when they come across it, although there may be particular theories that contradict convention in certain ways. In order to try to record the conventions of affinity theories it is important to try to elucidate how we come to their recognition, without, so far as possible, resorting to neo-Platonist notions of ideal forms. This leads to what I have called the 'logical common ground', as being the bundle of unvarying components common to all theories of affinity.

Components of the logical common ground include the general law of affinities originally articulated by Geoffroy in 1718, and the rather more nebulous concept of the affinity table. As Kim says:

> "In addition to its functions of summary description, prediction, and explanation, the table allowed dissent within a comprehensive framework."[62]

To map the framework of legitimate dissent is to delineate the various component-types, but to find the locus of consent is to reveal the common ground. The coincident components of the logical common ground help to further define the "comprehensive framework" of permissible dissent and variation by imposing criteria for the array of functional components built thereon. The logical common ground of affinity thus provided the identity between the assortment of theories held by chemists. My foremost task throughout this research has been to chart this topology of convergence and dissent amongst affinity theories.

My research also suggests that this phrase 'common ground' can also be used to describe the role played by the doctrine as a whole in helping to forge a coherent discipline of chemistry. Influenced strongly by chemical pedagogy, affinity became accepted as forming the foundation of the discipline. As each individual theory was based on the components of the logical common ground, the doctrine also provided a basis for communication and common understanding as a disciplinary common ground. Rather like Galison's 'trading

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[62] Kim 2003, 139.

zone', the common subscription to affinity allowed the exchange of knowledge in spite of individuals' differing theoretical formulations.[63] The doctrine was available to individuals espousing incompatible metaphysical or philosophical systems, intelligible and of use to each, but not necessarily with the same interpretive scheme acting in each case.

This role of affinity as the disciplinary common ground is most clearly evident in chapter 2 below. Here, the focus is directed rather at the wider context in which each affinity theory is most clearly manifested than at the details of each such theory. The original intention of this chapter was simply to provide a limited contextual and chronological background to the later chapters, which examine various components of individuals' theories largely in abstraction. However, it became clear during my research that certain themes were emerging that warranted further elucidation. A focus on these themes has enabled me to suggest answers to a number of important questions concerning the dissemination of affinity theories in Britain, as well as to offer a tentative explanation for the patterns of incompatibility amongst affinity theories.

Setting out in brief what I take to be the key points of Geoffroy's original presentation of his paper and affinity table and its initial reception in Britain, it offers a deliberately skeletal examination of the circumstances of the dispersion of affinity down a pedagogical pyramid headed by William Cullen. This chapter offers some thoughts on how Cullen and successive chemical pedagogues seized hold of an inexact generalisation and forged a coherent and carefully delimited discipline.[64] A pedagogical bias was clearly present from the start, the most explicit statements of the principles of individuals' affinity theories appearing predominantly in pedagogical sources. As these sources proved to be the most fertile ground for my study, they tend to outnumber other, non-didactic sources. The pedagogical ubiquity of affinity was not a fact that escaped novice chemists in the 18th century either; in 1766 Charles Blagden, taking notes from Cullen's chemistry lectures wrote:

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[63] Galison 1997.

[64] I use the word inexact in reference to Polanyi's early paper on the relations of chemistry to physics, Polanyi 1936.

> “to explain the subsequent Experiments, a portion of a Table of Elective Attractions was fixed up; but this being in almost every book of Ch^y is not worth repeating here”[65]

This in itself testifies to the status of these affinity theories as forming part of the norm of 18th century chemistry. The retrieval of such a norm is, as Knight has argued, "... itself interesting and must be the primary task of the historian”.[66] An insufficient understanding of the normal state of affairs will inevitably impinge unfavourably on any historiographical judgment.

Many of the outstanding questions about the diffusion of affinity theories in Britain can be best understood by a focus on the pedagogical context. I have been able to offer suggestions as to why there was such a lengthy hiatus between Geoffroy’s initial paper and the British recovery of affinity, and why indeed the recovery occurred at all.

Hannaway has stressed the importance of didactic writings in the development of chemistry as a science,[67] and more recently Bensaude-Vincent and her colleagues concluded that in 19th century France “textbooks played an important role in discipline building and in creating theories.”[68] My study shows that pedagogical activities, and specifically the use of affinity theories as pedagogical tools, contributed to the forging of a distinct discipline of chemistry in Britain. Rather than concentrating solely on textbook sources I have also drawn on lecture notes taken down by students. Although the circumstances of production of these sources are often far from clear, they offer indications of the reception of pedagogical endeavours, as well as of pedagogical intent. I have also been able to distinguish a number of tacit assumptions that were adopted by chemists as part of the disciplinary common ground. A common assumption of applicability and utility can be discerned, alongside a series of tacit boundaries that were projected from the logical common ground onto the discipline of chemistry. These assumptions reinforced the demarcation of the discipline from its disreputable older brother, alchemy, and its rather bumptious cousin, natural

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[65] Cullen 1766, Lecture 22.

[66] Knight 1975, 32.

[67] Hannaway 1975.

[68] Garcia-Belmar, Bensaude-Vincent, and Bertomeu-Sánchez 2005, 243.

philosophy. As Christie and Golinski have pointed out, "affinity theory, insofar as it really was a theory, was anti-reductionist and distinctively *chemical*."[69] These assumptions are explored in more detail in chapter 5.

There is a further set of components of affinity theories that I have labelled 'optional' components. This set of components I have deliberately excluded from my study, as they were largely irrelevant to the functionality of affinity theories. These types of theoretical component were not necessary for theoretical and operational coherence, but were often included in explanations of an individual's affinity theory in an attempt perhaps to enhance its philosophical status. Extending my metaphor somewhat, once the manufacturer has built his basic car, any number of 'options' can be added: CD players, satellite navigation systems, heated front windscreens, headlamp wipers and so forth. He can also paint it pink with blue spots, if that is what he likes. None of these optional extras are necessary to the car for it to be a car, and to function as a car, but they complete the image, they make it more desirable to others and they may perform a function that the manufacturer considers important. So far as affinity theories are concerned, metaphysical theories of matter fall into this class of components. During the 18th century there were a number of possible components of this type available, none of which were essential to the comprehension of an affinity theory as a whole, but any of which could be 'bolted on', so to speak. The ultimate structure of matter was not accessible to 18th century chemists; indeed many chemists set limits to ontological enquiry that upheld the demarcation of chemistry from other disciplines. Such speculations were metaphysical rather than scientific, and it seems to me to be crucial that we should give 18th century chemists credit for knowing the difference. This emphasises the importance of bearing in mind the intra-theoretical context: however fundamental a particular type of theoretical component might seem to be in the realist vision of the universe, it may well be wholly discretionary when viewed from the context of a theory or doctrine that is not dependent on it.

This is not to deny that optional components were influential upon an

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[69] Christie and Golinski 1982, 247.

individual's affinity theory in an indirect sense. The selection of one particular type of component would doubtless affect the choice of some other types of component. Theoretical coherence would require consistency between certain components; this conformity is primarily responsible for many of the labels that have been pinned to theories of affinity by historians. While it might be true that a particular affinity theory was composed of a sufficient number of Newtonian components to be labelled as wholly Newtonian, the multiple theory model requires the acknowledgment that other theories that could not be so labelled could, and indeed did, exist. While those historians (both modern and 18th century) who sought to plant affinity in the fertile ground of Newtonianism (for example) have sought to give it a metaphysical identity independent of individual usage, my research suggests that the reverse view is more appropriate; Newtonianism could be planted in the doctrine of affinity according to theoretical preference.

This approach to questions of the operational and didactic value of affinity, and the utility of affinity tables is more successful than the more traditional historical approaches have been. The initial consideration of the relationships between key British manufacturers of affinity theories in isolation from the details of such theories emphasises the pedagogical context as providing the primary framework for the dissemination and dispersal of affinity theories. The following abstraction of the components of affinity theories from their chronological, and social contexts has enabled me to determine their points of comparison. I would suggest that this 'a-chronic' (as it might be termed) approach indicates why particular components were included in affinity theories, what was important to the chemist manufacturing his affinity theory. In each case, components were found to be comparable on the grounds of their operational functionality, their practical utility. This is why affinity theories were omnipresent, and why they persisted throughout the century; because they were intended, and believed to be useful. Finally, the extraction and elucidation of the logical and disciplinary common grounds from the array of components of affinity theories reveals the role that affinity theories in all their infinite variety took in forging an autonomous discipline of chemistry.

1.5 The Plan

Chapter 2 sets out the contextual background to the affinity theories that are decompounded in the following chapters. I have throughout been extremely conscious that my thesis relies on an extremely artificial selection of actors and sources, the criteria for such selection being overwhelmingly pragmatic. As is the case with any historiographical endeavour, I have necessarily been restricted by the sources that are extant, and I have of course selected from these those sources that deal to some extent with affinity. To emphasise this artificiality, I have chosen to present this chapter in the guise of a theatrical production. My cast list is necessarily limited, confined predominantly to those whose theories are dissected and decompounded in the following chapters and I would not wish to pretend that this is history ‘as it happened’.

Chapters 3 and 4 set out some of the component-types discernable in affinity theories, offering examples of the variations to be found amongst components. The ‘functional component-types’ discussed in chapter 3 are common to all affinity theories. This sets out the variety of components that ‘operationalised’ affinity theory and provides important information concerning the use of such theories. These components differed in their intentions from those set out in Chapter 4 which began to be included rather later in the 18th century, in response to new discoveries in the field of heat.. These ‘supplementary component-types’ offer insights into what kinds of pressures prompted the introduction of new components into theories, as well as how such components were formulated. The reader should perhaps be warned that these chapters are extremely long, in particular chapter 3. In order to emphasise the distinction between the two groups of component types, each of these chapters, although rather long, need to retain their integrity. The division into component types structures the lengthy discussion, but I believe that any division into shorter chapters would inevitably obscure the distinction.

Chapter 5 focuses on the logical and disciplinary common grounds, setting out the bundle of components that I have found to be common to all affinity theories and the assumptions that, by consensus, linked the doctrine to the discipline.

And so … on with the show!

2. Affinity: A True and Accurate History of the Science as practised by the Philosophers of the British Isles

2.1 The Cast (in order of appearance)

William Cullen (1710-1790) Probably the most influential teacher of chemistry of the 18th century. Born in Scotland, educated as a surgeon, apothecary and physician, appointed lecturer in chemistry at Glasgow University in 1747. In 1755 he moved to Edinburgh University, where he taught chemistry until 1766.[1] Thomas Thomson called him "the true commencer of the study of scientific chemistry in Great Britain".[2] Appendix II gives some indication of the breadth of his influence.

Etienne François Geoffroy (1672-1731) Son of a Paris apothecary trained first as an apothecary and then as physician. Elected FRS in 1698 on a visit to London and in 1700 nominated to the Académie Royale des Sciences in Paris. Appointed élève by Homberg and later associé chemiste.[3] Presented 17 chemical papers to the Académie between 1700 and 1731.[4] He also worked at the Jardin Royal des Plantes and the College Royal where he was made Professeur en Medecine, Chirugie, Pharmacie et Botanique in 1709. Corresponded regularly with Hans Sloane and contributed to the *Philosophical Transactions* five times.

Robert Boyle (1627-1691) Wealthy natural philosopher of Oxford and London and Bond's "excellent chemist and celebrated philosopher".[5] Founder Fellow of the Royal Society, his most well-known work was the *Sceptical Chymist*[6] which set out arguments against the hypotheses of the four Aristotelian elements and three spagyric principles, propounding instead his

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[1] Thomson 1859.

[2] Thomson 1830, 305. Thomson was taught chemistry by Joseph Black, perhaps Cullen's most noted student, and he is the beneficiary of Thomson's most generous praise.

[3] Martin Lister, who met Geoffroy Senior commented "I must needs commend this Gentleman on his civility towards me, and for his care in Educating his son, who came over with Count Tallard, a most Hopeful and Learned young Man; whom our Society at Gresham College, at my request, honoured with admitting him Fellow, according to his Deserts". Martin Lister, *A Journey to Paris,* 242-243, quoted in Sturdy 1995.

[4] For a detailed account of Geoffroy's life and career, see Sturdy 1995.

[5] Bond, 1753, 186.

[6] Boyle 1661.

"corpuscular philosophy".[7] Remembered for his physical work on air, he was also a practising chymist and throughout his copious works, he endeavoured to explain chemical phenomena in mechanical terms.[8]

Sir Isaac Newton (1642-1727) Natural philosopher, alchemist, FRS 1672, President of the Royal Society 1703-1727, Lucasian Professor of Mathematics at Cambridge, Member of Parliament and Master of the Mint. Published *Principia* 1687,[9] *Opticks* 1704,[10] in the Queries of which he discussed chemical phenomena, using successive precipitation of metals to buttress his notion of interparticulate forces of attraction.

John Mickelburgh (c.1692-1756) Third professor of chemistry at Cambridge University. He took over his post in 1718 and it seems from notes of his 1726 lectures still held at Cambridge that courses were given in at least five years.[11] The lectures were given for the benefit of anyone who wished to attend, and presumably could pay the fees. The list of students for the 1726 course includes surgeons and apothecaries from Cambridge and the surrounding area as well as students of the various colleges.

James Crawford (1682-1731) The first lecturer in chemistry at the University of Edinburgh, from 1713 to 1726. Gave perhaps three or four courses in total.[12] Crawford spent five weeks in Leyden during 1707, and it is sometimes said that he was a student of Hermann Boerhaave, but this seems doubtful.[13]

Peter Shaw (1694-1763) From the late 1720s to the 1740s, Shaw produced English translations of the works of Hermann Boerhaave, Francis Bacon, Robert Boyle, and Georg Stahl, published a posthumous edition of John Quincy's

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[7] One of the earliest statements of Boyle's corpuscular philosophy was set out in his *Origins of Forms and Qualities (1666-7)* in Boyle 1999 Vol. 5.

[8] See also Newman and Principe 2002; Principe 1998.

[9] Newton 1995.

[10] Newton 1979.

[11] Haley 2002.

[12] There are two sets of lecture notes from Crawford's lectures extant, one held by Edinburgh University taken by Alexander Monro, and a further set held by The Wellcome Trust taken by a student named John Fullerton, MS 2451.

[13] See Doyle 2004. Doyle argues that historians have often mistakenly asserted that Crawford was one of Boerhaave's students as he graduated in Leyden, but points out that the majority of his medical training was done elsewhere, and that five weeks would probably not allow him sufficient time to attend Boerhaave's lectures.

Praelectiones Pharmaceuticae, and gave public lectures in chemistry. Only elected to fellowship of the Royal Society in 1752 many years after his last chemical publication[14] but after he had attained the heights of physician in ordinary to George II and George III.

Pierre-Joseph Macquer (1718-1784) Born in France, he was a member of the Académie Royale des Sciences and published in 1749 *Elemens de Chimie Theorique*, and its sister volume, *Elemens de Chimie Pratique* in 1751. Both works were translated into English and published in 1758 in a single volume.

William Lewis (bap. 1708-1781) Son of a Richmond brewer, educated at Oxford and Cambridge, where he obtained his M.B. Gave public lectures in chemistry in London from the late 1730s.[15] Publications include a *Course of Practical Chemistry* and the *New Dispensatory*. Elected FRS in 1745, he published three papers on platina in the *Philosophical Transactions*[16] for which he won the Copley Medal. In 1759 Lewis published what is said to have contained "the first exposition in English of Stahl's phlogiston theory"[17] in his edition of the writings of Caspar Neumann.[18] Consulted to the Society for the Improvement of Arts, Manufactures &c.

George Fordyce (1736-1802).[19] Born Aberdeen, learned chemistry as medical student from Cullen at Edinburgh. Graduated MD in 1758,[20] attended Leyden to study anatomy in 1759.[21] Began lecturing in chemistry from his London home circa 1760. From 1764 gave a lecture course in Materia Medica and in 1770 became physician at St. Thomas' Hospital. Harveian Orator at the Royal College of Physicians and Croonian Lecturer at the Royal Society.

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[14] Where his election certificate asserts that he is "A Gentleman well versed in Philosophical, Mathematical, and other Branches of polite and usefull Literature, as appears by his many learned Works already published". Royal Society 1752.

[15] Gibbs 1952, 124.

[16] Lewis 1754, Lewis 1757a, Lewis 1757b.

[17] Gibbs 1952, 130. This is particularly interesting when it is borne in mind that Shaw published a translation of Stahl's *Collegium Jenense* in 1730. This was one of the few of Stahl's works not to contain any reference to his phlogiston theory.

[18] Lewis 1759.

[19] Coley has produced the most comprehensive account of Fordyce's life and works, and much of the biographical information on Fordyce is culled from his 2001 paper. Coley 2001.

[20] Ibid, 402.

[21] Kelham 1968.

Torbern Bergman (1735-1784) Swedish chemist. In 1775 published *Disquisitio de Attractionibus Electivis.*[22] This was translated into English in 1785 as *A Dissertation on Elective Attractions*. Corresponded from 1780 until his death with Kirwan, whose attempt to quantify affinities may have been inspired by sight of Bergman's table.[23]

John Elliot (1747-1787) Born in Somerset, apparently becoming first an apothecary, and then M.D.[24] Settled in London, and began publishing in 1781 with his *Medical Pocket-Book* which was republished in at least five London, three Dublin, and four American Editions, continuing long after his death. Friendly with Kirwan, Joseph Priestley and Benjamin Franklin, he also contributed to the London Medical Journal. There is little information available on Elliot's life but there are numerous sources of the circumstances of his death in Newgate, in the aftermath of a trial for attempted murder.[25]

Richard Kirwan, (1733-1812) Wealthy Irish 'gentleman chemist', schooled in France[26] where he attended Rouelle's lectures.[27] Elected FRS 1780 and awarded the Copley Medal for three papers that set out his system for quantifying affinity.[28] Published *Elements of Mineralogy* which was translated into French, German and Spanish, and the handbook of the chemical revolution, *Essay on Phlogiston* (although on the 'losing' side). Founder member of the Chapter Coffee House Society which met from 1780 to 1787. Council for Royal Irish Academy from 1787.

William Higgins (1763-1825) Nephew of an established private lecturer in chemistry, Bryan Higgins. Educated at Oxford, where he had been operator to

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[22] Bergman 1775.

[23] Kirwan specifically mentioned Bergman in the paper that began his studies of affinity: Kirwan 1781.

[24] Partington and McKie have drawn attention to the fact that "a John Elliot attended the medical classes at the University of Edinburgh in 1766-1770 and another attended during 1773-1775." See Partington and McKie 1960, 266. Duncan notes that Elliot's attempt to quantify affinity was similar to Black's assignation of numbers to affinities, but it is unlikely he was a student of Black's, as he speaks of having gleaned Black's theory of heat from a set of notes of Black's lectures borrowed from a friend who had attended them. Duncan 1996, 198 and Elliot 1780, 122-123.

[25] For the full sad story, see Old Bailey News, *Times*, Jul 17, 1787,*Times,* Jul 24, 1787, Manning 1993.

[26] Scott 1979, 13. Scott's thesis is the most recent and comprehensive survey of Kirwan's life and work.

[27] Kim 2003, 269.

[28] Kirwan 1781, Kirwan 1782, Kirwan 1783.

the Professor of Chemistry. He left Oxford without a degree and seems to have spent some time assisting his uncle in London.[29] Published his *Comparative View of the Phlogistic and Antiphlogistic Theories* in two editions. Member of Royal Irish Academy 1794. Friendly with Kirwan.[30]

(and various supporting Natural Philosophers, Chemists, Apothecaries, Physicians and their Historians)

2.2 Prologue: Pedagogical Experimentations and Philosophical Investigations

The year is 1749, the place a lecture room at Glasgow University. A gentleman in a large wig presides over a room of students of diverse ages and styles.[31] The bewigged gentleman lectures to them on chemistry, interspersing his words with frequent demonstrations. One such demonstration appears to be taking place as we watch: he carefully pours a red brown liquid onto a brownish solid substance, standing back as the mixture bubbles, and fumes rise into the air. He draws the attention of the watching students to this phenomenon, explaining that the substances in the mixture are generating a sensible heat. Once the agitation has died down, he shows the students the resulting matter, a solid substance known as saltpetre, a compound salt that he has produced from the combination of potash and an acid called aqua fortis. The demonstration continues with the lecturer, William Cullen, taking this saltpetre, and carefully pouring another liquid, this time the acid oil of vitriol, over it. Once again, the mixture effervesces, and more fumes are produced. Cullen explains to the students what has occurred:

> "the Pot Ashes joins yet more readily with, or as we usually speak, is more strongly attracted by the Oil of Vitriol; so that if this be poured to Saltpetre the Pot Ashes or its fixed Part is joined with it and lets go the Aquafortis which therefore flys off according to its Volatile nature as we saw in our experiment. I say this is an Instance of Pot Ashes attracting Oil of Vitriol more

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[29] Wheeler and Partington 1960 *Life*, 4-5.

[30] It is difficult to ascertain when his friendship with Kirwan began, but it was evident by 1795 when Kirwan put forward a suggestion to the Dublin Society that they employ Higgins to arrange and supervise the Leskean cabinet of minerals. See Wheeler and Partington 1960, 17. Alternatively, Kirwan had been a customer of Bryan Higgins's chemical supply business during his time in London. See Kelham 1968, 110.

[31] Cullen's chemistry lectures were open to all those who had an interest in the subject, and this apparently included many from outside the university, whose interests were often commercial. Golinski 1988, 5.

> strongly than Aquafortis and this is what we call an elective attraction; & by the knowledge of such Elective Attractions many operations in chemistry are to be explained."[32]

Thus did Cullen introduce his students to the actions of affinity (or, as Cullen preferred it, elective attraction) and its role in chemical combination and separation. Almost 20 years later, in the final year of his chemistry lectures (by now at Edinburgh University), he drew on the same example. Some terms changed; instead of saltpetre, he referred to nitre, and he substituted the term 'nitrous alkali' for potash, this time mixed with 'nitrous acid', but the demonstration remained essentially the same.[33] This demonstration gave his students (by now numbering over 140)[34] a clear and powerful example of the action of chemical affinity in compounding heterogeneous substances, and of its associated power to separate compound substances.

A change of scene: England, in the years between Cullen's first chemistry lectures at Glasgow and his final lecture on the subject at Edinburgh. A discussion takes place in the pages of the *Philosophical Transactions* concerning an apparent transmutation of metals.

The art of obtaining copper from vitriol streams was familiar to metallurgical workers since Pliny's time.[35] They knew that if pieces of iron were placed in certain streams, often in areas where copper was mined, copper would be precipitated as the iron was apparently dissolved. A Dr John Bond, picking up on earlier discussions in the Philosophical Transactions,[36] attended at one such spring in Wicklow in Ireland, and carried out a number of experiments, reporting his results to the Society. Bond explained in a letter that:

> "This water flows from a rich copper mine, and is of a sharp acid taste, and light-blue colour. It is received and collected in pits, wherein iron bars are put, which, after lying in the water about three months, are intirely consumed, and at the bottom of the pits, a quantity of copper, greater than that of the iron is found, in the

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[32] Cullen 1749, f. 17.

[33] E.g. Cullen 1766, lectures 17 and 18.

[34] Golinski 1992, 17.

[35] Partington 1948, 110.

[36] Henry 1752.

> form of coarse sand."[37]

Bond carried out five experiments on the spring water, showing that the water contained an acid with copper dissolved in it. His explanations, while making use of some of the language of Newtonian philosophy, owe much to Locke's philosophy of active powers as well as the corpuscular philosophy of Robert Boyle.

> "From all these experiments it appears, that a mineral acid is the active quality in this water; which being diffused thro' the copper ore, unites itself with that metal, and forms a vitriol, which is dissolved by the water, and remains suspended in it, till it meets with the iron in the pits, by which this acid is more strongly attracted than by the copper, therefore it quits the copper, corrodes the iron, and changes it into a vitriol, which is again dissolv'd, and carried off in the stream continually flowing from the pits; while the copper, deserted by the acid, falls, by its specific gravity, to the bottom of the pits."[38]

The apparent transmutation of iron into copper is explained in Bond's letter as a neat swap of one substance for another. His account follows a similar model to Cullen's explanation of the decomposition of saltpetre, the model of the elective action of chemical affinity. But where Cullen offered his demonstration as an example of the action of a single familiar cause (and went on to explain the theory), Bond seems to have been unable to do the same. In comparison with Cullen's lecture, Bond's determined empiricism seems disingenuous. He alternates between an inconsistent set of concepts of active qualities, the acid-alkali dualism of the early 18th century French chemists and the animistic language of alchemy. Inevitably, the Newtonian 'attraction' is also present in his rather confused conceptual package. Later in his letter he asserts that:

> "the art of essaying, or separating metals from their ores, chiefly consists in evaporating an acid, which prevents the mutual attraction of the metallic particles: for when the acid is driven off by the violence of fire, the particles fall into their proper sphere of attraction, and assume a solid form."[39]

Newton's influence is evident in the purported 'spheres of attraction', although

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[37] Bond,1753, 182.

[38] Ibid, 186-187.

[39] Ibid, 187.

the attraction he mentions seems to be the cohesion of homogeneous particles rather than the elective attraction of affinity theory. The image is mechanistic, the acid envisaged as interposing itself between the particles of metal. Note that according to Bond, it is the role of the active acid to quit the copper as the passive partner rather than a mutual separation or a purely mechanical matter of forces.

These examples illustrate the role of pedagogy in dispersing[40] affinity theories throughout Britain. Cullen used the model of a preferential separation and combination to demonstrate the workings of affinity, the theory of which formed a general principle of the discipline. Although Bond, when presented with phenomena that followed the same model drew on similar ideas, his conceptualisation is vague. Bond wrote his letter in the early 1750s, thirty years after Geoffroy had presented his affinity table to the Académie Royale des Sciences (and four years after Cullen's first chemistry lectures) and yet he did not refer to affinity. This perhaps testifies to the Royal Society's relative lack of interest in chemistry during the first half of the century. In contrast, Cullen's inclusion of his affinity theory from his first lectures (which included a detailed exposition of Geoffroy's table) implies that his role in the dissemination of chemical affinity through Britain was significant.

2.3 Act 1: In Which a Frenchman builds a Table, and the Natural Philosophers of Britain Pay it no Heed

In 1718 Geoffroy presented to the Académie Royale des Sciences his "Table des Differents Rapports Observés en Chimie entre Differentes Substances" together with an explanatory *Mémoire*.[41] His paper inspired the Secretary of the Académie, Bernard le Bovier de Fontenelle to comment that "une Table Chimique est par elle-même un spectacle agréable à l'Esprit".[42]

The fact that some pairs of substances were more inclined to combine than

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[40] I have chosen the word 'dispersing' in reference to David Kaiser's work on the dispersion of Feynman diagrams through the realm of postwar physics. I have found striking similarities between the patterns of dissemination noted by Kaiser and those evidenced in the transmission of affinity theories. See Kaiser 2005.

[41] Geoffroy 1719.

[42] Fontenelle 1719, 37.

others was a fundamental chemical axiom. Geoffroy tabulated these relations, listing empirically based generalisations of this knowledge in a grid of sixteen columns (figure 1 on p. 93). Each column was headed by a particular substance, and below this were listed other substances in order of their tendency to unite with it, from the most eager at the top to the most reluctant at the bottom. Geoffroy's paper explained this and indicated in a very general way how the table had been created. He suggested that

> "Par cette Table, ceux qui commencent à apprendre la Chimie se formeront en peu de temps une juste idée du rapport que les differentes substances ont les unes avec les autres, & les Chimistes y trouveront une methode aisée pour découvrir, ce qui se passe dans plusieurs de leurs operations difficiles à démêler, & ce qui doit resulter des melanges qu'ils sont de differents corps mixtes."[43]

He did not at any point offer a causal explanation of how or why these relationships between substances operated. Instead, he proposed what he implied was a generalised 'loi' drawn from his observations:

> "Toutes les fois que deux substances qui ont quelque disposition à se joindre l'une avec l'autre, se trouvent unies ensemble ; s'il en survient une troisiéme qui ait plus de rapport avec l'une des deux, elle s'y unit en faisant lâcher prise à l'autre."[44]

According to the law, if two substances were combined and a third substance introduced that had more rapport with one of the combined substances than that substance had with its partner, it would oust the substance with less rapport from the combination and combine in its stead with the other. Knowledge of affinities could thus be used to manipulate matter, separating and combining different substances according to the chemist's desire.

Klein has shown that knowledge of these phenomena was habitually put to use in European metallurgical and apothecaries' workshops, where many of the relations listed in Geoffroy's table would presumably have been regarded as old news.[45] One half of the table drew on techniques of salt synthesis and analysis,

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[43] Geoffroy 1719, 203.

[44] Ibid.

[45] Klein 1996. Also see Newman 2006 which has recently shown that many of the same phenomena were recognised by chymists in the 17th century as well, as the much earlier Geber.

while the other emanated from the extraction of metals from their ores. Similar phenomena were also well known amongst the philosophical investigators of nature.

Bond's letter specifically cited Robert Boyle's mention of the displacement of copper from solution in vitriol by iron as an instance of what he called 'sympathetic precipitation' in his "Essay on Specific Medicines".[46] Boyle referred to a variety of similar chemical phenomena in an attempt to reconcile the notion of specific medicines with his corpuscular philosophy. By citing as examples the particular associations of particular bodies, he showed that:

> "there may be precipitations, where, whatever may be supposed, it does not appear that there is any tumult or contrariety."[47]

The lack of apparent strife between the substances would ensure their suitability for use as medicines. Boyle dealt more explicitly with metallic displacements in "Of the Mechanical Causes of Chemical Precipitation."[48] This set out a detailed mechanical explanation of a model of preferential combination that would have been recognized by Cullen and Bond.[49] The exemplary displacement at the core of an affinity separation can be distinguished in his explanation that:

> "another way, whereby the dissolving particles of a menstruum may be rendered unfit to sustain the dissolved body, is to present them another, that they can more easily work on".[50]

He continued by giving an example of how the recognition of the relationships between the dissolved body, the menstruum and the precipitant was of practical importance to the practitioners of metallurgy:

> "that in these operations, the saline particles may really quit the dissolved body, and work upon the precipitant, may appear by the lately mentioned practice of refiners, where the aqua fortis, that forsakes the particles of the silver, falls a working upon the

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[46] In fact, it seems that Bond's quotation was not entirely correct, as the phrase apparently used by Boyle (so far as Birch's 1744 edition and Hunter's most recent edition of the Works are concerned) was "silent precipitation". Boyle 1999, 10, 380.

[47] Boyle 1744, IV, 308.

[48] Ibid, III, 635-642.

[49] Levere has argued that in spite of Boyle's corpuscularian approach, "Boyle did give practical recognition to affinities … In explaining such phenomena, however, he remained within the limited and limiting frame of his natural philosophy". Levere 1971, 4.

[50] Boyle 1744, III, 640.

> copper-plates employed about the precipitation, and dissolves so much of them, as to acquire the greenish blue colour of a good solution of that metal. And the copper we can easily again, without salts, obtain by precipitation out of that liquor with iron, and that too, remaining dissolved in its place, we can precipitate with the tasteless powder of another mineral."[51]

Here Boyle set out in prose form what would be recognisable to later chemists as a short column of an affinity table, similar to the list included by Newton in the 31st Query appended to his *Opticks* of 1706. Boyle thus demonstrated his familiarity with the phenomena some 30 years before either Newton's Query or Geoffroy's *Mémoire* were published.

Christie and Golinski have argued that Boyle's works might be usefully viewed as posing the problem of how to apply a corpuscular mechanism to chemistry.[52] Boyle struggled to explain the preferential nature of these combinations and separations in terms of his corpuscular philosophy, having recourse (possibly in desperation) to a somewhat animistic idiom. He spoke of "seducing them [the menstruums] to work on other bodies, and to forsake those they first dissolved".[53] The inconsistency of this language with the ideal of corpuscularian mechanics is an indication of the difficulties natural philosophers, including later Newtonians, had in dealing with chemical behaviour. It was not a problem that Boyle was able to solve without recourse to mysterious, often anthropomorphic, affections. The corpuscularian metaphysic did not furnish a language or conceptual structure that could explain the affinities of individual substances other than by vaguely invoking "the shape, bulk, solidity and other mechanical affections of its particles."[54] In mitigation though, Boyle was certainly not alone in his linguistic difficulties. Newton himself spoke of:

> "a certain secret principle in nature by which liquors are sociable to some things & unsociable to others."[55]

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[51] Ibid.

[52] Christie and Golinski 1982, 245.

[53] Ibid.

[54] Boyle 1744, IV, 308.

[55] Newton 1678. It is probably important to bear in mind that this was early in Newton's thinking, and forms part of the famous 'aether letter'.

Like Bond, chemists far into the 18th century found it impossible to explain affinity in terms that satisfied the ideals of scientific discourse.

The issue of language was of some importance to Geoffroy and his contemporaries, and Duncan has explored its significance with regard to affinity.[56] As he notes, Geoffroy went to some lengths to avoid an implied connection to any type of philosophical system. Presumably aware of the difficulties inherent in explaining these phenomena in ontological terms, he tried to show that his generalised law could still be useful without drawing ontological implications. Throughout his 1718 *Mémoire* he avoided the use of the more loaded terms of 'affinity' and 'attraction'. Instead, he referred only to 'rapports', a word that can be loosely translated as 'relationship' but which seems to have been intended to be synonymous with 'disposition à s'unir'.[57] The implication of this term, that substances chose whether or not to combine together according to 'disposition', might itself seem rather animistic, but it was intended simply to indicate a varying tendency to combine.

It is interesting to note that in the *Proces Verbaux* of the Académie, where the paper was initially documented in manuscript, the change from the term 'affinité' to 'rapport' is recorded. Geoffroy began his reading of the paper on Saturday 27 August 1718, where the papers record that "M. Geoffroy a commencé à lirè un Ecris sur les differents degréz d'affinité des Matiéres Chimiquez"[58] After a single blank sheet, the proceedings of the next meeting on Wednesday 31 August 1718 appear, and that "M. Geoffroy a achevé L'Ecris … Suivant". The full text of the paper follows, in a different hand, titled as in the printed version, and referring to 'rapports' rather than 'affinité'.

In spite of Geoffroy's determinedly cautious terminology, by 1720 the Cartesian Fontenelle was speaking of 'affinities' even as Geoffroy was persisting in his references to 'rapports'.[59] In 1723, the anonymously published *Nouveau Cours de Chymie* of Senac referred to Geoffroy's "Table des affinities des corps".

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[56] Duncan 1981, Duncan 1996, ch.3 & 4.

[57] Geoffroy 1719, 202.

[58] Académie Royale des Sciences 1962, T37, f 231v.

[59] Fontenelle 1722, 32.

According to Senac, Geoffroy's table "a rendu plus de service à la Chymie qu'une infinite d'Auteurs par de volumes remplis de raisonnemens physiques."[60] Geoffroy's own term 'rapports' was, it seems, only ever used by him, being displaced by other, more controversial terms in almost every case.

Many historians have seen Geoffroy's paper as stemming from the Newtonian natural philosophy sweeping Europe. That Newton's notion of attractive force influenced many later chemists' affinity theories is undeniable; affinity lent itself too easily to an ontology of particles and attractive forces for it to be otherwise. Three strands can be discerned in the historiography that ties Newton to affinity theory. The first asserts that the idea of ordering affinities originated with Newton, and that Geoffroy merely rearranged Newton's words and ideas in tabular form. The second, in most cases deriving from the first, assumes that Geoffroy himself was a 'Newtonian'. A third assumption that any espousal of an affinity theory necessarily involved a commitment to a Newtonian ontology is also common.

The first position is epitomised by those who claim that Query 31 incorporated the first articulation of an affinity theory.[61] Thackray, for example, argued that:

> "Nor is it surprising that Newton's attempt to list the metals in the order of their attractive powers was to fascinate E.F. Geoffroy and lead, through the latter's table, to the host of late-eighteenth century attempts to quantify the forces of chemical affinity." [62]

Cohen adopted both the first and the second positions (which are clearly linked), asserting unequivocally that Geoffroy was a Newtonian and that his table reflected this orientation.[63] Smeaton however challenged this second position, adducing evidence from Geoffroy's materia medica lectures, posthumously published as *Treatise of the Fossil, Vegetable and Animal Substances that are Made Use of in Physick*,[64] to assert equally unequivocally that Geoffroy was

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[60] Senac 1723, lxvii.

[61] This Query appeared for the first time in the 1706 Latin edition of the *Opticks*. It was translated into French in 1720 and first appeared in English in 1717.

[62] Thackray 1970, 34.

[63] Cohen 1964.

[64] Geoffroy 1736.

very far from being a “Newtonian Chemist”.[65]

There is indeed little to support this particular origin myth. As Guerlac and Klein have shown, and my glance at Boyle’s writings above has demonstrated, there were many potential sources of inspiration for Geoffroy’s table besides Newton’s Opticks:

> “Much, if not most, of the information in the table he could have drawn from the seventeenth-century chemical tradition, as indeed Newton himself had done in accumulating the chemical facts that he set forth in Query 31.”[66]

So, in the face of this, why do historians insist on the Newtonian origin of affinity theory? There is a recognised tendency for ideas to be deliberately linked to revered authorities in order to acquire prestige or validation.[67] I would suggest that the ‘Newtonianisation’ of Geoffroy and his table is such a case. The third strand mentioned above seeks to extend this classification to all affinity theories. It is unfair, however, to condemn modern historiography for the widespread assertion that Newton ‘invented’ affinity. Many 18th century chemists asserted something remarkably similar. John Warltire, a public lecturer in chemistry, stated unambiguously that:

> "The Plan of this Table was first given to the World by the illustrious Sir *Isaac Newton*, in his Optics, Quere 31st; and has received many Improvements from *Stahl, Geofroy,* the Edinburgh Chemists, and others.”[68]

and even Cullen took care to assert Newton’s authority over the origin of affinity theories.[69] It is tempting to attribute this trend to nationalistic feelings, to suggest that British chemists wanted to claim such a useful chemical theory for their own, but there is no evidence in favour of this argument. Whatever the cause, it is clear that there is a strong tradition of ascribing the origin of affinity to Newton on the strength of the 31st Query. As those temporally closer to

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[65] Smeaton 1971.

[66] Guerlac 1968, 73.

[67] Kragh 1989, 111.

[68] Warltire 1769b, 25.

[69] See, for example, Cullen n.d. [1760?], in which Cullen asserts the role of Newton in the formulation of affinity.

Newton instituted this myth, so modern historians have accepted their assessment without demur, and the fiction has been propagated.

It might assist here to expand somewhat on just how far from 'theory' Newton's speculations actually were. The lengthy Query 31 contains Newton's speculations on matter and its attractions. About midway, he turned to chemistry, suggesting that inter-particulate attractions might be responsible for the successive precipitations of metals from solution in acid:

> "And so when a Solution of Iron in *Aqua Fortis* dissolves the *Lapis Calaminaris*, and lets go the Iron, or a Solution of Copper dissolves Iron immersed in it and lets go the Copper, or a Solution of Silver dissolves Copper and lets go the Silver, or a Solution of Mercury in *Aqua fortis* being poured upon Iron, Copper, Tin, or Lead, dissolves the Metal and lets go the Mercury; does not this argue that the acid Particles of the *Aqua fortis* are attracted more strongly by the *Lapis Calaminaris* than by Iron, and more strongly by Iron than by copper, and more strongly by Copper than by Silver, and more strongly by Iron, Copper, Tin and Lead, than by Mercury?"[70]

As we have seen, Boyle had published a similar 'series' of metallic precipitations some thirty years prior to this. Newton's series was not novel and it is clear that it was not set down as a general chemical theory. He merely sought to use well known phenomena to support his speculative matter theory. Looking back with hindsight, it might seem that he had set out in prose the equivalent of an affinity column showing the affinities of various metals for aqua fortis. But at the time, these phenomena were merely offered up as evidence for Newton's ontological hypothesis which also drew on meteorology, natural philosophy and geology for substantiation.

Newton's explanation of his affinity series can, however, be described as innovative. Despite his corpuscular philosophy Boyle had been unable to explain the elective nature of affinity. Newton was, it would seem, the first to suggest that an attractive force between particles accounted for series of precipitations. But his explanation was, in truth, no more successful. The notion of varying forces between particles explained no more than Boyle's language of seduction and abandonment. Newton's suggestion that there were

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[70] Newton 1979, 380-381.

attractive forces between corpuscles of different chemical substances displaced the causality, sliding a hypothetical stratum of measurement between phenomena and cause: this is not an explanation. As René Thom states:

> "Descartes with his vortices, his hooked atoms, and the like explained everything and calculated nothing; Newton with the inverse square of gravitation, calculated everything and explained nothing."[71]

Newton's example of generalisation without venturing into causality was, however, influential on later affinity theorists, as Duncan has pointed out.[72] The definition offered of 'force' clearly influenced later chemists, who adopted a similar stratagem of defining 'affinity' as "a term … designed to express, not the cause, but the effect."[73]

The explicit references of the Query were not necessary for philosophers to consider whether the methodology that Newton had applied so successfully in his *Principia* might be similarly applicable to chemical phenomena. The correlation of affinity with attractive force also implied regularity and consistency, as well as calculability. Rather than pointing to the content of Query 31 which was neither factually novel nor causally enlightening, historians might do better to argue that it was Newtonianism as a methodology rather than as a metaphysic that might have served to inspire, if not Geoffroy, certainly later British chemists such as Cullen and Kirwan. Those chemists who were later to point to Newton's Query as the origin of affinity theory drew from it the implicit suggestion that affinity might one day provide a respectably mathematical basis for a truly scientific discipline. The quantification of affinities would become one of the projects of the latter half of the century, the ultimate aim of affinity theories.

The third strand of historiographical misunderstanding, resulting in the Newtonianisation of affinity theory, arises to a large extent out of the adherence of historians to a single theory model of affinity. Such a model forces the historian into a rigid stance – if affinity is regarded as a construction of

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[71] Thom 1975. Quoted in Cartwright 1983, 75.

[72] Duncan 1967, 154.

[73] Lewis 1765, 27.

Newton's, affinity theory as a whole is assumed to be Newtonian. A clear and distinct correlation is then assumed, such that where chemical affinity is discussed, it is under a Newtonian historiographical umbrella. From the first historiographic strand we proceed to the third almost without pause for thought; if one affinity theorist avows a Newtonian allegiance, so must all affinity theories be founded on the same metaphysic. This is an over-simplistic formula, which takes account neither of the pre-history of affinity nor of the pluralistic nature of the doctrine throughout the century.

The historical record in fact points to a notable lack of interest of Newton and his circle in Geoffroy's *Mémoire* either on its publication or during the thirty years afterwards. Although Geoffroy produced the *Mémoire* during Newton's lifetime, there is no evidence that Newton noticed it. However, Newton's lack of interest cannot be singled out as being exceptional. In fact, he seems to have epitomised the response from the British natural philosophical establishment.

As Geoffroy was himself an FRS and corresponded with Hans Sloane until his death,[74] it might seem reasonable to expect to find some mention of his *Mémoire* in the papers of the Society. A number of his communications were published in the pages of the *Philosophical Transaction,* but there is no mention of his *Mémoire* therein. Neither here, nor in the Society's Letter or Journal Books can any reference be found.[75] Indeed, it is not until the work of Richard Kirwan in 1781 that there is any specific mention of affinity theory in the *Philosophical Transactions*.[76] The Society undoubtedly received copies of the Mémoires of their Parisian counterpart, and as the Journal Books show, they often read the papers out at their regular meetings.[77] Given Geoffroy's close ties with the Royal Society, it seems strange that his table was not afforded a welcoming reception in Britain on its publication; or indeed that it was not afforded any reception at all.

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[74] The Royal Society holds some of their correspondence, as do the British Library as part of the Sloane Collection.

[75] My researches into both the published and unpublished papers of the Royal Society have shown that although the Society did receive a letter from Geoffroy to Sloane in 1719 (Royal Society of London 1718-1721), no discussion of Geoffroy's paper or comment was noted.

[76] Kirwan 1781.

[77] See e.g. December 21st 1721, Royal Society of London 1718-1721.

Why then, was Geoffroy's table so comprehensively ignored by the natural philosophers of Britain? Duncan has suggested that

> "Geoffroy's table was presumably less well known in Britain … and perhaps also the notion of affinity which was thought to be expressed in Geoffroy's table (though he does not use the word himself) was still felt in Britain to be in some way contrary to the notion that chemical combination was due to attraction between particles."[78]

This comment is interesting in the light of the historiographical disputes mentioned above. Surely the apparent adaptability of Geoffroy's paper to the Newtonian world view (as demonstrated by both modern and contemporary historians) rather contradicts this argument. It seems unlikely that philosophical or metaphysical prejudice lay behind what can only be described as the deafening silence from the establishment in response to Geoffroy's paper.

Philip George has examined the chemical papers published in the *Philosophical Transactions* and his statistics suggest that the output was far from negligible.[79] However, the classification of papers as chemical (George adopts the classification applied in contemporary abridgements of the *Philosophical Transactions*) does not mean that this rather mechanistic 'chemistry' bore much relationship to that appearing in the Mémoires of the Académie in France. French chemistry was concerned with principles and elements, and there was a thriving programme of analysis of plant substances through the burgeoning technique of solvent analysis.[80] It should also be borne in mind that France had a centralised and professionalising infrastructure in which chemistry could be a means to achieve social standing. As Holmes has argued, the Mémoires of the Académie "consolidated the literary genre of the scientific research paper",[81] and Geoffroy's *Mémoire* certainly appeared in this context. It was conceived out of the investigatory impulse constitutional to the Académie Royale.

In contrast, in Britain, the Royal Society, the only formally constituted body whose auspices might be said to cover chemistry, provided no structure on

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[78] Duncan 1996, 114.

[79] George 1952.

[80] Holmes 1971.

[81] Holmes and Levere 2000, 34.

which a philosopher could fashion a career. The Society instead enshrined the spirit of the gentleman amateur, shunning the professionalizing spirit that characterized its French counterpart. If a chemist in England were to hold high status, he would be unlikely to have acquired it solely through his chemical proficiency.[82] The problem for the historian arises in part from the fact that in Britain there was little public forum for discussion of non mechanistic chemistry. This does not of course mean that there was no such art practiced, or indeed that its practitioners did not find Geoffroy's paper of interest. Unfortunately though, it does mean that there is little or no evidence on which the historian can draw to settle the matter. The silence may well be merely the silence of history and it is perhaps rather superficial to insist that it reflects the silence of the 18th century actors.

Bearing the historiographical difficulties outlined above in mind, I would nevertheless suggest another possible reason for the lack of response to Geoffroy's *Mémoire*. Although it was presented in a research context, Geoffroy did not dwell in detail on theory, and the table was described simply as a synopsis of chemical phenomena. These phenomena were familiar, as we have seen. At first sight, perhaps Geoffroy's table seemed little different from Boyle and Newton's lists of displacements. While it was historically innovative in that it was the first of its kind, it may not have been immediately seen as such by British natural philosophers. Appearing in a 'research' context, it appeared out of place, neither fish nor flesh. Presented as an aide memoire, perhaps it seemed just too familiar to be significant. To recall the common proverb, perhaps this familiarity bred contempt. Even in France, as Fontenelle extolled the utility of "une Table Chimique", he looked past Geoffroy's table, anticipating "une Table de Nombres ordonnés suivant certain rapports ou certaines proprietés".[83] Geoffroy's table can only retrospectively be seen as pioneering: to its contemporaries it was simply an articulation of knowledge that

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[82] While Golinski has argued (Golinski 1983) that Peter Shaw attained high social status through his chemical publications, Shaw was exceptional, and in the end his eminence was a result of his position as physician to Monarchy rather than his chemical work. Certainly it is true that chemistry formed many of the rungs on Shaw's ladder to success, but it was always as an adjunct to the medical career to which the ladder led.

[83] Fontenelle 1719, 37.

had been common for some time.

A comparison of the initial response to Geoffroy's *Mémoire* with the response of theorists to the 1948 introduction of Feynman's diagrams is also enlightening on this point. As Kaiser has explained, Feynman's initial audience was confused, asking:

> "in exasperation, what *rules* governed the diagrams' use. … Even some of Feynman's closest friends and colleagues had difficulty following where his diagrams came from or how they were to be used."[84]

Like Feynman, Geoffroy did not provide instructions for the building or use of his table, presenting it as almost atheoretical. Of course we have no access to the tacit knowledge available to Geoffroy's contemporaries. It may be that this incorporated many of the 'rules' that are apparently missing from the *Mémoire*. I would suggest that the geographical and later, generational, separation of Geoffroy from the British chemists who might utilize his table would mitigate against such tacit knowledge being transferred with ease. Perhaps the view of affinity tables as synoptic was taken through necessity rather than inclination.[85] Without rules for usage, without a clear understanding of the tacit theoretical assumptions lying behind the table, the immediate, and pragmatic tendency was to see them as a summary of familiar knowledge.

It is possible, of course, that the real point of Geoffroy's paper was not affinity at all. Some years earlier he had reported a series of experiments which he interpreted as showing that a sulphur principle combined with vitriolic acid to form common sulphur and with metallic calces to form the more familiar metals.[86] Bearing in mind that the former combination is specifically included in his affinity table, perhaps the 1718 *Mémoire* was in fact a piece of subtle propaganda intended to reinforce his views? In a later paper that defended certain aspects of his table against criticism, he identified the sulphur principle with Stahl's phlogiston.[87] Here he expressly focused on its combination with

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[84] Kaiser 2005, 45-6.

[85] Duncan 1970, 33.

[86] Geoffroy 1704, Geoffroy 1709.

[87] Geoffroy 1720, 29.

vitriolic acid as an instance of an affinity that was stronger than that of the acid for fixed alkali. His paper reinforced his interpretation of his 1704 experiments even as he was purportedly clarifying his rapports. These repeated references to his sulphur principle were embedded within papers that drew almost entirely on familiar, even unquestioned knowledge. Both papers thus implied that his new ideas were not only accepted, they were beyond question. This idea is, it must be admitted, purely speculative, although it usefully illustrates my point perhaps, that Geoffroy's own intentions for his table were irrelevant to its subsequent history.

Kaiser shows that it was via the pedagogical context that Feynman diagrams were eventually dispersed throughout the physical theoretical community.[88] I would argue that a broadly similar model of dispersion is evident with regard to affinity theories in 18th century Britain. Although Geoffroy was Professor of Chemistry at the Jardin du Roi, it was not in this guise that he presented his table. His *Treatise* refers neither to the table nor to affinities or rapports.[89] Nevertheless, he called it "une chose fort utile", and carefully distinguished between its use for "ceux qui commencent à apprendre la Chimie" (i.e. its pedagogical function) and its use for "les Chimistes".[90] The table was to provide novices with a general survey of the relationships between substances.[91] For mature chemists it would enable them to discover the "mouvements cachés" when substances are mixed, and to predict the results of their mixtures.

Cullen's pedagogical endeavours retrieved affinity from obscurity and instituted a new conceptualisation in which the two uses suggested by Geoffroy coalesced. The doctrine of affinity provided him with a didactic framework, structuring the teaching of the science as well as consolidating and assimilating innovation. Once the table was taught as part of an affinity theory, and only then, did it become significant as part of British chemistry. The affinity table and the law of affinity assumed a new status, forming the basis of a common ground between chemists as the foundation of otherwise diverse affinity

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[88] Kaiser 2005.

[89] Geoffroy 1736.

[90] Geoffroy 1719, 203.

[91] Ibid.

theories. It was through the pedagogical context that affinity became almost omnipresent in British chemistry.

2.4 Act 2: In which a Pedagogical Tool is Constituted and it is Discovered to beget the Great and Distinguishing Principle of the Science

The history of British affinity theories is throughout a tale with an overwhelmingly pedagogical theme correlative with the development of chemistry as an autonomous discipline. Simões has argued that

> "A discipline is built, consolidated and demarcated from neighbouring disciplines through the research and teaching activities of its practitioners. Especially in the very first steps of a young discipline, scientists are often involved in these two very different, and at times antagonistic, processes."[92]

My research suggests that in Britain affinity theories provided a structural framework which supported the new courses in chemistry that were being put together in the 18th century, as well as setting boundaries to the discipline. Eventually, through a 'trickle down' effect (Kaiser has dubbed the post-war version of this phenomenon the "postdoc cascade"),[93] they not only shaped the teaching of chemistry, but the practice of the science.

Chemistry teaching in Britain was limited early in the 18th century; Cambridge University founded a Chair in chemistry from 1702, but the occupants of the post seem to have taught sporadically for the first half century or so.[94] Teaching in Oxford (which opened a chemistry laboratory as part of the new Ashmolean Museum in 1683) was unofficial when there was any at all and the situation seems to have remained pretty dire until as late as the 1780s.[95] One of the few to have lectured in Oxford (at the Ashmolean), John Freind, published his *Chymical Lectures* in 1712.[96] These were perhaps the most dedicated of Newtonian attempts to force the teaching of chemistry into the Newtonian mode.

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[92] Simões 2004, 300.

[93] Kaiser 2005, 93-101.

[94] Archer and Haley 2006, ch 1-5.

[95] Golinski 1992 53-4.

[96] Freind 1712.

John Mickelburgh attempted a similar conflation a little later in the century. Mickelburgh's chemistry courses were the first to be given in Cambridge after the publication of Geoffroy's table and his lectures provide a further example of the deafening silence that characterized the British response for many years. He followed Newton in attempting to explain chemical behaviour by reduction to particles and forces. Much of his course was lifted directly from that of Freind whose methodology he praised unstintingly.

The notion of attraction is present throughout Mickelburgh's lectures, but it is a distinctively Newtonian or gravitational type of attraction; Mickelburgh fervently denied that it should be regarded as an occult quality "as the Lipsick philosophers do" just because the cause was not yet understood. He referred the doubters to Newton:

> "whosoever hath a mind to furnish himself wth Instances of this kind may only consult the 31st Quere of Sr Isaac Newtons Opticks, page 350th of the English Edition. ... how should this salt melt or run per deliquium if it did not attract to itself the watry particles wch float in the air in the form of vapours & why do not other Salts melt & run per deliquium but for want of such an attraction"[97]

Mickelburgh's Newtonian chemistry related attraction predominantly to physical factors. Sulphur, nitre and tartar were particularly mentioned as being possessed of a "considerable attractive force" which enabled them to "disunite & disjoyn the parts of hard & solid bodies."[98] In addition to the attractive force, he postulated a *vis repellens* that acted between the smallest particles and was augmented by the action of fire. Much of the distinctively chemical behaviour of substances was ironed out, with explanations in terms of these two opposing forces.

Christie and Golinski have compared Mickelburgh's lectures with those of Freind, arguing that Mickelburgh, although following a Newtonian reductionist programme, still adhered to the chemical didactic tradition instituted by Libavius.[99] His lectures provide useful evidence of how Newtonian chemistry

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[97] Mickleburgh 1726.

[98] Ibid.

[99] Christie and Golinski 1982, 246.

was taught to students, although it is unclear how long Mickelburgh adhered to this model. Following on from the 1726 set of fifteen lectures, there is another even shorter set of lectures apparently dated 1741. These lectures reverted to an Aristotelian matter theory; while matter was still attractive or repellent, the language was less mathematical and notably more chemical. The cause of this change can only be speculated upon, but by 1741 the heyday of Newtonian chemistry was passing. By this time there were a number of lecturers operating outside the English universities. They took a more distinctively chemical approach, emulating Boerhaave. Some were private, their lectures open to any who could pay, and others were affiliated to one of the four Scottish universities. One such, the first lecturer in chemistry at Edinburgh University, was James Crawford.

Crawford, lecturing before Geoffroy's paper was published, adopted a pragmatic attitude that seems closer in spirit to Geoffroy's than to his more Newtonian contemporaries'. He argued that:

> "ye partes of bodys by yr minuteness flying our senses, yr mechanicall pptys are unknown; qqontly yr can be but few of ye phenoa accounted for by mechanicall Laws: and our common mechanicall systems are nothing else but Phiphal Hypotheses, we only qclude, … figure, size and motion yt yy are pleased to assign ym, but whether yy really have ym or not, yy are utterly uncertain and can never be surely informed wtout a Revelarn"[100]

Crawford was undoubtedly familiar with Query 31, as well as with Freind's reductionist Newtonian chemistry. He was more than a little scathing:

> "… yet I despair of ye laws of attrac'n established by Kyle and Friend their ever being of any great use for explaining ye chymical phoea".[101]

Crawford, like Boyle before him, recognized "the problem of transdiction"[102] Whatever postulated systems or theories of matter a philosopher adopts, the linking of this to observed phenomena requires a leap of faith beyond the logically acceptable. As he continued:

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[100] Crawford 1713, f 3.

[101] Ibid.

[102] Guerlac 1968, 64.

> “ye Caelesteal Bodys being at a vast distance, it's easy to compare yr motions wt ye law of attracn; but here every thing by it's minuteness being insensible, it's impossible, I think, by expermt to establish laws of attracn wc can be compared wt ye notions of ye particules of bodys”[103]

Instead of dwelling on the rather bleak picture this presented for chemical philosophers, Crawford adopted a pragmatic methodology. Like Boyle and Newton he demonstrated his familiarity with the displacement of metals from acids:

> “Fr instance, if you dissolve merc. in sp vitr. and cast a plate of copper into ye solution, ye merc is precipitated to ye bottom, ye copp is dissolved, into a blew <unknown symbol possibly signifying ‘tincture’>,[104] if into ye <tincture?> you throw a piece of Iron, ye Copp falls, and ye Iron is dissolved and suspended, again if to this solution you join some of ye lapis calmaris ye iron falls and ye calarum is dyssolved and easily any alcobalt precipitates ye calarum."[105]

Crawford taught that chemists should take a position midway between full metaphysical theory and total empiricism – generalisation and order being emphasised, as well as the use of analogy that was to prove essential to affinity theory:

> "When both mechanicall and physicall causes fail us, we must be qtent to deduce ye phoen from ye chymical causes by referring ym to ye like effect yt qstantly and regularly happeneth in a thousand chymical experiments.”[106]

Crawford’s chemistry was epistemologically bounded by the search for “chymical causes”, from empirical generalization, rejecting causal speculation. He thus explained the precipitation series, on the grounds that each body was more or less easily dissolved by the acid, and those that were dissolved more easily would supplant the others. Such an empirically justified explanation was sufficient:

> “I think it more ingenious to rest here, referring a dark case to a

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[103] Crawford 1713, f 3.

[104] Several of the MSS I have examined utilised symbols for chemical substances. For clarity, where these appear I have used the full textual description surrounded by ‘< >’.

[105] Ibid, f 3-4

[106] Ibid, f 3.

> more known and familiar one, yn to vent a fictitious hypothesis about ye figure, size &c of ye partes of yse bodys or ye pores, and from yse supposed at pleasure w'out any proof, to pretend to solve ye pheoa, for it does not cure our ignorance to pretend knowledge yn we have none."[107]

Thus Crawford drew his disciplinary boundaries. His pragmatic empiricism contrasts with high-flown attempts to accommodate chemistry into a Newtonian scheme. Similar boundaries were later embedded in the doctrine of affinity and these were projected onto the discipline.

Chemistry in Britain was (happily) not confined to the activities of the Royal Society or the official teaching in the universities. There were of course many working chemists, whether apothecaries, assayers, physicians or any of the other skilled occupations that involved the manipulation of matter. These, in truth, were the artisans who might be more likely to describe themselves as 'chemists'. In spite of the lack of a formalized, specifically chemical 'establishment', there was also a thriving unofficial network of chemistry lecturers.[108] Many of its luminaries were self-educated while others had learned chemistry as part of their medical training. They contributed to the dissemination of chemistry through the performance of public lecture courses, and published their lectures and course syllabi.[109] By the 1730s, in spite of the lack of any establishment encouragement, Geoffroy's affinity table had begun to creep into this informal pedagogy. Its first mention in a British publication was by the most prominent (and successful) lecturer in chemistry of the first half of the 18th century, Peter Shaw.

Shaw's career illustrates the contrast between the social situation of the chemist within (or more accurately, without) the English scientific world when compared to France. He promoted himself as an indispensable intermediary between the proponents of chemical knowledge, and the society physicians who were his patrons.[110] As Golinski has noted, Shaw's choices of works for translation and publication did not emphasise a predominantly Newtonian

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[107] Ibid, f 4.

[108] For a general survey of 'itinerant' lecturers, see Gibbs 1960.

[109] For example, Saunders n.d. [1766?], Martin 1743, Shaw n.d. [1733?], Warltire 1769a, Wilson 1771.

[110] Golinski 1983, 19-21.

stance. Instead, they took for the most part what might be termed a ‘chemical’ position that followed the Baconian inductive method and emphasised a qualitative chemistry, often founded on systems of elements.[111] His entrepreneurial role served to bring him to the attention of the establishment, and enabled him to achieve similar social heights, at which point his interest in chemistry apparently had served its purpose and he published no more.

While still engaged in his role as public lecturer in chemistry, Shaw published a selection of headings for a proposed course in “philosophical chemistry”. Amongst the headings for this presumably theoretically biased course, he included:

> "III A View of the different RELATIONS, vulgarly call'd Sympathies and Antipathies, or Attractions and Repulses, observ'd betwixt different chemical Bodies; with the uses of this Doctrine in Philosophy and Chemistry. See Boyle, Hook, Homberg, Newton, Stahl, and the Memoir of Geoffroy in the Works of the Royal Academy for the Year 1718." [112]

Whether a course was ever given along these lines we do not know. Shaw did indeed give courses on chemistry for many years in London and later on in Scarborough, and he published the syllabus to one such course in 1733. Under the heading ‘synthesis’ he stated:

> “it is proper to enquire what other Bodies there are which may be perfectly separated into different Parts by the way of Menstruum, Absorbent, or Precipitant; so as to leave the separated Matters unalter'd in their Natures; and fit to compose the original substance again. This Enquiry depends upon finding out the secret Relations which exist betwixt particular Bodies; and these Relations can only be discover'd by particular Trials. * [* See M. Geoffroy's Paper to this purpose in the French Memoires].”[113]

These are the first references to Geoffroy’s *Mémoire* in any British publication, some fifteen years after its initial presentation. It cropped up again in Shaw’s 1741 translation of Boerhaave’s *New Method of Chemistry*.[114] Although

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[111] Ibid, 24-26.

[112] Shaw and Hauksbee 1731, 41.

[113] Shaw n.d. [1733?], 173-4.

[114] Shaw’s unofficial translation of the lectures (Boerhaave 1727) provided equally copious notes including references to some of the Memoires, but the latest reference is 1716.

Boerhaave's work advised his readers to consult Geoffroy's works, it did not comment specifically on the 1718 *Mémoire*. However, Shaw's notes (often vastly out of proportion to the Boerhaavian part of the work – some pages allow Boerhaave the top line, while Shaw's notes and updates occupy the remainder of the leaf) directed the reader to many useful chemical papers including Geoffroy's 1718 paper. He describes the table here as

> "a system or table of the mutual relations betwixt different substances in chemistry; which, if rightly understood, and carried on, might become a fundamental law for chemical operations, and guide the operator with success".[115]

It is clear that by the 1730s and into the 1740s Shaw, at least, was recommending Geoffroy's affinity table. He apparently viewed the table as a useful synoptic tool, albeit with the potential to provide a heuristic value, suggesting that it had the potential to form the basis of a "fundamental law" which could "guide the operator". The notion of discovering from the patterns of relations a law that could predict chemical behaviour must have been an attractive one, although Shaw apparently made no effort himself to deduce such a law and although he referred his audiences to Geoffroy's table, he did not reprint it in any of his various publications.

It was not until 1749, over thirty years after the original publication of Geoffroy's paper, that Macquer published his *Elemens de Chymie Theorique* in France which included not only a reproduction of Geoffroy's table, but also an entire chapter offering instructions for its use. Macquer's chemistry was notable for its consistency, making use of affinity theory throughout. He asserted that:

> "Nous avons vu dans le cours de cet Ouvrage, que Presque tous les phénoménes qu présente la Chymie, sont fondés sur les affinities qu'ont ensemble les différentes substances, sur-tout celles qui sont les plus simples."[116]

He added to Geoffroy's table, a set of six (seven in the English translation) rules or propositions relating to the action of affinity "quelle qu'en soit la cause". He

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[115] Boerhaave 1741, 58.

[116] Macquer 1749, 256.

referred to these propositions as "vérités fondamentales",[117] according them an unusual value that perhaps proceeded from the fact that they allowed him to link his affinity to his phlogiston theory as well as to his Aristotelian matter theory. Macquer took a holistic view of his chemistry, and his affinity theory provided a crucial link between the observations of matter as it tended to be found in the laboratory: messy, complicated, and a long way from the perfectly pure ideal of the Aristotelian elements; and the *a priori* ontology that he believed lay behind these untidy observations. Macquer's affinity theory, it would appear, was designed to solve the problem of transdiction.

Duncan has suggested that "the efficient cause of the revival of interest in affinity in the 1750s was probably the publication of Macquer's Elemens".[118] The work was undoubtedly influential; one of the few works that Cullen recommended to students, although with stern criticism of some aspects.[119] However, it was not until 1758 that the *Elemens* was translated into English by Andrew Reid, combined with its sister volume *Elemens de Chymie Practique* into a single publication.[120] Certainly the first (French) edition of Macquer's work would have been available to those British chemists who were prepared to obtain it, and it is likely that it played some role in the renewed interest in affinity that was to come. However, the components of Macquer's affinity theory differed in a number of important respects from those of more empirically inclined British chemists. Although Macquer's significance in disseminating affinity theory across Europe is not denied,[121] British chemists did not accept his affinity theory without question. Many would have learned of Geoffroy's table from alternative sources: Shaw had been prescribing it to his audiences since the 1730s, while in Scotland Cullen had been teaching his students Geoffroy's table for almost two years by the time the *Elemens* was published.

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[117] Ibid, 22.

[118] Duncan 1996, 115.

[119] Cullen 1766, Lecture 10.

[120] Macquer 1758.

[121] For detailed discussion of Macquer's role in the dissemination and propagation of affinity theory in France, see Kim 2003; Duncan 1996, Eklund 1971.

There are in fact two contenders for the first actual publication in Britain of an affinity table. Dr Robert Poole, physician and writer, included Geoffroy's table his *Chymical Vade Mecum* of 1748.[122] A better authenticated publication occurred in 1753, some years before the English edition of Macquer's textbook, in Lewis's *New Dispensatory*.

Both Gibbs and Golinski have noted similarities between the careers of Lewis and Shaw. Lewis also gave public lectures in chemistry during the 1730s and 40s, published methodized translations of the works of European chemists, and attained "a respected position as a research chemist".[123] His successful publications (or perhaps his personal preferences) did not, however, allow him to emulate Shaw and abandon chemistry. He continued to consult, advising amongst others the fledgling Society for the Encouragement of Arts, Manufactures, and Commerce,[124] and published until the 1760s. He was, at his death, working on an adaptation of Hoffmann's *System of the Practice of Medicine.*[125]

It seems likely that Lewis became aware of Geoffroy's table prior to 1748, when he published his proposals for printing his *Commercium Philosophico-Technicum*. This was an ambitious project, a periodical publication to be published in six parts per annum, and "designed as an attempt to advance useful knowledge."[126] Lewis's vision was of an empirical, pragmatically utilitarian chemistry, and the synoptic tabulation of knowledge formed an intrinsic part of his design. The *Proposals* specifically set out his intention to include in the work a

> "table of the relations or affinity which different substances bear to one another; with an experimental account of its uses".[127]

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[122] Poole 1748. The British Library's copy of this volume is undated (and as a manuscript note on the flyleaf states, it is a "very scarce book"), although Moore 1918, 77 mentions that it was published in 1748.

[123] Golinski 1992, 60.

[124] Society for the Encouragement of Arts n.d.a, ff 141-144, Society for the Encouragement of Arts n.d.b. His investigations on Virginian potashes was published as Lewis 1767.

[125] Gibbs 1952, 148-149.

[126] Lewis 1748, frontispiece. When the work finally appeared, this was amended to read "an attempt to improve Arts, Trades and Manufactures" (Lewis 1763, frontispiece).

[127] Lewis 1748, 18.

While this is a clear reference to Geoffroy's table, it is far too early to have sprung from any sight of Macquer's *Elemens*. Like Shaw, Lewis was obviously familiar with the table some time prior to the appearance of Macquer's work. It seems likely that, again like Shaw, it was included in his public lectures, but the historical record is silent on this. Sadly, only the first few parts of *Commercium Philosophico-Technicum* were published in 1763 and, in spite of the fact that an extensive explanation of affinity appears in the preface, no table was included.[128] However, as part of his report on the properties of platina that occupied almost half of the work, Lewis inserted fifteen separate columns, each of three substances, showing the affinities of this curious metal alongside explanations of how he discovered them.

Lewis was, as Cullen claimed in his lectures[129] responsible for the first publication of an English affinity table; an amended version of Geoffroy's table, in the first edition of his *New Dispensatory* of 1753. New editions of this work were published throughout the 18th century, and after Lewis's death they continued to be produced "with amendments by gentlemen of the faculty at Edinburgh".[130] They were recommended by Cullen to his students,[131] and were undoubtedly extremely influential in the medical world. Indeed, Cullen commented that the *New Dispensatory* was "the only English work that does any credit to the country, or had made any improvement in the Materia Medica."[132]

In the first edition of the *New Dispensatory*, affinity is mentioned only in the introduction with specific reference to the reactions of marine acid. Lewis commented that

> "the doctrine of the affinity of bodies is of very extensive use in the chemical pharmacy: many of the officinal processes are

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[128] The discussion of affinity appears as part of Lewis's explanation of the different types of "active powers" of bodies, chemical and mechanical. Lewis 1763, iv.

[129] The assertion apparently appears in the MS *Notes of Dr Cullen's Lectures on Chemistry, made by Dr John White of Paisley* (1754) held in City Library, Paisley. Sivin 1962, 67.

[130] Lewis 1786.

[131] See Cullen n.d. [1757/8], f 40.

[132] Cullen 1789, 51-52.

> founded on it"[133]

Lewis slightly changed the form and content of Geoffroy's table, using text rather than symbols, and setting out the orders of affinity in rows rather than columns. Sivin has carefully compared Lewis's table with Geoffroy's, highlighting those columns and substances that Lewis removed or added.[134] Sivin's analysis is unfortunately marred by his somewhat present-centred reference to affinity table columns as "displacement series". Thus he deplores Geoffroy's failure to recognise the effects of mass action, and rather oddly accuses both him and Lewis of inconsistency in the columns for, respectively, iron and antimony, and nitrous and marine acids.[135] Only Sivin's misinterpretation of the columns as "displacement series" can explain this mistake. It would appear that the theoretical assumptions required to enable the construal of affinity tables are counter-intuitive to those more versed in the chemistry of later centuries.

In later editions of the *New Dispensatory*, Lewis made further amendments to his table, which by this time bore little resemblance to Geoffroy's. He also extended his discussion of chemical theory, and the table appeared within a newly introduced 'Elements of Pharmacy', which constituted about a third of the total work. The table, now in the form of 19 textual lists, was included under a separate entry 'affinity' with a brief but clear explanation of how the table (but notably not affinity itself) worked. Lewis shied away from causal explanation, remarking only that:

> "the power in bodies, on which these various transpositions and combinations depend, is called by the chemists affinity; a term, like the Newtonian attraction, designed to express, not the cause,

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[133] Lewis 1753, 10. The word 'officinal' is defined by the OED as referring to a medicinal preparation "kept as a stock preparation by apothecaries or pharmacists (now *rare*); made to a standard prescribed in a pharmacopoeia or formulary, included in a pharmacopoeia." "officinal, a."*OED Online*, Mar 2004, Oxford University Press. 10 Oct 2006 http://dictionary.oed.com/cgi/entry/00330510.

[134] Sivin 1962.

[135] Geoffroy's table included a column headed with iron, with regulus of antimony immediately below it, and copper, silver and lead below that. The next column was headed by regulus of antimony, with iron immediately below it, and again copper, silver and lead below that. There is nothing inconsistent about this. Geoffroy was clearly showing that the strongest affinity lay between antimony and iron, and that this will lead to all other metals being removed from their union with either of these two metals. Indeed, there would have been something wrong with Geoffroy's table if these two columns had not borne this relationship to each other.

> but the effect"[136]

Although he referred to 'Newtonian attraction' in the same breath as affinity, it is clear that he was not conflating the two. The connection between the terms was in their reference to effect rather than cause. This is the same pragmatic approach to causality we saw in Crawford's lectures.

As Sivin has argued, Lewis valued affinity tables for their pragmatic usefulness to practical chemists, in the service of pharmacy, or industry.[137] Through *Commercium* he hoped to expand the use of chemistry to improve industrial processes and to extend knowledge of chemistry as a practical art. As lecturer and writer of textbooks, his pedagogical focus, his desire to teach and inform is clear. In publishing his affinity tables Lewis introduced chemists to affinity, while his pragmatic decision to set aside high level theory allowed these chemists to formulate their affinity theories almost anew. His own theory as he set it out in his works included little that did not appear in Geoffroy's original paper, although his table differed in both form and content. Nevertheless, his adoption of the affinity table as a useful tool led to one striking addition that clarified the link between the methodized knowledge encapsulated therein and the practice of chemistry. Geoffroy, in spite of a promise that he would publish details of the experiments on which his table was founded had never done so.[138] In Lewis's examination of platina, he carefully formulated new columns for his tables, showing by example how such information could be ordered in terms of affinity. In doing so, he filled in one of the lacunae of Geoffroy's theory by setting out in detail the experiments from which he derived his columns, and thus clarifying the empirical basis for his affinities.

Shaw and Lewis appear in this tale primarily as disseminators, introducing a new generation of chemists to Geoffroy's table, endorsing it as useful and worthy of their attention. Lewis's influence on chemistry in Britain is not sufficiently appreciated by historians, although his near contemporaries recognised the value of his chemical works. Throughout his teaching Cullen

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[136] Lewis 1765, 35.

[137] Sivin 1962.

[138] Geoffroy 1719, 212.

referred his students to Lewis's works, claiming in 1766 that "yet has there been no good chemist in England of yore except Dr Lewis who is perhaps at present the most considerable in Europe."[139] It was Cullen though who was to thrust the doctrine of affinity to the front of stage in British chemistry, by transforming it into a pedagogical tool that supported his complex and detailed lecture course.

Cullen was described by Thomson as "the true commencer of the study of scientific chemistry in Great Britain".[140] He was extremely well regarded throughout his life by his ex-students (and in many cases their ex-students) who did much to propagate their reverence for their master through the wider world. Thomson reported:

> "The appearance of Dr. Cullen in the College of Edinburgh constitutes a memorable era in the progress of that celebrated school. Hitherto chemistry being reckoned of little importance, had been attended by very few students; when Cullen began to lecture it became a favourite study, almost all the students flocking to hear him, and the chemical class becoming immediately more numerous than any other in the college, anatomy excepted."[141]

Thomson's claim is well supported; we know that Cullen's 1763/4 course attracted 145 students.[142] The popularity of his lectures are attested to by the unusually large number of sets of lecture notes held in libraries across the country. Lecture notes were routinely copied and sold to interested parties, often outside the student circle. Thus both Donovan and Golinski have argued that in the context of the 18th century both Cullen's and his former student Joseph Black's ideas as expounded in their lectures had effectively been placed in the public domain.[143] The diarist Sylas Neville, a medical student under Cullen, writes of the copying of lecture notes and of a thriving trade in the sale and purchase of reliable sets of notes.[144] Likewise, the apothecary and natural philosopher John Elliot admitted to having been able to study a set of Black's

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[139] Cullen 1766, Lecture 8.

[140] Thomson 1830, 304.

[141] Ibid, 307.

[142] Golinski 1992, 17.

[143] Golinski 1992, 42-3 and Donovan 1975, 271.

[144] Neville 1950, 151.

lecture notes belonging to a friend, although he complained that he ‘only wished they had been more perfect’.[145]

The extent of these archives allow the historian to make a fair account of his teaching[146] and Cullen’s chemistry teaching has been investigated time and again by historians, although only Crosland has concentrated in detail on Cullen’s affinity theory.[147] Most of the work done to date has been based on only a few manuscripts, held at the Royal College of Physicians Edinburgh, and there remains a great deal of information on Cullen’s affinity theory still to be elicited from manuscripts as yet unexamined.

Although he was briefly apprenticed to a surgeon apothecary as early as 1727/8, it seems likely that Cullen acquired some of his chemical knowledge from one of the public lecturers in chemistry during a brief stay in London in the early 1730s. It has been suggested that he may have attended one of Shaw’s London courses, at which he might have learned of the utility of affinity.[148] On the other hand, Lewis was also lecturing in London during the period that Cullen is known to have been there. Cullen’s habit of referring throughout his chemistry teaching to Lewis’s works[149] suggests that it is equally possible that Cullen attended Lewis’s lectures on chemistry.

It is certainly apparent that Cullen included affinity as an important part of his chemistry course at Glasgow University from the very first.[150] Cullen, like

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[145] Elliot 1780, 122-3.

[146] The Wellcome Library in London holds at least four fairly complete sets of lectures, as well as a number of more fragmentary sets Cullen 1766, Cullen 1765, Cullen n.d. [1760s], Cullen 1760. Glasgow University library holds a vast number of manuscripts, comprising Cullen’s own notes, as well as fragments of the lecture notes of students. The number of MS held at Glasgow University Library is too great to list each MS individually. Quotations from individual MS will be specified hereafter. Edinburgh University library and the Royal College of Physicians in Edinburgh are two further repositories for the enormous number of Cullen papers still extant. The fact that Cullen lectured in English rather than Latin confers the added benefit that most of the notes of his chemistry lectures are in that language. Neville wrote: “I find that Dr. Cullen notwithstanding his present eminence had but a poor education and had not acquired much learning before he was 40 years old. … Knowles heard that one J. Brown, a great Latinist, who writes many Theses for those who are not ashamed to bring out the composition of another as their own, assists Cullen in his Latin”. Neville 1950, 144. Although Cullen lectured in English, examinations were still held in Latin, and Neville also testifies to the fact that in spite of Cullen’s alleged lack of facility with the language he was nevertheless sufficiently proficient to hear examinations without assistance.

[147] Crosland 1959.

[148] Donovan 1975, 31.

[149] Cullen 1766, Cullen n.d. [1760s?], Cullen n.d. [1757/8], Cullen n.d. [1760?].

[150] Cullen 1748, ii.

Lewis, extended the practical range of Geoffroy's table, producing new columns setting out the affinities of substances not previously included. But where Lewis conceived of affinity as a utilitarian ordering or classification of empirically based facts, Cullen developed a complex theory, linking it explicitly to his observations of chemical practice. He extended its theoretical range by the inclusion of new components covering such matters as complex affinities and the role of heat and it moulded and dictated much of his didactic strategy.

Cullen taught that the chemist investigated the "particular properties of bodies"[151] and the structuring role that he allocated to this theory is clear from his carefully worded definition:

> "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."[152]

As we saw in the prologue, one of Cullen's most important demonstrations, cropping up every year in the lecture notes, was the combination of aqua fortis and potash to form nitre, and the decomposition of this into its constituent aqua fortis and potash. He went on to compare the properties of the acid, alkali and the neutral salt, showing that, contrary to what Macquer believed, the properties of the constituent substances were not carried through into the compound. Tables appear in the lecture notes showing that aqua fortis is volatile, while the alkali is fixed (solid) and nitre, the compound of these two, is also fixed. Both the acid and the alkali are acrid, where the neutral salt is mild. Qualities then, were not dependent upon the constituents of substances, but could be changed by combination or separation. And both combination and separation were performed by the judicious exploitation of the affinities of substances.

Cullen explained that combination was produced due to a natural tendency present in all bodies or substances to approach each other. Separation too, was due to either the action of affinity (or elective attraction as he preferred to call it) or fire. Fire was the traditional agent of chemists in the analysis of bodies, but while heat was still used cautiously in operations such as distillation to

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[151] Cullen 1766, Lecture 9.

[152] Ibid, Lecture 19.

analyse compounds, it had been recognised that fire was a rather blunt instrument for many separations. For Cullen, affinity was a more precise tool for separating bodies that were chemically combined, as he demonstrated with the decomposition of nitre.

Cullen also classified the specific operations and processes in terms of his affinity theory. In both analysis and synthesis, the primary tool of the chemist was the power apparently inherent in substances to combine together, but fire had a place in affinity theory too, promoting fusion or solution to enable the affinities to act.:

> "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."[153]

Cullen's theory included the rather mechanistic assumption that as the particles of bodies had to be close together to exercise their affinities, one or both substances in any operation must be fluid. In a fluid state, the particles of each substance could mingle and approach each other close enough for their natural attractions to act. This necessary fluidity was adopted by the majority of chemists, although Nicholson later objected to its axiomatic status as having been too hastily adopted.[154] 'Fluid', in this context, meant either in fusion, in solution, or in the form of an elastic fluid, or vapour. Thus, Cullen's affinity theory determined the specific operations to be carried out and he grouped chemical processes and operations under three headings accordingly.[155] Combination could be performed either by solution, fusion or exhalation (a term used for evaporation), and separation could similarly be performed by solution, fusion, or exhalation. In all operations though, the agents of the chemist were affinity and fire.

Guerlac claims that Cullen was the first to combine Newton's "attractionist atomism with those chemical facts of affinity assembled and sifted by chemists

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[153] Cullen n.d. [1760s], f 66.

[154] Nicholson 1795, I, 337.

[155] Cullen n.d. [1760s], f 66-67.

on the Continent."[156] It is certainly true that Cullen was the first to explicitly link something like a Newtonian notion of attraction with affinity. However, as with Lewis, Cullen's attraction "rather denotes a Force, than a Cause; & in this sense was used by Newton".[157] His affinity theory did not depend on any notion of action at a distance, and indeed his ontological preferences seem to have been an uncertain blend of Boyleian corpuscularianism and Newtonian aetherial speculation.[158]

For the purposes of most of Cullen's chemistry lectures, causal speculation was set aside. His motivation may have been as much based on social as on theoretical or pragmatic considerations. Throughout the 18th century in Britain there was a strong impulse towards the use of knowledge for useful, improving purposes, for the general and individual good. This was the drive that led to what historians call the agricultural and industrial revolutions, and it was particularly strong in Scotland. There was a strongly utilitarian theme emerging in the philosophies of David Hume and Francis Hutcheson, both of whom were highly influential in the Scottish philosophical hothouse where the doctrine of affinity was given its new lease of life.[159]

Moral philosophy sought to guide the acquisition and application of knowledge, and in Scotland a kind of utilitarian empiricism was advocated. British natural philosophy had been distinguished from the time of Bacon by its strongly empirical tendency, and chemists in particular were less interested in formulating a great metaphysical theory that would explain everything, than with finding ways to order their vastly accumulating 'matters of fact' and to make their knowledge practically useful.[160] The associated reluctance to 'frame hypotheses' (or at least to be perceived as so doing) was similarly a residue of the Baconian ideal espoused by so many of the philosophers of the previous

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[156] Guerlac 1968, 81.

[157] Cullen 1766, Lecture 19.

[158] See Christie 1983 and Taylor 2006.

[159] Indeed Hutcheson's *Inquiry* of 1726 included the claim that "that Action is best, which procures the greatest Happiness for the greatest Numbers" some fifty years before Bentham adopted the notion for his utilitarianism. See Hutcheson 1726, 177.

[160] Matters of fact loom large in Hume's philosophy. See in particular Hume 1931, 172. For the 17th century origin of this concept, see Shapin and Schaffer 1985.

century.[161] Hutcheson cautioned against "rash precipitate assenting"[162] to authority, and this admonition was further rationalised in Hume's sceptical philosophy.[163]

From these points of view, affinity theories were philosophically appropriate. In harmony with the Scottish *zeitgeist,* they were empirically founded and offered a philosophically acceptable systematisation of chemical knowledge, while at the same time setting clear limits to enquiry.

Cullen was engaged in fashioning a career, as had been Shaw before him. As the first chemistry lecturer appointed by Glasgow University, his was one of only a few officially appointed positions. It was undeniably in his interest to demarcate his discipline from other fields. We know from the manoeuvring that took place over Cullen's move to Edinburgh University, as well as his association with 'improving' patrons that he was an ambitious man.[164] To preserve his status, it was important to keep his students' minds on the objects and offices of chemistry. Chemistry needed clear disciplinary boundaries to distinguish it from natural philosophy as well as to distinguish Cullen in his career. He explained:

> "some of the moderns have endeavour'd to reduce Chemical Philosophy to Mechanical Principles, thus they are apt to confound Operations, reckoning many as Chemical w^{ch} properly belong to Mechanics."[165]

It is clear from all the extant sets of Cullen's lectures that his affinity theory performed a vital role as a pedagogical tool. It enabled the demarcation of chemistry and its methods from the mechanical philosophy. Here was a basis for the classification of operations as well as a way of explaining how substances combined together, and how the natural tendencies of matter could be manipulated to achieve the desired result. Cullen added new components to his theory that introduced 'double elective attractions', dealing with the prediction

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[161] Newton 1995,442.

[162] Hutcheson 1747, 64.

[163] Hume 1931.

[164] See Guthrie 1950, Christie 1976, Golinski 1988.

[165] Cullen n.d. [1760s], 79a, f 5.

and explanation of complex combinations. These proved to be of great influence in the years to come.

Throughout his chemistry teaching, Cullen marched his students through the columns of an affinity table, commenting on its contents. In the earliest sets of notes dating from 1748-50, he used Geoffroy's table. In these lectures he also referred freely to the columns contained in Lewis's tables, comparing them with Geoffroy's, and where necessary correcting both. There is also evidence that Cullen printed his own table for students from the late 1750s.[166] A copy of a printed table of fifteen columns survives in the archives of the National Library of Wales, and it is possible that this was the table sold to students.[167] Later lectures include a much enlarged and amended table of Cullen's devising, which was apparently pinned up to be copied down by the students. One such can be seen in figure 2 (see p. 94 below).[168]

We have noted Charles Blagden's blasé comment indicating that affinity tables routinely appeared in any publication on chemistry worthy of the name. When Cullen began his lectures at Glasgow, no affinity table had been published in Britain. By the final year of his chemistry lectures at Edinburgh, they were omnipresent. By this time Cullen had been teaching affinity theory as a general principle of the discipline for eighteen years. Many of his early students had themselves become lecturers, and they too taught their students to use affinity tables, and wrote the very textbooks that presented affinity to an even larger audience. Cullen's pedagogy was crucial to the dispersion of affinity theories throughout Britain, as can be seen from the plan of the pedagogical pyramid at Appendix II.

Geoffroy's passive recording of chemical behaviour should be contrasted with the later vision, instituted by Cullen, of the active chemist who manipulates the natural tendencies of matter. Similarly, the status of affinity theories and the knowledge they offered changed. Geoffroy and his contemporaries had long been familiar with the phenomena covered by his table while Cullen's students

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[166] Cullen 1759b.

[167] Cullen n.d. [1750s?]. This table includes a column for fixed air, which would date it around 1757-1759.

[168] Cullen 1765, MS 1921. See also Cullen n.d. [1760s].

were presented with his theory at the start of their induction into chemistry. Cullen taught his students right from the start that attraction and fire were the agents of the chemist. All the various chemical processes involved these two agencies and chemical knowledge of particular substances consisted primarily of a knowledge of their affinities. Students heard about the affinities of bodies, and learned to use an affinity table long before they saw the precipitations and displacements that gave rise to the table. They approached this stage of the course with Cullen's affinity theory firmly lodged in their minds, and a copy of his table grasped equally firmly in their hands. Everything they learned from that point onwards about the particular substances was seen through affinity tinted spectacles.

It was specifically Cullen's marshalling of affinity theory in the service of his pedagogical role that led to this change in the status of affinity theories. In setting affinity at the centre of his lectures as one of the general principles of chemistry, he assigned it a new explanatory and predictive role. At the same time its *a priori* aspect gave it a new standing in the eyes of his students. This in turn set in train a mode of explanation by affinity that would oblige affinity theories to account for more, to explain and predict more.

Cullen's students were making their presence felt in the scientific world by the 1760s and 1770s: Black was teaching at Edinburgh, at the same time as George Fordyce was lecturing in London. William Saunders, another of Cullen's students, was also lecturing in London, while Charles Blagden, who seems to have attended chemistry lectures at Edinburgh given by both Cullen and Black[169] was working with the chemist Henry Cavendish by the early 1780s. Other students of note include William Withering, James Lind,[170] James Anderson and Will Falconer.[171] Cullen's emphasis on affinity was to be disseminated far outside his immediate sphere of influence through the activities of his students.

From the late 1760s alternative organisations to the Royal Society had begun to

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[169] The Wellcome Library for the History and Understanding of Medicine holds sets of lecture notes taken by Blagden for both Cullen's 1766 lectures in chemistry and Black's 1767 lectures.

[170] Lind's notes of Cullen's lectures are held by the British Library. Cullen n.d. [1760?].

[171] Falconer's notes of Cullen's lectures are held by the Wellcome Library, London. Cullen 1765.

spring up, in London and provincial towns. The most famous of these, the Birmingham based Lunar Society, had links to both Cullen and Black through Withering, James Watt, and James Keir. In 1771 Keir published a translation of Macquer's *Dictionnaire de Chimie* which was heavily littered with footnotes correcting (and in some cases refuting) Macquer's assertions, particularly on affinity. He also rectified Macquer's failure to include an affinity table in his *Dictionnaire*, adding Geoffroy's table as well as Gellert's table of solutions.[172] It is unclear whether Keir learned his chemistry from Andrew Plummer, Cullen's predecessor at Edinburgh University, or Cullen himself.[173] Keir arrived at Edinburgh in 1754 and was still there when Cullen arrived to begin teaching chemistry in 1755. Black was undoubtedly present in Edinburgh at the same time as Keir attended the university,[174] and given Keir's passion for chemistry, it would be strange if he had not met both Cullen and Black. While the correspondence networks of organisations like the Lunar Society further disseminated chemical ideas beyond the realms of the universities, publications such as Keir's translation also served to propagate a distinctively British type of affinity theory.

My emphasis on the importance of affinity theories for 18th century chemistry might be deemed to be somewhat underdetermined on the evidence afforded by research publications. The historian is in danger of being misled when she searches for evidence of the use of affinity in many of the usual sources, for in these sources, the details of affinity theory are rarely, if ever, alluded to. Similarly, in the correspondences of chemists, with each other and with the outside world, affinity is only referred to infrequently. This dearth of overt discussion of affinity might suggest (and indeed has suggested to some historians) that affinity theory was not viewed by chemists as being of particular importance to their discipline.[175] The doctrine of affinity may not have been explicitly mentioned in every discussion of chemical phenomena, but this does

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[172] Macquer 1771, 2, 449-450.

[173] Moilliet and Smith 1967. It is stated here that Keir was taught chemistry by Plummer and left Edinburgh in 1755, but the DNB states that Keir did not leave until 1757, which would leave ample time for him to attend Cullen's lectures.

[174] Donovan 1975, 72-5.

[175] Melhado 1985.

not mean that it was unimportant. On the contrary, as even the most cursory glance at chemical works of the time confirms, it was vital to any understanding of the practice of chemistry in the 18th century. To borrow a phrase from Perrin, it was "taken for granted".[176] By the 1760s, the doctrine of affinity was enshrined as part of the norm of 18th century chemistry and a tool of the same status as the ubiquitous furnace.

In spite of the regard in which Cullen was undoubtedly held, his students did not simply adopt their master's theory wholesale. This is particularly evident in Fordyce's very individual theory. Fordyce's influence on his contemporaries, is often underestimated. Coley describes him as:

> "a man of considerable intellect, wide learning and enormous energy, who made valuable contributions to medicine and science."[177]

Not the least of his contributions was his long career as a chemistry lecturer in London. Coley tells us that:

> "for almost 30 years he lectured from 7am to 10am six days a week, devoting an hour to each subject. Each course of 100 lectures lasted four months and he repeated them three times a year."[178]

When Fordyce began his lecturing in the early 1760s, although chemistry was being taught at most of the universities in Scotland, in England there was much less formal provision for students interested in the chemical art. John Hadley was lecturing at Cambridge in 1759, but his lectures would probably have been regarded as somewhat old fashioned, being based in part on Aristotelian matter theory.[179] Fordyce's heroic schedule and his apparent success, testify to the demand for chemistry teaching in England. He was able to fashion an impressive career from his chemical and medical teaching and was clearly a man of parts; his *Elements of Agriculture* was copiously cited, as were his works on heat. In 1787, Black wrote eagerly to James Lind and Thomas

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[176] Perrin 1990, 266.

[177] Coley 2001, 396.

[178] Ibid, 398.

[179] Hadley 1759.

Beddoes asking for news of Fordyce's experiments on the weight of heat.[180] He taught chemistry to Jeremy Bentham and advised on the design of his panopticon[181] and advised during Lunardi's balloon ascent of 1784.[182] He was a trustee of William Hunter's estate,[183] and a close friend to Mary Wollstonecraft.[184] His interests were varied, ranging from agriculture to the effects of heat on the human body, but throughout his career Fordyce remained at heart the student of Cullen, regularly referring in his lectures to his greatness in the discipline and as a man. As late as 1786, he told his students:

> "The first Dawn of Science in Chemistry was introduced into it by Dr Cullen & hardly any Improvement has been made in the Science since his time … the Science of Chemistry as far as it is render'd perfect is entirely owing to him."[185]

However, Fordyce was far from being an unthinking disciple. Letters held at Glasgow University Library show that he was not averse to criticising his old master, and attempting to show him what he thought were better methods or theories, striking a precarious balance between deference and obstinacy.[186] Shortly after he had left Edinburgh, Fordyce developed his affinity theory into a lengthy paper which he sent to Cullen, and this forms the subject of most of the Glasgow letters. The paper itself was presumed lost and has not previously been examined, but I have been able to ascertain that in fact it is still extant, but mis-identified.[187] I have thus been able to examine Fordyce's early affinity theory for the first time, and to read Cullen's (unfavourable) comments with the benefit of the paper itself to hand. Both these documents are examined in detail in the following chapters.

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[180] Lind to Black [n.d.], Joseph Black Correspondence 1783-1990 and Black to Beddoes 24/11/1787, Joseph Black Correspondence 1780s Fordyce's joint experiments with Charles Blagden to discover the effects of heat on the human body were of sufficient interest to be reprinted in the second edition of the Encyclopaedia Britannica. See Encyclopaedia Britannica 1778-1780, *Heat*, 3548.

[181] Bentham 1791, 308, 311-312. There is a set of lecture notes on chemistry taken down by Bentham which bear unmistakeable marks of having been Fordyce's lectures. See Fordyce 1769 f.55 ff.

[182] Anon 1784, 3.

[183] Hutchinson 1799, I, 470.

[184] Godwin 1798, 72, 178.

[185] Fordyce 1786a, Lecture 1st .

[186] Fordyce 1759-1774.

[187] Fordyce 1759 Catalogued as "Account of Mr. Slake's paper to the chemists at Paris on compound Elective attractions. With notes appended by G. Fordyce."

By 1765, Fordyce had apparently revised his theory, at least for pedagogical purposes, and the basis of the theory that was to be continually adjusted and amended throughout his career is contained in a set of lectures from that year also held by Glasgow University Library.[188] Fordyce's 1765 publication *Elements of Agriculture* also provides valuable information on his affinity theory at that time.[189] This work included an explanation of his theory and its application to the problems of agriculture.

Eklund has asserted that affinity formed the "second pillar" to 18th century chemistry, together with phlogiston.[190] My examination of Cullen's and Fordyce's lectures casts this view into serious doubt. While Eklund rightly highlights the importance of affinity theories to chemistry (at least for the second half of the 18th century), my research suggests that he somewhat overstates the importance of phlogiston. Phlogiston was rarely mentioned by either Cullen or Fordyce in their lectures, and it certainly does not seem to have performed the role suggested by Eklund. Cullen, as I have shown elsewhere, developed a unique theory of heat and combustion which (almost as an aside) replaced the principlist phlogiston of Stahl with a compound of fixed air and acid; if anything, this theory might be characterised as anti-phlogistic.[191] He still referred occasionally to phlogiston in his lectures, but students were always counselled to be cautious of this substance that had "never been got by itself".[192]

Fordyce too included phlogiston in his early lectures, but was extremely cautious about assigning it the status of an element,[193] and he seems to have been quite prepared to give it up without a fight; by 1788 he was teaching phlogiston theory in tandem with oxygen theory.[194] For both Cullen and Fordyce, it was their affinity theories that served to structure their science and

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[188] Fordyce 1765. Further sets of lectures are held by the Royal Society of Chemistry, by King's College London and by the Royal College of Physicians in London. Fordyce n.d. [1770s?], Fordyce 1786a, Fordyce 1786b, Fordyce 1788.

[189] Fordyce 1765.

[190] Eklund 1975, 96.

[191] Taylor 2006.

[192] Cullen 1765, MS 1920 f.72v.

[193] Fordyce 1786a.

[194] Fordyce 1788.

their lectures to students while their attitudes to phlogiston were at best ambivalent, and at worst sceptical.

For Fordyce, affinity theory was absolutely central to chemistry and to any understanding of matter and its behaviour. Like Cullen, he explicitly linked chemical operations or practices to affinity, arranging the first part of his 1765 lectures by dividing the operations common in chemistry according to whether they provoked affinities to act through heat or solution. His affinity theory was carefully formulated to correspond with the rest of his chemistry, and indeed it dictated much of it, whether in terms of the practical solutions advanced to chemical problems, or the details of his complex matter theory.

Fordyce's ontology was inextricably tied to his affinity theory. He was quite specific in his assertions that affinities acted between particles of substances. In chemical combination one particle of one substance united with one or more particles of another. This interesting particulate ontology was combined in some unspecified way with an Aristotelian qualitative sensibility. For Fordyce,

> "the properties of ye compound are very different from either of its Elements, altho' ye Elements exist essentialy (sic) tho' not formaly (sic) in ye compound."[195]

Kelham claims that Fordyce's ontology followed (chronologically) Bryan Higgins's 'atomic' hypothesis that "one atom combined with one atom, and that at this point saturation occurred."[196] It is unclear when Higgins developed this idea, first published in 1775, but he had only obtained his MD in Leyden in 1765. Fordyce's 'atomic' ideas were already present in the first edition of *Elements* of 1765, and in his 1765 lectures Fordyce taught that:

> "in ye chemical combinatn every Particle of one substance is united with yt of ye other"[197]

Kelham cites Priestley to suggest that Higgins was taught by Cullen,[198] and this

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[195] Fordyce 1765, f 51.

[196] Kelham 1968, 114.

[197] Fordyce 1765, f 47.

[198] Priestley did not actually suggest that Higgins had been one of Cullen's students, but that he had acquired a view of fixed air as being composed of common air and phlogiston from Cullen. This was certainly not Cullen's view in the late 1760s, but of course he may have changed his thinking later. Priestley 1775.

is undoubtedly possible, but I would suggest that given his age, his London base and the undoubted similarities between their matter theories, it is also possible that he was taught by Fordyce. Fordyce's sphere of influence, particularly given his prodigious lecturing programme, must have been wide, like that of his early mentor. Fordyce's career offers an example of how Cullen's emphasis on affinity was dispersed down the pedagogical pyramid. Even if Cullen's own theory was not transmitted *in toto*, its crucial role as one of the general principles of chemistry was.

2.5 Interlude: In Which a Swede builds a Bigger Table

Disquisitio de Attractionibus Electivis,[199] Torbern Bergman's detailed study of elective attractions as (like Cullen) he called them, included affinity tables that stretched to 50 columns (in the 1783 edition of the table to 59 columns). This table took an unprecedented step for printed affinity tables: it was divided into two halves, one for affinities acting "in the wet way" and the other for operations carried out "in the dry way".[200] This division derived from the apparent necessity for fluidity in one or both substances, but although it was often interpreted operationally (that is, showing affinities in solutions and in fusions) this was not Bergman's intention.[201] The "humid way" referred to a situation where:

> "one of the substances, at least, is fluid in the heat of the atmosphere, or at least in a heat not much greater than that of the atmosphere"[202]

rather than one necessarily involving solution. The distinction is minor, but might well have proved important when comparing the affinities operating in amalgams, for instance. Bergman also included diagrams that showed double elective attractions and were extremely similar to those that Cullen had introduced around 1757, dealing with combinations of four separate or two

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[199] Bergman 1775.

[200] In fact, both Black and Cullen had been in the habit of dividing their affinity tables similarly. See Section 4.1.1 below.

[201] Nicholson 1795, 157 stated for example that "we may observe that water is concerned in all the operations which are called Humid; and beyond a doubt modifies all the effects of such bodies as are suspended in it."

[202] Bergman 1783, 13.

compound substances.[203] Black and Fordyce had also presented similar diagrams to their students as part of their chemistry lectures.

Bergman, although not a British chemist, is an influential figure in my story through the 1785 English translation of his work which was widely disseminated amongst British chemists. The 1775 version of his tables had been published in 1782 by Elliot.[204] His extensive affinity table began to appear in many of the textbooks published in Britain,[205] and replaced Geoffroy's as the unofficial standard. Duncan has suggested that his table, due to its sheer size, must have cast something of a dampener on the drive to produce new affinity tables.[206] After 59 columns of affinities, how many more would be required? And as Bergman himself explained, a truly accurate version of his table would require "above 30,000 exact experiments, before it can be brought to any degree of perfection."[207] Duncan points to the fact that there were only a few attempts to better Bergman's table, all by "stout-hearted Germans".[208] In fact, George Pearson, a former student of Black and lecturer in chemistry at the Royal College of Physicians,[209] produced a yet larger "table of precipitations" based on Bergman's but incorporating anti-phlogistic theory, represented by columns for oxygen and 'calorific'. This was included in his anonymous translation of the *Chemical Nomenclature* of Fourcroy et al.[210] This table seems to have taken over from Bergman's in the post-Lavoisier chemical world and was reprinted in chemical textbooks, 'pocketbooks', and dictionaries.[211] Pearson coupled affinity theory to the new chemistry and, it would seem, British chemists were thankful. Not all chemists were satisfied with the qualitative approach of traditional affinity tables and theories though. The limitations, even of such tables as Bergman's made it clear that a more precise measure of affinity was

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[203] Crosland 1959.

[204] Elliot 1782.

[205] Including, for example, Elliot 1786 and Nicholson 1795.

[206] Bergman 1970, Introduction.

[207] Ibid, 70.

[208] Ibid, Introduction, xxxv.

[209] Coley 2003.

[210] Anon [George Pearson] 1799.

[211] E.g. Parkinson 1800, Nisbet 1805.

required. The focus of many chemists moved to developing a system of mathematising affinities, of quantifying the attraction between substances.

2.6 Act 3: Attempts by some Ingenious Chemists to Bring a Scientific Precision to the Pedagogical Tool that was Proving of such Great Utility

Bergman's (or perhaps Pearson's) table marked the zenith of the development of qualitative affinity tables. Bergman's division of his table into the 'wet and dry ways', rather than increasing certainty of affinities, rather emphasised the uncertainty that chemists were beginning to recognise was inherent in affinity tables. In spite of the apparent increases in accuracy of the new table, it still did not succeeded in enabling chemists to predict the results of more complex interactions. A large proportion of double elective attractions were still only knowable *a posteriori*. Only a quantification of affinities would supply accuracy here. Perhaps this is where we find further signs of Newtonian influence amongst affinity theorists, in the drive to carry forward the hitherto qualitative art of chemistry into the quantitative territory of a science. Unlike the original push to incorporate affinity theory into chemistry, this urge to quantify was not pedagogically driven although it was built on a conviction that affinities held the key to the discipline that was instilled by pedagogy. The actors in this part of the drama were what we might call research chemists, overtly interested in shaping new theory, in taking the qualitatively useful affinity theories and giving them a 'grown up' precision.

There had been earlier attempts to assign numbers to affinities, although in most cases these were plucked out of the air for demonstrative purposes rather than predictive. Black, for instance, had accompanied his lectures with diagrams that included such arbitrary quantities.[212] Similarly, Fordyce had included conjectural figures in a 1759 letter to Cullen.[213] There seem to have been two methodologies available to the quantifying chemist, the first theoretical and the second experimental. It does not seem unreasonable for an enterprising theoretician to believe that algebra could represent the various relationships

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[212] Black 1966 59-60.

[213] Fordyce 1759-1774.

between substances shown in affinity tables and from this it would be an easy step to assign numbers to the affinities represented. Other chemists had recourse to experiment and measurement of affinities. Although affinity itself was unobservable, its effects were not, and measurement of these effects, it was believed, could supply quantified affinities.

John Elliot, apothecary and MD,[214] was by nature it seems a theoretician; indeed his natural philosophy was often speculative in the extreme. Another chemist who is relatively undiscussed by historians, he is unfortunately most known, because of the dramatic circumstances of his death in Newgate prison. His lack of scientific fame is somewhat compounded by the fact that he is regularly confused with Sir John Eliot, who as Partington and McKie have pointed out "published nothing".[215] The *English Short Title Catalogue* in fact still connives at Sir John's misappropriation of Elliot's works and the historian is on many occasions forced to extend her search to both names. This miasma of drama, claimed insanity and simple confusion has clouded the fact that Elliot's chemical and scientific works, although limited in extent, are of great interest on their own account.

Elliot, like Fordyce, was something of a polymath, publishing on chemistry, medicine, optics, physiology, mineral waters and astronomy. He developed a complex theory of heat and combustion that anticipated Adair Crawford's theory in certain respects, although unfortunately Elliot was unable to publish his ideas until after Crawford's own had appeared in print.[216] Elliot's *Elements* sets out his affinity theory (although a portion is borrowed directly from Fordyce), with his own affinity table and Bergman's first table of 1775.[217] Elliot's table is itself worthy of special note, as it is the only published table to include the compounds formed by the various combinations shown. This may reflect the uncertainties of substance identification and nomenclature of the 'revolutionary' period, when identities that had been regarded as certain by

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[214] Elliot's working history is far from clear, but his works describe him first as "apothecary" and later as "MD". Partington and McKie 1960.

[215] Partington and McKie 1960.

[216] Elliot 1780. See also Partington and McKie 1938, 350-354.

[217] Elliot 1782.

Cullen's students had become subjects of frenzied debate. Elliot also included Bergman's diagrams of single and double elective attractions together with a single extra diagram of double elective attraction which assigned numbers to the affinities. Elliot's numbers combined in a balance of forces to show the result of the combination of compounds. Duncan explains Elliot's assignation of numbers as 'trial and error':

> "the figures were not found by experiment, but by assigning arbitrary numbers, as Black had done, for one reaction and adjusting them by trial and error to fit other reactions."[218]

Elliot's quantification was a simple form of the 'algebraic', or theoretical approach, but he does not seem to have pursued it any further. The second edition of his *Elements* incorporated a large fold out sheet setting out his friend Kirwan's quantifications of affinity from experimental evidence. It seems likely that Elliot, had he lived, would have pursued this route to quantification in preference to the theoretical one. It is unfortunate that the undoubtedly fascinating story of Elliot's life and death have overwhelmed interest in his work. It is perhaps better to highlight a notice that appear in the *Times* which suggests that a far better focus for our attention is on Elliot's work:

> "Thus has ended the life of a man whose enlightened mind was an honor to philosophy; and that it was tinged with frenzy is to be attributed to his unremitting ardour in abstruse learning. – Dr. Priestly (sic), Dr. Franklin, and a number of the first characters of the age, honoured him with particular attention and esteem."[219]

Kirwan's quantifying endeavours were more comprehensive than Elliot's, and occupied him for much of his life. His theory was first set out in papers delivered to the Royal Society from 1781-3,[220] and thereafter amended in further papers published in the *Transactions of the Royal Irish Academy*.[221] He developed a theory which assumed that the proportions with which acids and alkalis combine to form neutral salts indicated the strength of the affinities between them.

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[218] Duncan 1996, 198.

[219] *Times,* Jul 24, 1787, 3.

[220] Kirwan 1781, Kirwan 1782, Kirwan 1783.

[221] Kirwan 1790.

His 1782 paper claimed that chemistry was founded on the doctrine of affinity[222] and his *Essay on Phlogiston* similarly demonstrated the importance of affinity in his chemistry. By the time he published the *Essay,* Kirwan already had a history of rehabilitating phlogiston. His early papers had identified inflammable air as the elusive phlogiston and he had formulated a complex system to buttress the doctrine.[223] The *Essay* drew on affinity theory to point out the inconsistencies of Lavoisier's claims, pointing out that they did not accord with what he had presented as the affinities of the oxigenous principle. Affinity was here set forth in terms evoking Cullen's 'general principle' or Macquer's 'fundamental truth'. In this context affinities were regarded as axiomatic; if a theory contradicted the observed affinities, then the theory must be at fault. So the argument went.

The to-ing and fro-ing between Kirwan and the French chemists in the *Essay on Phlogiston* emphasise that this point of view was shared by both sides of the debate. Some years later, Thomas Thomson wrote:

> "Though chemical affinity constitutes confessedly the basis of the science, it had been almost completely overlooked by Lavoisier, who had done nothing more on the subject than drawn up some tables of affinity, founded on very imperfect data."[224]

In fact, as Beretta has shown, Lavoisier's avoidance of affinity theory is a fallacy.[225] A memoir entitled "Vues Générales sur le Calorique" published in 1805 by Madame Lavoisier together with other previously unpublished work shows that Lavoisier did consider affinity as of vital importance to his chemistry.[226] In this memoir he unambiguously related affinity to universal gravitation, linking it to his caloric theory of heat.[227] The details of his theory are beyond the scope of this thesis, but it is clear that affinity was considered, by

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[222] Kirwan 1783, 34.

[223] Kirwan 1782.

[224] Thomson 1830, 157.

[225] Beretta 2001.

[226] Lavoisier 2004, I, 1-28.

[227] Briefly, the particles of caloric tended to separate particles of matter (molecules), while the force of attraction pulled them together. The states of matter and its behaviour were a consequence of the balance of these two forces. Thus, for Lavoisier the two "pillars" were presumably caloric and affinity: this would seem to cast some doubt on the true extent of Lavoisier's 'revolution'. Ibid, 5-7.

Lavoisier as well as Kirwan, to form the basis of chemistry, with or without phlogiston.

The French chemists saw Kirwan's publication as an opportunity to set out in detail their claims, and rebuff the arguments of the phlogistonists point by point. In 1788 they republished the French translation of Kirwan's work with their refutations of his arguments. Finally, in 1789, Kirwan republished his original *Essay*, together with the English translation of the French refutations, and yet further rebuttals by Kirwan. This very public row over a non-existent substance is unfortunately the work for which Kirwan is most remembered. Kirwan's reasons for his less public renunciation of phlogiston between March 1790 and January 1791 are unclear, although it is thought to be unlikely that the arguments of the French chemists were responsible.[228] It is interesting to note that Kirwan's works published after 1791 are not particularly different from those published before. Aside from the absence of phlogiston, his chemistry changed little. This in itself would seem to indicate that the row over phlogiston rather exaggerated the importance of the postulated substance in the chemistry of the combatants.

Affinity remained Kirwan's primary interest throughout his career. In 1790 he read a paper to the Royal Irish Academy on the composition of salts that continued the work of ten years earlier presented to the Royal Society.[229] In 1797 he continued this theme with an extremely lengthy paper which again attempted to discover the proportions of 'real' acid, water and alkali in a number of salts.[230] This was his last chemical paper. Shortly after his death in 1812, a contemporary 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."[231]

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[228] Scott 1979, 259.

[229] Kirwan 1790.

[230] Kirwan 1800.

[231] Quoted in Scott 1979, 122.

This type of assessment has dogged Kirwan's memory perhaps in consequence of his having been on the 'losing side' in the phlogiston debate. Recent scholarship takes a more charitable view, as Kim has argued:

> "Though Kirwan usually emerges in the historiography of the Chemical Revolution as a loser who supported the phlogiston theory, his 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."[232]

A new focus on Kirwan's affinity theory, which occupied him intermittently for much of his scientific career, may serve to rehabilitate his reputation. But in addition to his work on affinities, his role as a collector and disseminator of information on chemistry and chemical developments should be given due regard. Throughout his life, Kirwan built up an enviable system of correspondents. He occasionally visited Birmingham and corresponded with members of the Lunar Society, keeping its members abreast of developments in London and at the Royal Society.[233] Scott claims that:

> "There are many indications that Kirwan kept up an immense correspondence with scientists in Europe; regrettably only a small fraction of it is known."[234]

We know that he corresponded at length with Bergman in Sweden as well as with Guyton de Morveau in France.[235]

Kirwan's influence on the Chapter Coffee House Society is clear from a perusal of the minute book.[236] He missed only 20 meetings, and led the discussion on many occasions – and the subjects of discussion clearly reflected Kirwan's chemical interests. The topic of affinity arose regularly, and Kirwan's affinity theory was often marshalled in support of his arguments. The Society did not long survive Kirwan's return to Ireland,[237] but during its six year lifetime, its membership was a roll-call of the great and the good of British chemistry at this

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[232] Kim 2003, 269.

[233] Scott 1979, 60.

[234] Ibid, 71.

[235] Guyton de Morveau and Kirwan 1994.

[236] Levere and Turner 2002.

[237] Scott 1979, 36.

period, including Priestley, Watt, Jean-Hyacinthe Magellan (himself the centre of a Europe-wide network of scientific communication), Nicholson and Keir.[238]

Kirwan then, formed the ‘hub’ of a European-wide network of scientific correspondents. With links to German, French and Swedish chemists he was well placed to keep in touch with the most recent developments in chemistry and natural philosophy. His role as a disseminator can only be conjectured, but it seems likely that his correspondence linking geographically far flung chemists was of great importance. In this role his affinity theory provided a discursive common ground that enabled the effective communication of scientific information between a variety of correspondents and acquaintances. He was thus able to draw together various strands of chemistry for his own benefit. His role, seen in this light, seems not so very different from that of Lavoisier himself. In addition, he placed his laboratory at the disposal of young gentlemen who wished to familiarise themselves with chemistry.[239]

Thus we can see in Kirwan’s career traces of a pattern that by now is clear: the partnership of affinity and pedagogy. Those who were most particular in forming and developing affinity theory in Britain were also almost always involved in the teaching of chemistry. Britain’s unstructured scientific world, with its private societies and private lecturers combined with chemistry’s peculiarly unsettled status led to a rather chaotic didactic landscape. In spite of this outward chaos, however, affinity theories offered a common ground to novice chemists of immense pedagogical utility. Such theories also provided a shared basis for communication amongst British chemists.

Like Kirwan, William Higgins used his affinity theory as a weapon in the debates over the existence of phlogiston. But Higgins’s theory was used to oppose Kirwan’s, in support of the affinities that Lavoisier claimed for oxygen. Higgins’s theory appears in a lengthy Kirwan-baiting tract, *A Comparative View of the Phlogistic and Antiphlogistic Theories.*[240] published in 1789 in direct response to Kirwan’s *Essay on Phlogiston*. Surprisingly, Higgins’s later

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[238] Watt, Keir and Priestley, all members of the Lunar Society of Birmingham, were honorary members.

[239] Scott 1979, 72.

[240] Higgins 1960.

successful career was in part the result of Kirwan's sponsorship. Perhaps this is a measure of the fact that disputes over phlogiston were of less importance to Kirwan than his *Essay* might lead us to believe.

The *Comparative View* defended the claims of the antiphlogistians, marshalling both experimental evidence and theoretical support, in the form of a complex and ingenious affinity theory. Higgins's theory presupposed an early type of atomic theory, similar to those of his uncle Bryan and Fordyce. He presented diagrams showing how each particle joined to form a 'molicule'.[241] The affinities were shown as lines between the atoms, similar to modern depictions of chemical bonds. The figures were not experimentally determined, but were chosen to conform to the orders of affinity[242] that Lavoisier had presented in a 1782 Memoir.[243]

Higgins seems to have been an impressive self-publicist, with a considerable ability to offend. From a retrospective viewpoint, the 'atomic theory' set out in the *Comparative View* bore a close resemblance to Dalton's atomic theory as it appeared in Thomson's *System of Chemistry* of 1807.[244] In the *Comparative View* the atomic theory was subordinated to Higgins's affinity theory, which took centre stage, but in 1810 Humphry Davy suggested that Dalton's theory plagiarised Higgins's, and Higgins himself took up the cudgels in 1814.

The details of the dispute are beyond the scope of this study, but it is undoubtedly true that Higgins's polemic against phlogiston drew on an affinity theory that was itself closely tied to a particulate theory with a clear similarity to Dalton's atomic theory. On the other hand, other chemists had speculated along similar lines, including Cullen and Fordyce, as well as Higgins's own uncle. As chemists contemplated affinity and formulated their theories, it was a plausible direction for their thoughts to take. Kirwan's use of saturation proportions to determine the strengths of affinities can be seen to demonstrate a like concern for combining proportions and ratios. Although most such speculations cannot

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[241] Ibid, 45.

[242] Wheeler and Partington 1960, 93.

[243] Lavoisier 1785, 535.

[244] Wheeler and Partington 1960, 129.

be regarded as fully fledged theorising, the Higgins/Dalton affair suggests that Dalton's atomic theory might be better viewed in the light of these types of hypotheses in the tradition of affinity theories. Indeed, Henry Guerlac has traced the development of Dalton's theory through a series of affinity theorisers.[245] The pluralist nature of the doctrine of affinity encouraged chemists to hypothesise freely without fear of compromising the affinity theories which were of such importance to their chemistry.

2.7 Epilogue: The Pedagogical Pyramid: Those who can …

As I have remarked, a pedagogical theme undoubtedly runs through this investigation of 18th century affinity theories. When Geoffroy's paper was first presented, chemistry in Britain was under something of a cloud. The Royal Society were apparently not interested in chemical theories. With little or no tradition of teaching chemistry in the universities, its teaching was sporadic, temporally and geographically, and in many cases it was outside any institutional context. It is not surprising that it is extremely difficult for the historian to find evidence of contemporary responses to Geoffroy's table. Those who might have favoured it had no public forum to discuss it, and this early in the century there was no established social or professional network in place to disseminate it. For these reasons perhaps, Geoffroy's seed fell on stony ground.

Nevertheless, chemistry had to be taught: apothecaries provided an important service to the medical profession, and physicians also had an need for some familiarity with the substances they prescribed. In Scotland, men of industry, prompted by new legislation on manufactures, were beginning to discover a need for greater understanding of chemistry.[246] Entrepreneurial spirits abounded in Britain at this time; private lecturers like Shaw and Lewis

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[245] Guerlac links Dalton's work through Kirwan's, Cullen's, and other affinity theories to Newton. He argues that chemical affinity offered the best opportunity to solve the problem of transdiction and it was through attempts to link the unobservable entities postulated with the observable behaviour of different substances that Dalton eventually arrived at his New System. Guerlac 1968.

[246] Two Acts of 1727, the first for the better Regulation of the Linen and Hempen Manufactures in Scotland, and the second for Encouraging and promoting Fisheries and other Manufactures and Improvements in Scotland were crucial here. The latter Act resulted in the creation of the Board of Trustees for Manufactures, a body which paid both Cullen and Black premiums for investigations into bleaching. See Clow and Clow 1952, 165-177.

perceived the great potential utility of chemistry, and both turned it to their own advantage. In their eyes, a synoptic table that summarised so much practical chemical knowledge could not fail but to be useful. Thus it fell to the pedagogues, the presenters of lectures and the writers of textbooks to introduce Geoffroy's table to British chemists.

It has been noted that the periodic law and table first appeared in Mendeleev's textbook *Principles of Chemistry* and that it was likely that it was the specific pedagogical demands of preparing a "general survey of chemistry" that prompted his discovery of the law.[247] Bensaude-Vincent has argued that Mendeleev's position as a teacher confronted him with questions unlikely to face other chemists: "How to summarize chemistry? How to order the chapters?"[248]

Chemists of the 18th century, before the rationalisation of chemical nomenclature, were in an even more confusing environment. Those who began to teach the science in Britain had to formulate answers to similar questions, and their affinity theories were manufactured to provide these answers. The theories had to be manufactured, as Geoffroy's 1718 paper had left a great deal unexplained. It was pedagogical utility that led chemists like Shaw, Cullen and Lewis to drag affinity theory forward and to start filling in the gaps left by Geoffroy.

Cullen's role was the most crucial to the 'revival' of affinity through his recruitment of affinity theory as a pedagogical tool. But for Cullen's purposes, Geoffroy's *Mémoire* alone was insufficient. The table and the law were insufficient for affinity theories to be useful. He added components to his theory, articulating tacit assumptions, and generally fitted it for a useful purpose. As pedagogical tools affinity theories dictated the structure of courses, the explanations of observations, and guided the students in their operations. New tables were produced, and new components were formulated to account for new observations. Newly discovered phenomena were explored and assimilated into affinity theories as new components.

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[247] Bensaude-Vincent 1986, 3.

[248] Ibid.

I would interject a note of caution here, however. I have examined those affinity theories that are set out explicitly, and these are only to be found in early textbooks or in lectures to novices. As the modern chemist does not usually find it necessary to restate their understanding of chemical bonds in their research, so practising chemists of the 18th century were not in the habit of setting down their affinity theories in their notebooks. I argue that they were fundamental to chemistry; that any definition of 18th century chemistry has to include some type of commitment to an affinity theory. But at the same time, it must be conceded that they were so fundamental that they rarely appear in what might be termed 'research'. Rarely, though, is not never, and the presence of affinity in Lewis's work on platina, and Cavendish's on the composition of water and inflammable air,[249] undoubtedly testifies to its significance, however veiled, in 'research' publications. As pedagogues developed their affinity theories, and linked them closely to their teaching, affinity became embedded in British chemistry. As Fordyce and Black learned from Cullen that affinity theory formed the basis of their discipline, so too would his other students, and their students *ad infinitum*. Affinity theories may have begun as pedagogical tools, but were eventually dispersed from the lecture halls to the laboratories.

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[249] Cavendish 1784, 20-21.

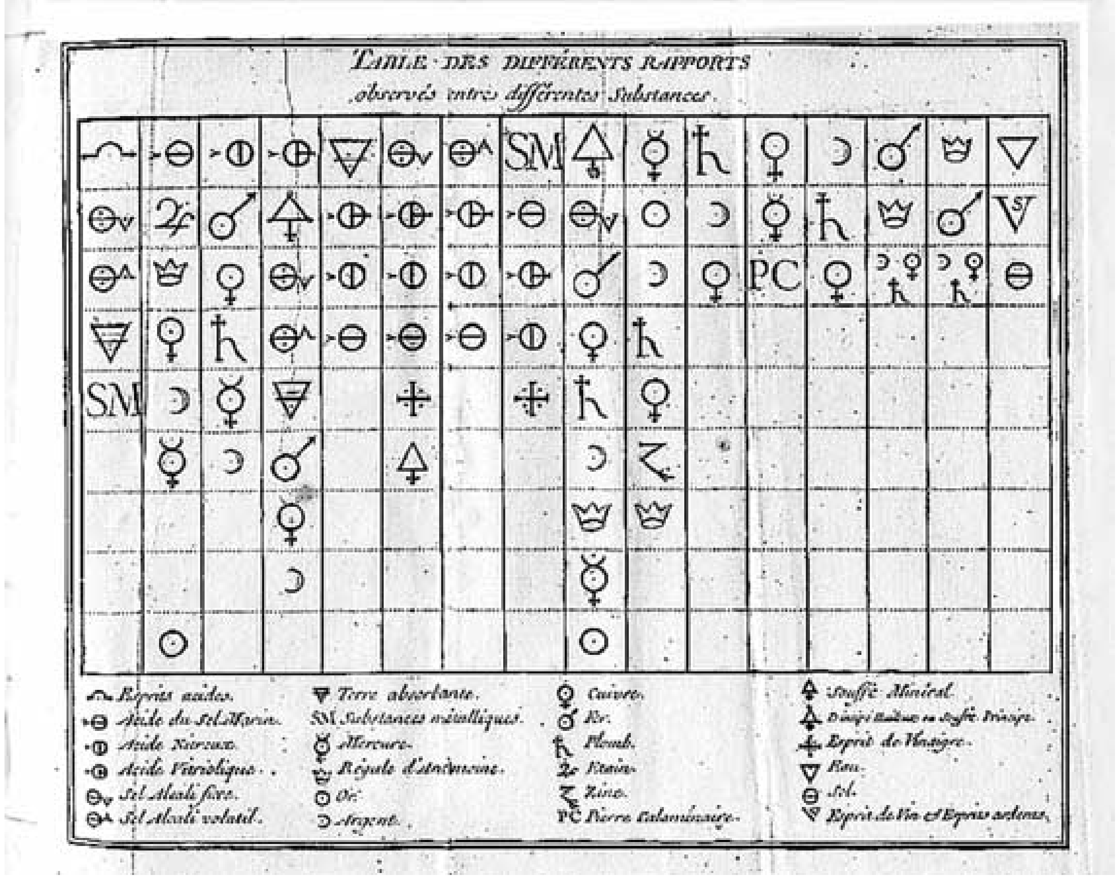

Figure 1: Geoffroy's 1718 Table as reprinted in Macquer, 1749.

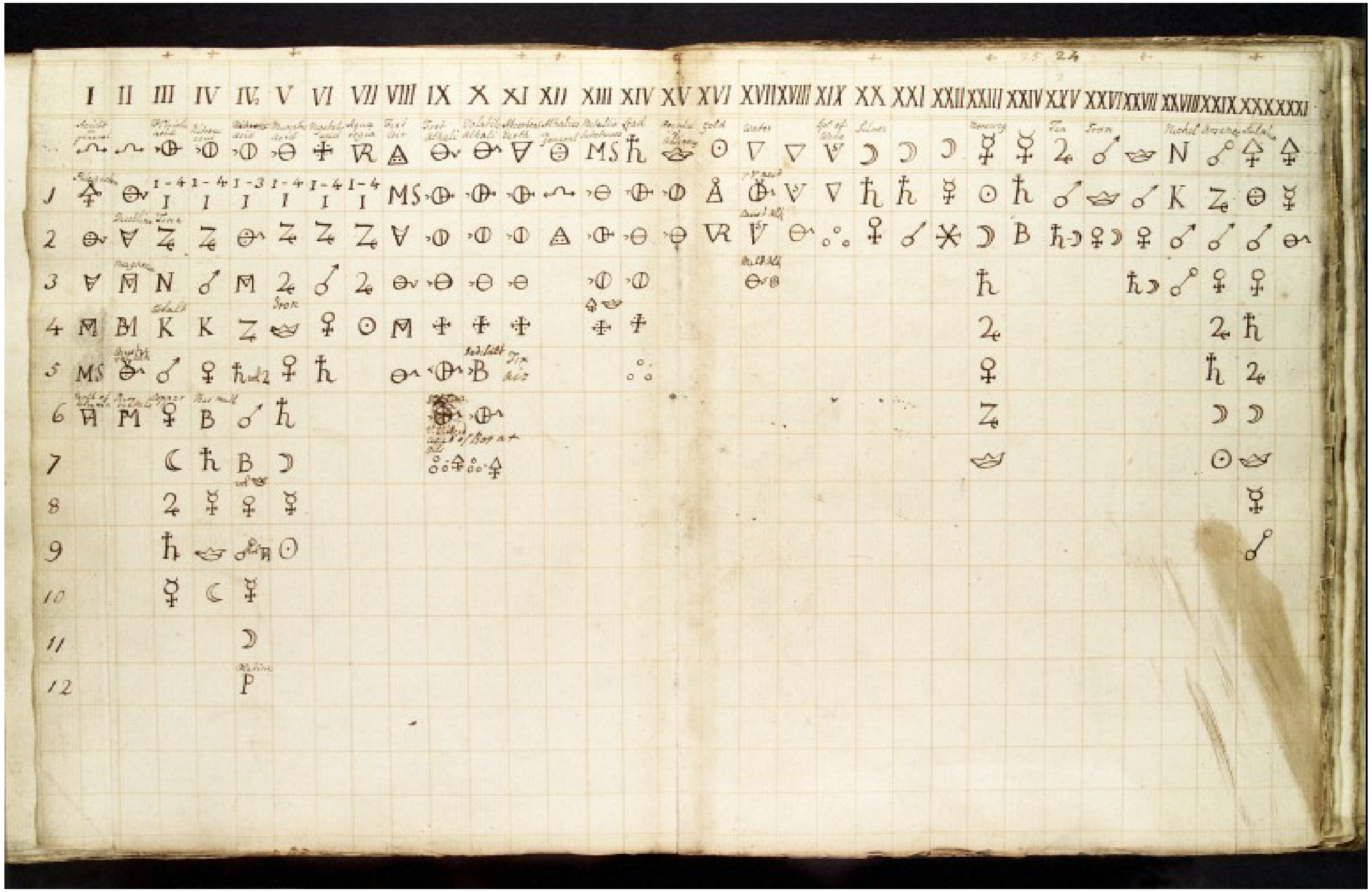

Figure 2: Affinity Table, Cullen 1765, MS1920, Wellcome Library, London

3. “Tho’ all things Differ, All Agree”[1] –Variety and Conformity within Functional Component-Types

The previous chapter indicated how affinity theories, originally adopted as a pedagogical tool, were disseminated down the pedagogical pyramid until they became planted with deep roots in the discipline. My research has also shown that although all the chemists who played a part in Acts 2 and 3 of the narrative held to some theory of affinity, their theories were not the same.

This chapter is intended to show two things:

(1) the extent to which many affinity theories were at variance; and

(2) that there was, nevertheless, an underlying correspondence, albeit unexpressed.

Affinity theories can be broken down, decompounded like matter into their constituent components, and these components can in turn be compared in order to detect the correspondences and divergences between individual theories. This is my strategy in this chapter; thus accomplishing (1) above. But if an inter-theoretical comparison of components is to result in any meaningful insight, the basis for such an examination must first be distinguished. The detection of contrast is only valuable when based on an underlying familial relationship, a similarity behind the veneer of diversity. There would be no point, for example, in carefully comparing the *wisteria sinensis* growing up the side of my house with the incumbent President of the United States. Nothing useful could be achieved by such a comparison – it is highly unlikely that any point of similarity or relation could be found. As an essential act preparatory to an inter-theoretical comparison of components we must therefore identify a frame of reference within which a family resemblance can be discerned.

My research indicates that otherwise divergent components from different theories are nevertheless comparable by reference to the theoretical or conceptual function they were intended to perform. I have therefore endeavoured to construct a component taxonomy based on these intra-theoretic functions, classing components into functionally similar ‘types’. Individual

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[1] Pope 1713, 1.

components played a functional role within their affinity theories, and these roles are the same or similar as those of other components in other theories, and define the type to which each one belongs. Providing rules and instructions for the utilisation of affinity theories, these 'functional' types of component were vital to the operational validity of affinity theories. The detection of this tacit kinship between otherwise disparate components offers a valuable glimpse of the hitherto unseen intentionality behind the doctrine of affinity. Affinity theories were chemical tools, employed in pursuance of an operational goal and as such, like technical artefacts, they have a teleological aspect, dependent on human intentionality.[2] The types into which I have classed the components of individual affinity theories are similarly closely linked to the assumed functions of the theories. My taxonomic strategy highlights the correspondences that underlay the diversity of components of affinity theories; thus fulfilling the second intent of the chapter. As the very differences are outlined, patterns of similarity are delineated.

My examination emphasises the fact that certain component-types of affinity theories were unnecessary for such theories' functional utility. The line of demarcation between these 'optional' and 'functional' component-types is not always clearly defined, but nevertheless in broad terms they are distinguishable. The ontological or metaphysical commitments that historians have in the past regarded as so crucial to affinity theory were, operationally speaking, irrelevant. The relationship between the intended function(s) of the affinity theory as a whole, and the function of each individual component-type is crucial to this distinction. Where the component-type does not contribute in any way to the application of the theory, it can be assigned an 'optional' status. My discussion departs from historiographical tradition in disregarding these optional component-types. Instead, the following chapter concentrates entirely on the functional component-types that emerged as affinity theories became pedagogical tools around the middle of the century.

We have seen that Geoffroy offered a 'law' of affinity in his 1718 *Mémoire*:

> "Every time that two substances which have some disposition to

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[2] Kroes and Meijers 2006.

> join with each other happen to be united together, if there supervenes a third which has more relationship *[rapport]* with one of the others, it unites with it and makes it release its hold on the other"[3]

However, there were other assumptions that needed to be made before Geoffroy's ideas could be adopted and applied usefully. Certain concepts were required to be 'filled-in' for affinity theories to be operationally intelligible. Many of these were tacit assumptions that had been made by Geoffroy in putting his paper together. For example, Klein argues that Geoffroy's original affinity table articulated a new conception of "chemical combination, compound, and reaction".[4] In this scheme, the chemical compound was made up of empirically "homogeneous chemical substances", i.e. relatively stable substances which could be combined to create new substances, and recovered from these new substances without alteration.[5] Klein's analysis indicates three functional component-types that were necessary to affinity theories for their functional application.

The first is a conception of substance identity. This component-type encompasses epistemological conceptions as well as more empirical ontological analyses of the substances that most commonly featured in affinity tables. Following on from this is a further component-type of concepts of combination. This is closely linked to the former, and the interplay between the individual components of each component-type will be obvious. The third component-type necessary for the operational utility of affinity theories is a conception of order. As substances are ordered in affinity tables, how is this order established? And on what empirical basis?

While Geoffroy's 'law' might appear to answer these types of questions, in fact there was a theoretical lacuna between the law and the practical applications of affinity theories. Geoffroy's affinity table would be effectively useless without some conception of substance identity, of combination of substances and of the order of affinities. Those who intended to utilise affinity theory in their

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[3] Duncan 1996, 116.

[4] Klein 1996, 282.

[5] See also Klein 1995.

chemistry thus formulated components to answer these questions. This chapter examines in detail these components, classed into component-types, as articulated within a variety of affinity theories.

3.1 Concepts of Substance Identity

As Klein has recently pointed out,

> "what counted as a single substance, and the practical and epistemic methods of defining its boundaries are among the key historical-ontological questions we must ask if we wish to understand historical transformations of chemistry on a broader cultural scale."[6]

Her own work has greatly contributed to answering these questions, beginning with her analysis of the substances represented in Geoffroy's affinity table which, she argues, epitomised a new concept of the "pure chemical substance".[7] These could be either compounds or elements, but when combined together, they "must remain unaltered as substance-specific entities".[8] This concept may form one of the most basic and essential types of components of affinity. Inevitably, however, it is rarely specifically articulated.[9]

There are two layers of conceptualisation here. Firstly, there are questions posed by the epistemology of the "homogeneous chemical substance", whether compound or elemental. Note the emphasis on homogeneity rather than simplicity. Homogeneity implied a level of mixture beyond a mere mechanical *mélange*, but without insisting on simplicity or elemental status. As Cullen explained to his students:

> "we have no Criterion by which we can know, whether we have hit on the truth in the Division of the Elements of Bodies; there certainly are Elementary Bodies, tho' they cannot be number'd, nor do I think there is a necessity for it, as they have done no good, but rather misled the Chemists."[10]

The notion of ultimate simplicity was not only impossible to ascertain, but was

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[6] Klein 2005, 114.

[7] Klein 1994, 168.

[8] Ibid, 170.

[9] Klein 1996, 269.

[10] Cullen n.d. [1760s], f 16-17.

believed to be a harmful concept. Much better to simply concentrate on those substances that the chemist commonly encountered. But what epistemic criteria could be applied to such substances? Was homogeneity enough, or were admittedly homogeneous substances further classified as simple substances or more complex compounds? The first sub-section below explores how far affinity theories relied on notions of simplicity or corresponded to abstract or operational concepts of elements and compounds.

On a more practical level, there is the question of substance identity: how did a chemist know what a substance was, how did he label it? It was vital that the chemist who was to use the table knew what ingredients were constitutive of what compound. This is perhaps a difficulty that 21st century readers find it difficult to appreciate, possessing as we do a chemical nomenclature that clearly indicates the constitution of any compound substance. The second section below explores the fashioning of identities for newly discovered species of matter, and the role of affinity theories in recognising and identifying such species through their chemical behaviour.

3.1.1 Correspondences and Divergences: Elements, Principles and Affinity

As Boyle's determined critique indicates, metaphysical systems of elements and principles were traditionally crucial to chemical theory.[11] And yet, by the end of the 18th century, Nicholson could write

> "the limits of art are not the limits of nature. At present we hear little concerning elements."[12]

From the very first, affinity theories relegated such abstract notions to a much lower level of importance. Geoffroy's table included in its header row both admittedly compound and purportedly simple substances without distinction.[13] The criteria for their inclusion, Klein asserts, was their homogeneity and relative stability; the latter signified by the facility of being recoverable from combination, in reversible chemical operations. This suggests that affinity

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[11] Boyle 1661. See also Boas 1954.

[12] Nicholson 1795, 155.

[13] Klein 1995, 92-3.

theories were divorced from any hierarchy of complexity. However, there was scope in affinity theory, indeed it might be called a requirement, for such a notion, and this section explores those components that endeavoured to clarify relations between the substances found in affinity tables and more traditional elemental concepts.

In his earliest lectures on chemistry, Cullen initiated a strategy that was later adopted by many of the writers on chemistry throughout the century. He began his lectures with a discussion of "the objects of chemistry", which were specifically opposed to bodies only possessed of general mechanical properties.[14] A similar distinction underlay that between constituent and integrant parts. The first were the results of chemical division of bodies, and the second of mechanical division only. This distinction (also made by Stahl, Shaw and Macquer)[15] emphasised the disciplinary boundary between chemistry and natural philosophy by reference to their differing objects and practices. Chemistry was concerned with the production of particular properties in bodies by means of their combination and separation.

In 1748 Cullen told his students:

> "… we should give an account of the Elements but the Real Elements not known because of their minuteness shewn above.
>
> …
>
> Chemistry resolves Bodies into difft pts. These have been supposed Elements but that doubtfull & we give them only as the Chemical Principles usefully known & now to be explained."[16]

Cullen at this time listed the chemical principles as salt, sulphur, mercury, earth, water, air and fire, but this seems to have been more a nod to convention than a core tenet of his chemistry. His chemical principles were not supposed to be simple, as:

> "… no Chemical Resolution exhibits the most Simple Elements

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[14] Cullen n.d. [1748/9]. In some years, Cullen included a series of lectures on the history of chemistry, which discussed the origins of chemistry, and its most well known practitioners up to his own time. On Cullen's historiography, see Christie 1994.

[15] Shaw n.d. [1733?], .Macquer 1749, Stahl 1730.

[16] Cullen n.d. [1748/9?], Lecture IV.

> of Bodies. … Chemistry however is usefull in explaining the higher degrees of Composition."[17]

The aforementioned 'chemical principles' were only referred to again in his lectures as classes in his taxonomy of chemical bodies.[18] In later courses, Cullen adopted a pedagogical stratagem of discouraging speculation on the metaphysical elements or principles:

> "Opinions concerning Elements shou'd not be regarded as they mislead the Student. … our Business at present is only to know the meaning of the Classes already defined"[19]

The classes had been amended early in his teaching career to salts, inflammables, metals, earths, waters and airs.[20] Perhaps as a result of his avowed scepticism with regard to elements, in later years Cullen's use of the word 'principle' developed to encompass a binary definition. This distinguished his absolutely elemental 'meta-principles' from a more empirically justified conceptualisation. The 1748 lectures explained this second, pragmatic definition:

> "In order to compose Cinnabar or Vermilion it is enough to know that Brimstone & Quicksilver are the proper Ingredients nor for this purpose does it much concern me whether the Brimstone & Quicksilver are Elementary Bodies or mixts."[21]

Thus, brimstone and quicksilver might or might not be meta-principles, but there was little doubt that they were the 'ingredients' of cinnabar. It was with these pragmatic constitutive principles that Cullen wished his students to be concerned. The contingent nature of this knowledge did not detract from its utility:

> "tho by Chemical Resolutions we do not arrive at the Real & most simple Elements of all Bodies yet it is usefull to know the

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[17] Ibid, Lecture VI.

[18] Ibid.

[19] Cullen n.d. [1760s], MS/MSL/79a, f 29.

[20] Cullen's taxonomy notably did not adopt the traditional tripartite classification of natural 'kingdoms'. In this he seems to have differed from most of his pedagogical contemporaries in Europe. See Klein 2005, 110-117.

[21] Cullen n.d. [1748/9?], Lecture IV.

> principles of Compounds."[22]

We have two competing notions of 'principle' here, the absolute, meta-principles, and the 'principles of compounds'. By the 1760s, he had adopted a third conceptualisation, and a different term, 'chemical element':

> "Bodies can however be divided into certain parts different fm each other, which may be called Chemical Elements or the smallest parts that Bodies can be resolved into by Art; … We sometimes call the parts of Compounds Elements".[23]

Cullen's 'chemical elements' were dependent on the state of the 'Art', and the degree to which it was possible to resolve bodies into different parts by chemical means. Chemical elements were thus defined at least in part by the methods and practices of chemistry as a discipline. This strong operational influence on the epistemological status of individual substances reinforced Cullen's demarcation between chemistry and natural philosophy. Cullen's formulation implies that he did not distinguish between chemical elements and the more immediate 'principles of compounds', and yet they did not correspond with the substances that he included in his affinity table. Like Geoffroy, he included substances in his tables that he knew to be composed of other bodies, (including sulphur, aqua regia and the metals). It seems that his notion of chemical elements was rather intended to replace the traditional systems of elements than to classify the substances included in his affinity table.

Lewis explained the difference between mechanical philosophy and chemistry by asserting that where the first "seems to consider bodies chiefly as being entire aggregates or masses; as being divisible into parts, each of the same general properties with the whole",[24] the second:

> "considers bodies as being composed of such a particular species of matter; … or consisting of dissimilar parts, which may be separated from one another, or transferred into other bodies. The properties of this kind are not subject to any known mechanism, and seem to be governed by laws of another order."[25]

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[22] Ibid.

[23] Cullen n.d. [1760?], f 3-4.

[24] Lewis 1763, iv.

[25] Ibid.

This tallied with Cullen's separation of the chemical from the mechanical domain. Lewis, however, made no attempt to relate his distinction to any notion of elements or principles; chemistry was concerned with bodies as 'species' possessed of differing properties or qualities, or as made up of 'dissimilar parts' into which they could be separated by the operations of chemistry. Lewis's statement implied a hierarchy of simplicity, contrasting "particular species" of matter with those bodies that consisted of "dissimilar parts" which could be separated. This was essentially the same analytic relation as Cullen's implied hierarchy of simplicity, from cinnabar to brimstone and quicksilver, from one body to its 'ingredients'. It was an empirically ascertained status, a pragmatic assumption of relative simplicity that was unrelated to any abstract notion of principles or elements.

To his conception of substances as distinct chemical 'species' Lewis added the notion of a "grand active power",[26] chemical affinity, which he specifically stated "obtains between bodies as being composed of parts, and as being of a different species of matter from one another".[27] Affinity was thus inextricably linked to the difference of chemical species.

Some chemists worked backwards, drawing ontological conclusions from the apparent strength of affinities. Hadley asserted, on what were certainly logically sound grounds, that those substances with the strongest affinities were simplest in nature:

> "The most distinguished and considerable affinities are those of the simplest bodies whence it follows that the least compounded bodies are with the greatest difficulty analyzed"[28]

This assumption originated with Becher and Stahl, and was also adopted by both Boyle and Newton.[29] It also appeared in Macquer's list of fundamental truths of his affinity theory. It is clearly an *a priori* assumption rather than an empirical law, as a logical extrapolation from the definition of simple substances. This principle rests on the further assumption that the so-called

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[26] Ibid.

[27] Ibid, v.

[28] Hadley 1759 f 51.

[29] Duncan 1996, 184.

simple substances were no such thing, enshrining the common assumption amongst chemists that their most ‘simple’ substances were far from fundamental as a general law.

A more complex definition of the substances that were the chemists’ concern was set out by Fordyce in his lectures of 1765. He picked up Cullen’s notion of the chemical element, but rather than invoking a system of absolute meta-principles, or elements, he contrasted it with an implicitly mechanical notion of Physical Elements:

> "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.”[30]

Thus Fordyce’s definition of chemical elements pre-empted Lavoisier’s historically lauded definition of simple substances as:

> “simple in the present state of our knowledge, and so far as chemical analysis has hitherto been able to show.”[31]

He explained in more detail in 1786:

> “If I put a piece of Iron into a Solution of blue vitriol, I make another Division, viz into Copper which is on the surface of the Iron, & if the Division was complete the other Part would be vitriolic acid, which is colourless. I therefore Divide the Solution of blue vitriol into Parts which are dissimilar in their particular Properties from the whole. Copper is red, vitriolic acid is colourless, both together are blue. This is a chemical division. Copper then & vitriolic acid are substances which form blue vitriol. Whether the vitriolic acid be capable of Division into two Parts, or no, we do not know. No person has divided it yet, but it does not follow from thence that it is not divisible any further. … we know nothing a priori in Chemistry, therefore we can judge of no Division but what has actually been made. There are a number of substances which we cannot divide further but it does not follow from thence that they are not further divisible. The Substances which are as simple as we can make them we call chemical Elements.”[32]

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[30] Fordyce 1765, f 37.

[31] Lavoisier 1965 177.

[32] Fordyce 1786a, Lecture 2.

Lewis's conception, concerned only to distinguish substances from each other as different species, and making no claim concerning the absolute simplicity of substances, had been notably more cautiously empirical in tone than was Fordyce's. Fordyce's harnessing of Cullen's term 'chemical element' to his own much more positive conceptualisation reflects his rather daring attitude to hypotheses – an attitude which can be detected in many of the components of his affinity theory. Nevertheless, the type of pragmatism demonstrated by Fordyce and Lewis perhaps testifies to the power of the empirical ideal in chemistry. As Lewis stated, affinity was a power that 'obtained' between different species of matter. It was the difference of species that was essential here, not the simplicity of the matter.

The set of chemical elements that Fordyce assumed were, of course, dependent on the current state of chemistry. In 1786 he offered his students a list of 49 substances divided into the same six classes used by Cullen.[33] A substance was assumed to be elemental so long as it could not be analysed further by chemical means. But the possibility must be faced that a substance previously believed to be a chemical element might in future days be discovered to be a compound substance. As Nicholson explained:

> "Those substances which we have not hitherto been able to analyse, … are indeed considered as simple substances relative to the present state of our knowledge, but in no other respect; for a variety of experiments give us reason to hope that future enquiries may elucidate their nature and composition."[34]

Fordyce and Nicholson had before them an example of such a scenario, in Black's discovery that the common alkalis, substances that had not previously been decomposed, were compound substances composed of pairs of very different constituents.[35] Quick-lime, which had previously been thought to consist of the native calcareous earth combined with fiery particles (acquired during prolonged heating, and causing the causticity of quick-lime), was discovered to be the simpler substance of the two, with calcareous earth a

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[33] Fordyce 1786b, f 22

[34] Nicholson 1795, 155.

[35] Black, 1910.

combination of quick-lime and fixed air. The hierarchy of substances had been inverted. Combinations involving such substances were thus more complex than had previously been believed. Fordyce fully expected this type of discovery to happen again, and indeed Lavoisier's work overturned a similar hierarchy of complexity.

Such changing perceptions of the relations between substances might require the amendment of affinity tables, but they did not and would not undermine Fordyce's affinity theory. Whether or not a substance was perceived as elemental was irrelevant to affinity, as Fordyce clearly understood. His works testify to a second conceptualisation of his chemical element that was operationally context-dependent, and corresponded to the behavioural classification implicit in the use of affinity tables. Even substances known and agreed to be compound might still be regarded as elements in particular contexts. Thus "A Compound may become an Element".[36] When an admittedly compound substance combined with a different substance (whether simple or compound), to make a third, even more complex substance, the first (compound) substance, was seen as an element of the third. Certain substances, such as brimstone, were elements of compounds (e.g. cinnabar), but were themselves believed to be compounds or mixts (as brimstone was composed of vitriolic acid and phlogiston). Although brimstone was not believed to be elemental, in its combination with mercury to produce cinnabar, it was acting as a chemical element. Fordyce also presented this system, in reverse, as an explanation of the complex changes seen in such processes as fermentation.[37] Thus a hierarchy of more and less simple substances was proposed, an entirely relational ordering with no absolute basis. Fordyce's description of these 'operational elements' reveals one of the (predominantly) tacit components of all affinity theories, a component forming part of the common ground discussed in chapter 5, but it is important here to note two points. Firstly, that this conceptualisation was entirely separate from notions of ultimate or even contingent simplicity; and secondly, that although few chemists articulated the

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[36] Fordyce 1765, 3.

[37] Fordyce 1786b, Lecture 15.

idea as Fordyce had, it was necessarily implicit in every affinity table.

Fordyce used the term ‘element’ indiscriminately, to signify both the contingent chemical element and the operationally specific element. Torbern Bergman was (admittedly rather later) much more comprehensible. He explained:

> “Those elements, into which; by chemistry, a body may be resolved in the first instance, may be termed its proximate principles or elements; …
>
> By decomposing again each of those *proximate* principles of cinnabar, one may attain its *remote* principles …
>
> If the principles, into which a body has been thus resolved, are capable of no further resolution, they may be called primary, or ultimate principles or elements.”[38]

Bergman’s ‘proximate principles/elements’ corresponded to Fordyce’s operational elements, while the ‘ultimate or primary principles/elements’ equated to the contingent ‘chemical elements’.[39] Bergman’s hierarchy incorporated a conceptual link between the chemical and the operational elements. However, in so doing he obscured the relation that was most important to affinity theorists, that between a body and its proximate principles (and vice versa). His system was complicated by the fact that the layers of relative simplicity were not mutually exclusive; according to the particular circumstance, proximate principles could also be both remote principles and ultimate principles, while remote principles could also be ultimate principles. Where Fordyce’s system effectively distinguished the taxonomy of affinity tables from even contingent notions of absolute elements, Bergman’s apparently sought to conflate the two. The common ground component that explained the substances appearing in affinity tables, tacitly present in all affinity theories, but only briefly exposed in Fordyce’s teaching, was thus veiled once more by Bergman, hidden behind a hierarchy of relative simplicity.

Fordyce (and later, Bergman) expressly defined both contingently simple substances and the proximate ingredients of compound substances as

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[38] Bergman 1783, 6-7.

[39] As Newman has recently shown, this distinction (and indeed the very same terms used by Bergman) drew on a long chymical tradition. Newman 2006, 52.

‘elements’. This elided definition served to justify the substances that appeared in affinity tables. For Fordyce it was these operationally contextual ‘elements’ that appeared in affinity tables, as the substances that actually combined by the action of affinity. He adopted a taxonomy based on his affinity theory that further classed substances as either menstrua or solvends, according to their roles in each chemical combination. This bifurcation (discussed in more detail under section 3.2.1 below) provided a classification system that would assist in the assimilation of new discoveries into his theory. Interestingly, although Elliot appropriated Fordyce’s operational elements (quoting directly from his *Elements of Agriculture*, with acknowledgement) for his own work, he carefully left out this further layer of classification.[40]

It should be noted here that these contingent systems of ‘elements’ were not the only approach taken by chemists. Bryan Higgins, for example, lectured that there were seven “primary distinct elements of matter, *viz*. Earth, Water, Alkali, Acid, Air, Phlogiston, Light” which attracted and repelled each other in a complicated system. Higgins claimed that some familiar substances, like caustic volatile alkali, were absolutely elementary. Perhaps unsurprisingly, he also included a lecture in which

> “the incompetency and errors of the tables of elective attractions demonstrated; and comprehensive tables commenced, in which the blanks are to be filled up as fast as experiment will authorise.”[41]

By the late 1780s, Fordyce’s attitude towards affinity tables was also somewhat jaundiced. This was in part a consequence of the shifting status of substances from elements to compounds as substances like water, the archetypal element, were decomposed, and metals were assigned simple status. While none of this affected his theory, he could hardly deny that it cast a shadow of doubt over most affinity tables thus far produced. He explained:

> “A great number of substances which we consider simply chemical Elements are really & in fact Compounds. So that when we are performing a simple elective attraction as we suppose, it frequently is not a simple elective attraction but a compound one.

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[40] Elliot 1782, 103-4.

[41] Higgins 1775, 29-30.

> This makes great derangement of great Difficulty in forming Tables of elective attraction; for the same substances do not combine together by compound elective attractions as we should expect from simple elective attractions"[42]

In such scenarios, numerous affinities competed together in ways that were imperfectly understood. Affinity tables were intended to show the actions of single affinities and as so many substances had now been shown to be compound, the tables that had been produced on that basis were likely to be incorrect. More importantly, it made the production of new affinity tables, always a complex process, a tangled maze of competing affinities.

Fordyce perceived the problem to be temporary, the result of deficient knowledge of substances and their relations rather than anomalies within his affinity theory. The idea of affinity tables was relatively impervious to changes in the absolute ontological status of particular substances, as the matrix allowed the easy inclusion of chemical elements whatever their realist status. As knowledge grew about the composition of individual substances, so the tables of affinity could be amended, bringing them closer to perfection.

We can see evidence of some of the difficulties that Fordyce mentioned in Bergman's affinity tables. Substances such as aqua regia, a mixture of nitrous and marine acids, appeared in Bergman's tables of 1775 and 1785, alongside various substances which were presumed to be combinations of simpler substances with phlogiston. Bergman's tables reflected both the phlogisticated nature of the chemistry of the late 18th century, and the operational basis of his table. As he believed that metals dissolved in acids lost their phlogiston (to the acids), the successive displacements were of the calx rather than the metal itself. While his 1775 table had listed metals in the columns beneath the acids, the 1785 version listed the calces. As he argued:

> "That these substances are attracted and dissolved by acids, is known even to beginners; but let it be remembered that they are not, as was supposed, taken up entire, and in their complete form by menstrua: for some particles of the acid carry off the superfluous phlogiston, while others dissolve the calcined metal. Since therefore they exist in the menstruum mutilated, and in a

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[42] Fordyce 1786a.

> great measure deprived of one of their principles, the condition under which the process may be referred to single attractions, does not exist."[43]

For Bergman, as for Fordyce, it was essential that affinity tables set out the results of single affinities only, and he amended his table to ensure that this criterion was rigorously observed. Thus the distinction between single and double affinities, initially set out in Cullen's lectures, served to reinforce the epistemological criteria for the 'operational element'. As it was metal calces rather than metals that combined with the acid menstrua, so it was metal calces that should appear in affinity tables. On the other hand, as sulphur combined in the dry way with metals entire rather than their calces, so it was these, compound, substances that appeared in the appropriate column of Bergman's tables. Bergman's table thus adopted behavioural criteria for inclusion that conformed closely to Fordyce's 'operational element', although with an additional level of distinction beyond those Fordyce specified, between the 'wet way' and the 'dry way'. Which substances were deemed to be acting as chemical elements in particular combinations depended not only on which substances combined together, but also on the type of operation that combined them.

Cullen, Fordyce and Bergman all spent time formulating their own affinity tables. They were all keenly aware of the difficulties arising where more than three affinities were in competition. Cullen though, had the luxury of feeling relatively confident of his 'chemical elements', as yet untroubled by the multitude of new airs that boiled up from the late 1760s. In contrast, for Fordyce and Bergman, these discoveries emphasised that they were standing on slippery ground. It became increasingly clear that affinity tables must be rigorous in depicting only single affinities, and that the substances that appeared in their columns must be those that actually combined or were separated out. Hence perhaps Fordyce's decision to offer his students in 1786 an affinity table of only seven (extremely generalised) columns.[44] Where Fordyce argued that accurate affinity tables must await greater knowledge of substances, Bergman

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[43] Bergman 1970, 82-3.

[44] Fordyce 1786b, facing f 49.

apparently believed that greater rigour in depicting the combinations and separations of matter in affinity tables would produce the accuracy desired.

We have seen in this section, a variety of attempts to bring the theory of chemistry closer to its practice. Chemists formulated pragmatic conceptualisations of chemical elements and compounds based on the methods and practices of the art. As we have seen, Lavoisier's definition of simple substances contingent on the state of the art had a long history. These contingent chemical elements can be roughly discerned in Cullen's lectures, overlapping with more traditional notions of elements and principles. As they were based on the limits of chemical analysis, they were distinctively chemical, bound to chemical methodology and practices. While a substantial overlap undoubtedly existed between this set of contingent or analytical elements and the substances that chemists commonly encountered in their affinity tables, there was also a notable disjunction. No single level or scale of complexity corresponded to that contained in the affinity tables, and any taxonomical structure that described the contents of affinity tables would seem to have been based on something other than a hierarchy of simplicity. We have seen here a glimpse of one of the components of the common ground in Fordyce's operational notion of elements. Those substances that combined (without their own decomposition) to produce a new substance were the elements of that new substance, and these were the substances that appeared in the tables. It was that simple. These elements were distinctly based on affinity theory. They were dependent entirely on the operational context in which they appeared rather than on a single distinct ontological level of analysis. This second sense, I suggest, originated from the routine employment of affinity tables, and tacitly provided the criteria for the inclusion of substances in such tables.

Affinity theories encouraged a shift of emphasis onto the dynamics of chemical operations and the behaviour of substances, rather than their ultimate composition.[45] From the new dynamic viewpoint, compound substances could be characterised as simple or elemental within the bounds of particular

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[45] Kim has discussed the opposition in French chemistry during the 18th century between compositional 'principlist' chemistry and affinity chemistry at length. See Kim 2003.

operations in which they behaved as such. Substances that were undoubtedly compound from a realist point of view, could thus be regarded as elements within the context of a particular operation ('operational elements'). In the chemistry of the 18th century, notions of simplicity and combination were fluid, determined largely by context.

Bergman's and Fordyce's concerns to ensure that their affinity tables reflected the behaviour of substances accurately indicates the importance of the chemist's facility of recognising substances and where necessary classifying them. If a substance was incorrectly identified, as Fordyce pointed out, the affinity theory would be founded on error. The specific identification of each individual substance that appeared in affinity tables was thus crucial to their practical utility. The next section explores components that set out some of the rules for such identification.

3.1.2 Identity and Recognition: The Specific Character of the Chemical Substance

The Nobel prize winning chemist, Roald Hoffmann, calls identity "the central problem" of chemistry. He explains:

> "The very first question a chemist asks when faced with a sample of anything new under the sun – some dust brought back at fantastic expense from the surface of the moon, an impure narcotic off the street, an elixir extracted from a thousand cockroach glands – is always the same: "What do I have?"[46]

In the 18th century, as now, identity was the crux of chemistry. A chemical understanding of a body was founded on the correct identification of its constituent substances. This section explores the concepts used by chemists to assist with the processes of identification and recognition of particular substances. I begin by looking at the establishment of a substance's identity, its chemical character. Next, I explore the process of recognition and identification of familiar substances, and finally I shall draw attention to some conceptual difficulties resulting from the use of affinities in the process of identification.

For the 21st century chemist the identification of a new substance is made simpler by the existence of a standardised set of elements that set a boundary to

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[46] Hoffmann 1995, 7.

reduction and form, according to that old cliché, the 'building blocks' of matter. As we saw in the previous section, a clearly defined set of elemental substances, and the confidence that such an explanatory resource must inspire, was not available to 18th century chemists who were (to continue the metaphor) still trying to extract the material for their bricks from the ground. Nevertheless, the ability to identify certain key substances, whether elemental or not, was still essential to both the chemistry of familiar bodies and for investigations into new and unknown materials. 18th century chemists were reliant for identification on a combination of macroscopic physical properties and a knowledge of the affinities that offered a glimpse of the microscopic world.

Bergman argued that criteria for recognition and identification of substances were essential in ascertaining what actually happened in chemical combinations. As he said:

> "Here the knowledge of the form, taste, solubility, tendency to effloresce, and other properties, even those which, in other respects, appear of no consequence, of the substances, is of great use in enabling us to judge safely and readily, whether any, and what decomposition has taken place."[47]

Bergman made his statement in the section of his *Dissertation on Elective Attractions* where he explained how he had interpreted the experiments on which he had based his enormous affinity table. His ability to recognise and name the substances emerging from a mixture was crucial to this endeavour. It is surely no coincidence that Bergman was one of the earliest chemists to attempt to produce a new nomenclature for chemistry that would accurately reflect the composition of substances.[48]

Klein argues that

> "Eighteenth-century chemists formulated new chemical conceptions for the identification and classification of chemical substances in place of the old ones derived from natural history. In contrast to traditional natural history, the identification of natural bodies within chemistry was done by intervening in the

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[47] Bergman 1970, 66.

[48] Crosland 1962, 142-152.

> constitution of natural bodies with chemical tools."[49]

Individual substances were identified and classified by their chemical behaviour, through chemical intervention. Lewis set out a list of properties that differentiated one chemical species from another:

> "dissoluble, liquefiable, vitrescible, combustible, fermentable, &c. impregnated with colour, smell, taste, &c."[50]

Distinctions were drawn between substances based on their properties. Looking at Lewis's list, we see two different types of properties. He distinguished something similar to Locke's sensible qualities which produce an effect/change on the observer (Lewis's 'impregnated' properties). The other type of property conforms broadly to Locke's powers: the power to produce observable changes either on themselves or on other substances. The power of burning, combustibility, the power of dissolution, and the power of fermenting; these, as well as more sensible properties, distinguished the different species of matter.

It was important that more than just a few properties were examined in any attempt to identify a substance. In a discussion that took place during a 1785 meeting of the Chapter Coffee House philosophical society, Thomas Cooper described an unusual appearance of sulphur during a chemical process, to which Kirwan responded:

> "Mr Kirwan is of opinion that the floating matter is not Sulphur, and recommended the examination of it to Mr Cooper. Mr C. confesses that he formed his conclusion only from the feel & appearance without attending either to the smell or burning it."[51]

Cooper did not manage to procure the mysterious substance again to examine it, and so it remained an anomaly.[52]

Lewis's experiments on platina, concerned as they were to find out its properties, offer a useful example of the establishment of a character for an

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[49] Klein 1996, 281.

[50] Lewis 1763.

[51] Levere and Turner 2002, 102.

[52] Ibid, 110.

unknown substance.[53] Lewis published six papers in the *Philosophical Transactions* in three tranches in 1754 and 1757 in which he set out his studies of the "white metallic substance said to be found in the gold mines of the Spanish West-Indies"[54] Platina was at this time a new substance, its properties being little known and Lewis's investigation provided the most considerable account of its behaviour yet available.

Initially, Lewis described the Platina in the state in which he had received it, intermingled with earthy matter, gold and mercury. He deduced that it had probably been contaminated with mercury during the process of extracting the gold from the ore, but the major proportion of the mixture was

> "white, shining grains, of seemingly smooth surfaces, irregular figures, generally planes with the edges rounded off. … the grains … are the true platina."[55]

Lewis classed the new substance as a metal without difficulty. His *New Dispensatory* indicates that the criteria for metals were based initially on physical characteristics. He cited specifically their "peculiar bright aspect, perfect opacity and great weight"[56] and explained that when metals were heated with access to air, they were slowly converted "with different degrees of facility, into a powdery or friable substance, called *calx*, destitute of the metallic aspect, and much lighter, in proportion to its bulk, than the metal itself."[57] Finally, he asserted that all metallic substances dissolve in acids, although some only in particular acids. Only this last taxonomical criterion refers to affinities.[58] Lewis assessed the malleability, specific gravity, and fusibility of the 'grains' of platina. When attempting, fruitlessly, to force it into fusion, he tried every method of promoting fusion that was available to him, including the

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[53] Eklund has argued that Lewis's investigation of platina epitomises the new technique of operational identification, that is the development of operational techniques allowing substances to be identified by their relationship to other substances. Eklund 1971 See also Kirwan 1786 which followed a very similar pattern.

[54] Lewis 1754.

[55] Ibid, 638.

[56] Lewis 1768, 23.

[57] Ibid, 24.

[58] Although for many later chemists, the penultimate characteristic, the calcination of metals, could be explained by reference to the affinities of phlogiston for various metals and for atmospheric air.

addition of plaster of Paris, which was used to enable the fusion of "the most difficultly-fusible metallic body hitherto known, forg'd iron".[59] He tried reducing the platina with nitre, "which reduces all the known metallic bodies, except gold and silver"[60] and with sulphur, again without success.

Many of these experiments suggested that platina was analogous with gold. Like gold, the platina would only dissolve in Aqua Regia, and on the addition of various salts and metals, a variety of precipitates were produced. This quickly observed kinship between platina and gold formed a starting point for Lewis's experiments, and he tailored his investigations accordingly. For example:

> "As fix'd alcaline salts enable sulphur to dissolve gold; platina was expos'd to the fire with a mixture of sulphur and alcali, called *hepar sulphuris* …".[61]

Lewis's intuition was justified – like gold, the bulk of the platina was dissolved by the hepar sulphuris. There is a clear strategy here to compare the unknown with the known, both in physical properties and in their conjunction with other substances. It is the latter type of comparison that predominates in Lewis's investigations. Conjunction of different species of matter held a particular resonance for Lewis, as it was in such circumstances that affinities became evident. Affinity, for Lewis, was necessarily the result of the interaction of two different substances. In 1763 he explained that if gypsum (itself composed of vitriolic acid and quicklime) was mixed with charcoal, and heat applied,

> "a strong chemical affinity begins to take place: the acid quits the lime, and unites with the inflammable principle of the coal, forming therewith another new compound, common brimstone."[62]

Lewis saw affinity as a power that arose between two different species of matter, rather than a power or property that was inherent in each particular species. On this view, affinities were properties of particular conjunctions rather than of individual substances. In his examination of platina, he was

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[59] Lewis 1754, 644.

[60] Ibid.

[61] Ibid, 645.

[62] Lewis 1763, vi.

concerned to compare conjunctions rather than to seek absolute powers:

> "it is propos'd to examine the effect of acid spirits, simple and compound, applied after various manners; in order to determine not only its relation or *habitus* to them, but likewise its less obvious agreement or disagreement with the metallic bodies, whose history is more known."[63]

He compared the results of most of his experiments with what might be expected of gold in a similar experiment. Thus new substances were compared with other, more familiar materials with recognised and well understood properties.[64]

Lewis showed that gold and platina could be mixed without any physical means of detection. Colour, ductility and specific gravity were unimpaired, and as the behaviour of platina in conjunction with other substances was so similar to that of gold, many of the standard chemical tests for the purity of gold were feared to be ineffectual. Platina and gold were so similar, both physically and chemically, that there were doubts as to whether they were truly different chemical species. Lewis was keen to show that although platina resembled gold to a large degree, it nevertheless did not contain gold, and that the usual tests for gold remained effective, even in the presence of a large amount of platina. Confident identification of the new metal only became feasible after the publication of an investigation such as Lewis's. As he explained,

> "… platina is not, as some believe, gold naturally debased by the admixture of some other metallic body, but a metal of a peculiar kind, essentially different from all the others. Before the discriminating characters of platina were discovered, such a notion was highly plausible, and direct experiment seemed to confirm it".[65]

The persistent comparison of platina with gold must have reflected commercial concerns as well as Lewis's scientific intuition, as platina was still considered a

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[63] Lewis 1754, 646.

[64] Jon Eklund has noted that Lewis lists his experiments in an order that seems unlikely, and that his ordering of the experiments mixing platina with acids is most likely a decision related to style. See Eklund 1971, 117 fn.. Lewis's concern for the style of his paper is interesting when we note that he did not offer specific affinity triplets in his papers given to the Royal Society, although they were included in his later *Commercicum Philosophico-Technicum* (see below). Perhaps Lewis felt that the Royal Society were not concerned with affinity tables and that their inclusion would be inappropriate.

[65] Lewis 1757b, 165.

worthless contaminant of gold. In 1766 Cullen told his students that:

> "All the sources of it are shut up by the Spaniards, because it was used in such a notorious manner for adulterating their <gold>; but as the late labours of the most eminent chymists of Europe have found out the method of discovering such debasement & of separating the platina from the <gold>, we hope the sources will be again opened, that further observations may be made on this curious substance."[66]

Cullen was possibly referring to Lewis's 1754 paper here, as it included four methods for detecting the presence of platina in combination with gold. The first relied on the fact that an amalgam of a platina/gold mixture would separate the platina, which did not unite with the mercury. Thus the affinity of mercury for platina was weaker than its affinity for gold. The second method depended on the fact that gold could be precipitated from aqua regia while a similar precipitation of platina was incomplete, and the presence of the platina tinged the solution yellow. The third method was more effective in separating the two substances; inflammable liquors were added to a solution of the mixture which precipitated the gold, while the platina remained in solution. The final method suggested by Lewis was the addition of green vitriol, which precipitated gold from solution, but not the platina.[67]

Lewis established that the affinities of platina were different from gold. It displaced gold from particular combinations, and in other combinations where gold remained combined, platina was displaced. These concrete differences in affinity showed that platina was a single homogeneous chemical species entirely distinct from gold. It was also affinity that provided the methods for distinguishing and separating the two metals most assuredly. It was the <u>behaviour</u> of matter that gave away its secrets, setting different chemical species apart from each other.

Affinity thus offered a solution to the problem of transdiction. Observable physical qualities could not be imposed on the microscopic world; particles of gold, for example, were not imagined to be in themselves yellow, shiny and malleable. But the affinities of gold were observable and could, chemists

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[66] Cullen 1766, Lecture 89.

[67] Lewis 1754, 656.

believed, be extrapolated to the microscopic world. Such extrapolation was not crucial for the coherence of affinity theory, although it was an entirely rational step. A combination of Humean scepticism and the activities of charlatan alchemists had perhaps served to destroy chemistry's faith in identification by physical characteristics. Affinities were observable and, by their very nature, comparative, and thus were particularly suited to describing the identities of new matters.

Almost contemporaneous with Lewis's work on Platina was Black's 1756 paper "Experiments Upon Magnesia Alba, Quick-Lime, and other Alcaline Substances"[68] drawn from his 1754 MD Dissertation. This reported Black's investigations into an earth, magnesia alba, and its comparison with other chemically similar substances. Black reported various experiments in which he combined magnesia with the various acids to produce what he called neutral salts.[69] One of the complicating factors in any discussion of earths at this time was that calcareous earths were seen as a whole class of substances, widely varying in origin and appearance (Black listed lime-stone, marble, chalk, spars and marbles and animal shells). These substances were all "converted into a perfect quick-lime"[70] on exposure to strong fire or heat. Magnesia physically resembled the calcareous earths, but was shown in Black's experiments to produce noticeably different compounds with acids. In spite of its physical resemblance, Black argued from these differences in chemical behaviour that magnesia could not be classed as a calcareous earth. He set about establishing its positive character through a series of experiments designed to determine its affinities and behaviour. Magnesia was compared with the calcareous earths, and alkaline salts, all substances which it resembled in particular ways. Like the calcareous earths, it seemed to produce a quick-lime upon strong heating, and like the more familiar quick-lime this was caustic and combined with acids without effervescing. Like the alkaline earths it could 'sweeten', or make mild,

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[68] Black 1910.

[69] Ibid, 10. Purists, Cullen amongst them, would probably not have called a compound of an earth and an acid a neutral salt, reserving this status solely for those combinations of acids and alkalis. Black's decision may have reflected his observations of the behavioural similarities between the traditional fixed and volatile alkalis and the calcareous and absorbent earths.

[70] Ibid.

the caustic quick-lime. Black's observations on magnesia led him to re-examine the familiar alkaline salts, comparing their behaviour with that of magnesia and calcareous earths.

Black's paper, like Lewis's was based on analogies drawn between known and unknown substances. These were tested by experiment, clarifying the chemical similarities and differences. His eventual conclusions have been thoroughly discussed by historians,[71] and there is no need for me to repeat their work. His paper ended with two short affinity columns, the first amending the column already present in most tables for acids, showing their various affinities to the three alkali substances that he examined. The second was an entirely new column for his newly identified substance, fixed air.[72] While engaged in determining the chemical properties of magnesia alba, Black had postulated the existence of this 'elastic fluid'[73] that combined with the earths and changed their properties. What is often ignored in discussions of Black's work is the fact that, neither in his MD dissertation nor in his 1755 paper did he show any interest in collecting the fixed air. In 1754 he had described to Cullen an amusing phenomenon that he had observed, when chalk and vitriolic acid were combined:

> "the strong effervescence produced an air or vapour, which, flowing out at the top of the glass, extinguished a candle that stood close to it; and a piece of burning paper, immersed in it, was put out as effectually as it if had been dipped in water"[74]

In spite of this chance observation, as Donovan has noted, Black was uninterested in the properties of fixed air in its free state.[75] By the end of his paper, however, he had succeeded in establishing a chemical character for fixed air just as he had for magnesia. He was able to argue convincingly that fixed air existed and differed from normal atmospheric air, being possessed of a set of ascertainable affinities which dictated its chemical behaviour. Black apparently transferred it from one substance to another, e.g. from fixed alkali to quicklime,

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[71] E.g. Cranston 1950, Donovan 1975, Donovan 1976, Golinski 1992, Read 1950.

[72] Black, 1910, 46.

[73] Or possibly 'an exceedingly subtile powder' Black 1910, 30.

[74] Quoted in Donovan 1975, 201.

[75] Donovan 1975, 200.

but it was only ever moved from one combination to another. When he measured the quantity of air expelled from an alkali dissolved in acid, the weight was ascertained by weighing the apparatus together with the acid and alkali both before and after the operation. The character of this substance was composed of its affinities, its combinations and the chemical effects of these combinations. A substance that had not been seen (strictly speaking), touched or tasted, was deemed to be a distinct chemical species on the basis of its effect on the properties of more tangible substances in combination. The affinities of this almost (in positivist terms) unobserved entity were determined and set down as lawful relations.

At this stage in its existence, fixed air was strikingly similar to phlogiston, as a substance that was recognized only through its relations to and effect on other substances. As with phlogiston, the presence of fixed air was indicated by particular properties in the compound substance. Fixed air differed from phlogiston in that it could be indirectly 'observed' escaping from combination in the form of effervescence, and of course it would later be collected using Priestley's pneumatic apparatus. But when in combination, as it was in most of Black's investigations, its presence or absence was signified by the chemical behaviour of the compound substances, according to its determined affinities.

Lewis and Black's analyses indicate that as chemical behaviour resulted from affinities, so the characters of substances as chemists knew them were, in part, identified with their affinities. New substances were characterised by their combinations and their behaviour. Familiar substances were also recognised by their affinities. Thus an unknown commentator on a 1765 set of Cullen's lectures disposed of his suggestion that all inflammable substances contained a phlogiston composed of fixed air and vitriolic acid with the comment:

> "they can't be mephitic air and acid because we know ye y^{d} do not unite"[76]

Certain standard tests began to be used, with standard reagents, such as the limewater test for fixed air which was based on Black's characterization of fixed air. Fordyce's tables in his *Elements of Agriculture* explicitly identified

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[76] Cullen 1765, MS 1920, f 75r.

properties with affinities. His table of the salts found in soils is divided into three columns, showing the names and synonyms of each salt, their origin, whether natural or artificial, and "Their PROPERTIES". For vitriolic acid, this column read:

> "It unites with
>
> 1st, Fixt vegetable Alkali, forming vitriolated Tartar.
> 2d, Fixt Fossile Alkali, forming true Glauber's Salts.
> 3d, Iron, forming Green Vitriol.
> 4th, Copper, forming blue Vitriol.
> …
> It attracts Alkali's and Earths, stronger than any other Acid."[77]

By the latter part of the 18th century, most airs were regarded as easily identifiable by their affinities. Fordyce gave his students characteristic combinations to identify 'gas' (fixed air), inflammable air, and nitrous air. Phlogisticated air remained problematic as it "cannot be ascertain'd."[78]

In an earlier paper, Fordyce had advocated the use of affinities in identifying a mixture of unknown metals. He suggested that if the mixture be dissolved in acid,

> "we may try to make a precipitation with the metal which is lowest but one in the order of elective attractions, and so proceed to the next above it, until we come to the highest; and by this means we shall obtain all the metals in the mass.[79]"

As this use of the recognised ability of metals to unite with acids indicates, classifications too were often based on affinities. Robert Dossie's taxonomy (discussed further below in 3.3.1) was contingent upon his affinities, and his orders of affinity were in turn contingent (to some degree at least) on his taxonomy.[80] Dossie unusually classified silver, copper and iron as alkalis rather than metals. This is explained by the fact that his taxonomy, classing substances into genera and species, was itself based on demonstrable affinities. As he argued:

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[77] Fordyce 1765, 19.

[78] Fordyce 1786a, Lecture 88.

[79] Fordyce 1780, 36.

[80] Dossie 1759.

> "a similar agreement is found, in a great number of bodies, that vary much in their general nature, and have nothing in common but such attractions: and this agreement, with respect to the object of their attractions, constitutes them nevertheless of one genus, considered with relation to their menstrual nature."[81]

It became more common for acids to be recognised as such by the fact that they combined with alkalis, and vice versa. Nicholson explained:

> "Acids were formerly distinguished by the popular criterion of taste which is peculiar to them, … Modern discoveries have, however, exhibited acids, in which the leading properties are too obscure to be of any great utility in determining their nature when unknown; and it is only from the general assemblage of properties that they can be distinguished."[82]

Out of the five criteria he listed to distinguish acidity, three were based on affinities. In 1786, Kirwan classed sulphur as a (mild) acid, due to its ability to unite with

> "alkalies, calcareous and ponderous earths, and most metals, as a weak acid might; and except a manifest solubility in water (a property which some other concrete acids also possess in a very weak degree) it exhibits every character of acidity".[83]

Even the strength of this theoretical acidity was measurable by its affinities. Sulphur must be an extremely weak acid, as "it decomposes only acetous, and not marine baro-selenite, and is separable from alkalies and earths by all other acids".[84] 'Strong' acids were those which were high up in affinity columns, while those towards the lower ends were 'weak'.

Kirwan recategorized sulphur on the basis of its similar affinities to those of a recognised class of substances. But the distinction between individual and class was not always clear. For the chemists of the late 18th century, a consensus over the identification of 'phlogisticated air' remained unattainable. According to Fordyce, the problem was that any vapour of a greater specific gravity than respirable air was described as such.[85] This, of course, is a physical criterion,

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[81] Ibid, 15.

[82] Nicholson 1795, 2.

[83] Kirwan 1786, 146.

[84] Ibid, 146-7.

[85] Fordyce 1786a, Lecture 88.

and Fordyce recognised that it referred rather to a group of substances than one unique species of matter. Affinities could be ascertained for individual substances and then generalised across a class where there was clear repetition (witness the columns in most affinity tables for 'acids in general'),[86] but generalisation could not be assumed *a priori*. In the case of the variety of substances named 'phlogisticated air', there was not that much similarity amongst their affinities. Substances could be classed together on the basis of similar affinities, but similar affinities could not be assumed amongst substances that were classed together on alternative grounds. The characteristic group of affinities that would distinguish 'phlogisticated air' could not be determined until the substance itself was distinguished sufficiently for these to be discovered.

This highlights a conceptual problem with these methods of substance identification. The relative affinities between substances shown in affinity tables were based on assumptions of substance identities. And yet, as I have shown, in many cases identification was in turn founded on affinities. So, while a substance was recognised by its affinities, its affinities had presumably been discovered on an assumption of identification. Anderson has drawn attention to this complex set of relations in the work of Macquer where

> "Analysis, principle, and affinity work only as a complex, each term defining and justifying, or serving as the reference for, the others"[87]

Anderson argues that Macquer's way out of his circular argument was his categorisation of tables of affinities as matters of fact. For most chemists, the distinction between qualities and identity was elided. Spector has noted that

> "For chemists, the names/symbols contained in affinity tables were assumed to stand in for the thing observed without the philosophical implication that judgment intervened. In actuality, … what are perceived are not the isolated chemical entities themselves but the experimentally observed qualities of the chemicals."[88]

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[86] E.g. Geoffroy 1719.

[87] Anderson 1984, 61.

[88] Spector 2003b, 222-223.

In many cases where a chemical operation had produced a doubtful result, chemists were forced by the vicious circle in which they were placed to adopt a hierarchy of characteristics. Other tacit assumptions and observations were brought into play. Earlier in the 18th century, the forms in which metals appeared were rarely critical to their identification. In Lewis's examinations of platina, the addition of a large amount of mercury to a solution of platina in aqua regia eventually resulted in the precipitation of the platina "in the form of a dark brownish powder".[89] Although platina was a new substance, Lewis was unconcerned at its apparent change of form. The brownish powder was unhesitatingly identified as platina. Lewis drew on a fairly limited assortment of chemical elements. Changes in form were commonplace amongst his constituents, and for the most part seem to have been disregarded. Airs did not feature in Lewis's battery of substances. Powders or earths were simply regarded as calces, which were deemed to be the metal under a different, accidental form. In this case, he knew that the only ingredients in the mixt were mercury, platina and aqua regia. Thus, he assumed, only mercury, platina or aqua regia could emerge. This assumption exemplifies the unarticulated assumption that matter was conserved, that certain substances were stable in most circumstances as pragmatic chemical elements.

Bergman's table, as we have seen, attempted to accommodate the type of anomaly that Lewis had glossed over. Between Lewis in the 1750s and Bergman in the 1770s it seems chemists became more rigorous in their expectations of chemical explanation. It was no longer sufficient to recognise that a substance was mercury, but in a different form; it was now necessary to explain how the mercury had come to be in this different 'form'. Phlogiston theory, as incorporated by Bergman and others into affinity tables, performed this function. The displacements of metals from acids required a strict accounting. Nevertheless, Lewis's identification of his "brownish" powder serves to remind us of the important fact that chemists were not operating in a historical vacuum. Their predecessors had recognised at least six metals, and certain other substances since beyond written memory. The array of substances

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[89] Lewis 1754, 658.

which the chemists of previous centuries had known were recognised in a great variety of forms through, for the most part, their sensible qualities. Identification of these substances was part of chemical heritage, and this provided a route out of the dilemma between affinity and identity. In the same way as the unvarying volume of gaseous substances was to provide an access point into the relative mass of non-gaseous substances in the 19th century, the recognition of long familiar substances provided a foundation on which to build the identities of less familiar ones. In some ways affinity theories hung on the identification of these historically more-than-familiar substances. Where even these traditional marks failed, as in the case of Fordyce's 'phlogisticated air', determination of affinities was impossible, and identification remained doubtful on any ground.

3.2 Concepts of Combination

It will be immediately apparent that conceptions of substance identity will impinge on conceptions of combination. This component can be divided into three according to the different types of question that might be asked about combination. The first is epistemological: how does the chemist know whether substances are combined or not, and are there different types of combination? Clearly, any answer to this question will be linked to the components discussed in Section 3.1.1 above. Accordingly I have not dwelled on this at length. The second is concerned with the products of combination: what happens to the affinities and properties of substances once they are combined? And the third focuses on the mechanics of chemical combination: how does combination work? How do more complex substances combine together?

3.2.1 Complexity: The Epistemology of Combination

As both Bergman and Fordyce made clear, any interpretation of chemical operations required the ability to decide whether the substances employed were acting as elements, in which case the model of single affinity was appropriate, or as complex substances, when double or compound affinities would be acting. We have seen that the problem of whether a substance was complex or simple in an absolute sense was believed to be insoluble. Although most chemists, like Cullen, paid lip-service to some metaphysical system of elements, few would have attempted to claim that their ‘chemical elements’ were in reality truly simple. Cullen disposed with some scorn of Stahl’s classes of mixt, compound, decompound and superdecompound as:

> “these terms useless, as the Degree of Composition not known”[90]

The key point here, as we have seen from Fordyce’s operational elements and Bergman’s proximate principles, is the notion of relative degrees of composition. Cullen and his contemporaries were convinced that the apparently simple substances that they manipulated in their operations were far from such in metaphysical or absolute terms. Nevertheless, they were able to draw upon their observations to determine the relative complexity or simplicity of substances.

We have seen that there were two subtly differing pragmatic notions of simplicity in circulation; the ‘chemical elements’ that had so far remained impervious to the chemist’s art, and ‘operational elements’ which acted as such in clearly defined operational circumstances. An array of substances able to behave as elements formed the basis for much of 18th century chemistry. These acids, alkalis, metals, and earths were often compounded together to form neutral, metallic, or earthy salts, hepars and other mineral substances. Knowledge of which elements combined to produce which compound substances was crucial to any affinity theory. Cullen talked his students through a table showing the combinations of the acids and alkalis, advising them to learn it by heart.[91] Lewis published a more comprehensive table that covered earthy salts as well as neutral.[92] These tables told chemists how to use their affinity theories to analyse compound substances as well as to recombine them to produce the desired body. They helped to counter the difficulties inherent in chemistry’s disorganised ancestral nomenclature. They also provided a matrix for further investigation and discovery; Lewis’s printed table showed for the combinations of magnesia “purging salts, not distinguished by any particular

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[90] Cullen n.d. [1748/9?], Lecture IV.

[91] Cullen 1766, Lectures 44 and 45.

[92] Lewis 1765, 458.

name".[93] Such unidentified substances required chemical identities and names. Nicholson's *Dictionary* included a series of tables of combinations covering 21 pages that is notable in part for the number of empty cells showing how many identities remained to be fashioned for these compound substances. They also included the combinations of more complex substances (acting as operational elements) to produce "compounds consisting in general of more than two Principles".[94]

It might seem obvious that when two substances were combined together that the resulting substance would be complex, and could be legitimately regarded as so. But the discoveries of the second half of the century meant that there were very few operations that could be regarded so straightforwardly. The use of fire and heat to promote union and the fact that acids were always combined to some degree with water, meant that there were very few combinations that could be performed by the simple mixture of two, and only two, substances. In the majority of the examples we have already seen, the water that was invariably present was regarded as a passive agent of solution. Complicating matters further, very few substances were easily obtained in a pure state, and many operations performed a dual role of separation and combination through the action of affinities.[95]

> "It sometimes happens that to separate all the Constituent parts of Bodies we are obliged to make use of mixts wc indeed separate the parts of the Body but make a new Combination betwixt each of its two Principles & these of the Body we cannot separate."[96]

This difficulty was to become increasingly apparent throughout the century, particularly with the discovery of the range of new 'airs'. This brought into play a whole class of substances that had previously been believed to be a single passive substance. To illustrate; if, for example an unfamiliar substance AB is combined with a substance believed to be simple, C, the results could be either AC and B, BC and A or in exceptional circumstances, ABC. If either A or B

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[93] Ibid.

[94] Nicholson 1795, 1076-1093.

[95] A glance at Chapters I-VI of Clow and Clow 1952 emphasises the difficulties chemists faced in acquiring certain of their 'chemical elements' in a relatively pure state.

[96] Cullen 1757, f 40.

are familiar to the chemist, then some light is shed on the constitution of AB. If, on the other hand, C is not as simple as previously believed, but is composed of DE, then the results of the operation could be highly misleading. Lewis's experiment combining mercury, aqua fortis and platina (section 3.1.2 above) would have been explained by Kirwan as involving not three operational elements, but anything up to eight.[97] Elliot highlighted a further complication in a letter to Kirwan (published in the *Philosophical Transactions*) which showed that the use of different menstrua led to amended affinities:

> "in the *moist* way the affinities take place differently, according as water, or spirit of wine, is used. Perhaps a like difference would be found on using other liquids, each of which would probably afford a different table: for much depends on the attraction which the ingredients themselves have to the liquid employed".[98]

The multiplication of chemical entities, and the doubts cast on customary assumptions about the passivity of menstrua and substances traditionally regarded as simple sat uneasily with the notion of simple affinity.

The law of affinity implied that only two substances combined together at once and that all compound substances could be divided into two, simpler substances, and in some cases these (or just one of them) could be further divided into two. As Klein has noted, on this view each cell in Geoffroy's table stood for a complex substance.[99] It was clear that vitriolic acid combined with phlogiston, sulphur with fixed alkali, and mercury with gold. Geoffroy presumably assumed that his audience, experienced chemists as they were, would understand the relations between the compound substances that were only tacitly included in his table.

Much later, Elliot's affinity table of sixteen columns articulated the details of combinations that Geoffroy had left out.[100] His table included for each column a parallel list of the substances formed by each combination. Elliot's table thus

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[97] Kirwan would have enumerated (prior to his rather reluctant acceptance of the anti-phlogistic system) mercury calx, phlogiston, platina calx, muriatic acid, nitrous acid, and water, which in turn could have been composed of inflammable air (or phlogiston combined with matter of fire) and dephlogisticated air.

[98] Elliot 1786, 158.

[99] Klein 1995.

[100] Elliot 1782, 105

showed explicitly that vitriolic acid combined with phlogiston to form sulphur and sulphur in turn combined with fixed alcali to form hepar sulphuris. According to both Elliot's table and (albeit implicitly) Geoffroy's, hepar sulphuris could be decomposed initially into sulphur and fixed alcali, and the sulphur could then be analysed further into vitriolic acid and phlogiston. This testifies to a structured hierarchy of bodies increasing in complexity stepwise – reminiscent of Stahl's ontological hierarchy of principles. Bergman's and Fordyce's 'orders' of elements suggest a similar understanding.

Fordyce taught his students that no more than two substances were able to combine at any one time. He inserted a caveat though, that this only applied to the more 'perfect' combinations. In his view the division between chemical combination and mechanical mixture was indistinct to the point of futility:

> "No man would doubt a man being an animal or a cabbage being a vegetable; but when we consider sponges & some other substances it is difficult to say whether they are animals or vegetables. So in some combinations, there are some so nearly mechanical, that we can hardly say whether they be mechanical diffusions or chemical combinations. In such kind of chemical Combinations sometimes the Menstruum will combine with two Solvends at a time; but it does not happen in those Combinations which are very perfect. Moreover it may happen that two substances may have an equal attraction to Menstruum & neither one nor the other separate from one another."[101]

Fordyce's insistence on binary combination seems to have been a late addition to his affinity theory as a footnote was added to the fourth edition of *Elements of Agriculture* that had not been present in earlier editions:

> "It can be conceived that three particles, each of a different species of matter, may unite together, so as to form one compound Particle; but there is no given example of this in Chemistry, but when a compound contains three elements, two combine and form a Menstruum for the third."[102]

Weisberg and Wood have drawn attention to Priestley's use of the word 'confusion' for this type of combination or mixture.[103] This notion was further

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[101] Fordyce 1786a, Lecture 8th.

[102] Fordyce 1789, 8.

[103] Weisberg and Wood 2004, 701.

extended by John Anderson, controversial professor of natural philosophy at Glasgow,[104] who wrote to Cullen in 1766 enclosing a portion of a textbook dealing with elective attractions, with a request for comments and corrections. Anderson included amongst the propositions of his affinity theory:

> "If the third Substance attracts both of the compounding substances equally or, if it attracts one of them as much as that one attracts the other, then no Decomposition will follow, but a compound will be formed consisting of three Principles."[105]

Anderson thus distinguished two separate scenarios:

where a third substance C has equal affinity to combined substances A and B (i.e. CA = CB); and

where that third substance C has an equal affinity to A as A's affinity to B (CA=AB).

In either of these cases, according to Anderson, a compound of all three substances would be produced. This contrasts with Fordyce's theory which simply stated that the newly introduced substance in such a scenario would have no power to separate the already combined substances.

The idea that three substances could combine in certain circumstances formed an important component of many chemists' affinity theories. As Nicholson claimed:

> "it often happens, that bodies which have no tendency to unite are made to combine together by means of a third, which is called the Medium."[106]

Soap offered an example of this type of combination by the aid of an intermediate substance where water and oil combined through the action of the alkali. This could still be explained by Fordyce's binary theory, by dividing the combination into two stages. This implies a mechanism for combination that will be discussed further below.

Contemporaneous with Fordyce, Kirwan also suggested that in certain situations

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[104] Oxford Dictionary of National Biography 2004, s.v. "Anderson, John (1726–1796)" .

[105] Anderson 1766.

[106] Nicholson 1795, 157.

"triple or quadruple salts" might be produced. Specifically, he argued that neutral salts had a power of uniting to certain other substances "without suffering any, or but a very small, decomposition".[107] The results of this type of combination he described as 'anomalies' with regard to his system of quantified affinities (see section 3.3.3 below) which required further investigation.[108] Anderson's and Fordyce's qualitative affinity theories, proceeding from empirical evidence to hypothetical assumption, allowed them to formulate their theories in response to their observations. Kirwan on the other hand, with a carefully worked out quantitative theory *a priori*, was clearly reluctant to admit that his quantitatively determined affinities were incorrect, in spite of the fact that they conflicted with observation.

As Fordyce's theory indicated, it was not always easy to distinguish combination from other forms of mixture. Cullen offered an apparently simple formula: chemical combination, or 'proper mixture'[109] as he called it, always resulted in a homogeneous substance whose properties were different from those of its constituents. He distinguished between mechanical solution, chemical solution, and proper mixture. Mechanical solution was an impermanent diffusion which required the prior mechanical division of the solid body into particles, while chemical solution was permanent, and the solvend was divided as part of the process. In chemical solution, both the solvend and the menstruum retained their particular properties or qualities. As Cullen explained:

> "A Solution of common salt in Water is not a proper mixture; because …, it still retains its peculiar properties nor is a solution of alkali in water, for the same reason; but if it be combined with acid, … a proper mixture ensues; & this may be distinguished from Ch^{l} solution, by the loss which each of the combined Bodies suffers of its peculiar Qualities."[110]

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[107] Kirwan 1783, 43.

[108] Kirwan did promise that his next paper would in fact examine some of these anomalies, but it does not seem that he ever completed this work. See Kirwan 1783, 43 fn.

[109] This use of the term 'mixture' to signify combination was regarded by Nicholson at the end of the century as somewhat old fashioned. By this time it was used to describe only mechanical 'aggregation'. Nicholson 1795, 505.

[110] Cullen 1766, Lecture 25.

The question of whether Cullen considered affinities to be responsible for solution is a complex one. In Geoffroy's affinity table, column 16 showed the displacement of neutral salts from solution in water by spirit of wine. In comparison, Cullen's table included two columns for water, showing comparative affinities of various alkalis and spirit of wine. Cullen routinely taught that the action of affinities always resulted in new properties. Thus it would seem that only where affinities were acting did 'proper mixture' take place. Nevertheless, his table included cases where the requisite change in properties did not occur. There is no indication that he ever resolved this inconsistency; perhaps he did not consider it to be of any moment.

Fordyce also used the example of common salt dissolved in water, but he drew rather different conclusions. He divided types of union into mechanical mixture and chemical combination although, as we have seen, he does seem to have envisaged some type of continuum between the two extremes. In his scheme, a solution of salt in water counted as chemical combination. He turned Cullen's argument around, claiming that:

> "if you make a solution of Salt in water, we are apt to say that the Salt gives the Taste to the water; but it does not. Salt is as insipid as water. If you apply dry Salt to the Tongue provided the Tongue likewise be perfectly dry so that no Part of the Salt shall be dissolved in water, it has no taste. The Taste which is acquired is the Taste of the Compound & not the Taste of either of the Elements."[111]

For both Fordyce and Cullen the distinguishing factor in proper mixture or chemical combination lay in the loss of the properties of the constituents in combination. Although they agreed on the criteria, Fordyce saw solution as combination, while Cullen did not. Cullen's position, although at first sight anomalous, was in fact quite consistent with his affinity theory. As, of course, was Fordyce's. Their divergence was in their comparison of the properties of salt before and after combination, and their contradiction perhaps typifies the difficulties that must arise when taking such a subjective property as sapidity into account.

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[111] Fordyce 1786a, Lecture 5.

Nicholson was even more categorical than Fordyce, stating that solution was "the perfect union of a fluid substance with any other body."[112] He distinguished between combination and mixture, and solution was a fluid instance of the former. The latter, in contrast, "the union of bodies in a gross way"[113] involved no action of affinity.

In his mineralogical study, Kirwan specified four "principal marks of Chymical Union"[114] These were a high specific gravity (higher than the specific gravity of the heaviest ingredient), transparency (although not in all cases), crystallization and "a more difficult solubility"[115] (relative, that is, to the solubility of other earths). These rather vague marks were apparently intended to assist in ascertaining whether an earth was one of the five simple earths enumerated in Kirwan's taxonomy, or one of the innumerable possible compound earths. In practice, one has to doubt their utility as requiring some knowledge of the constituent bodies as comparators; this would presumably have made their use doubtful as naïve indicators.

Kirwan elaborated on the familiar 'loss of properties' method for distinguishing chemical union with regard to salts. It was crucial to his quantification of affinities that the precise point at which the affinities between two constituents were satisfied was marked. Thus he drew attention to the phenomenon of saturation. Nicholson enumerated two slightly different senses in which the term was used, the first solely in the context of solution, where a solid substance is added to a fluid until saturated, and the second in the context of combination where the loss of properties was crucial.[116] Cullen had earlier used these two senses to emphasise the distinction between solution and mixture:

> "the Saturations of Solutions & Mixtures are different. In the former we regard only the Solvend, when the greatest Qu^{ty} of Water dissolves a certain Proportion of Salt, until it be saturated therewith; but greater Quantities of one Salt than of another are requisite for this Purpose; & if more be added after the Water is

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[112] Nicholson 1795, 852.

[113] Ibid, 155.

[114] Kirwan 1784, 16.

[115] Ibid, 17.

[116] Nicholson 1795, 799-800.

> saturated, it falls down to the bottom in its natural form. … But in the Saturation of Mixtures several different Phenomena are observed. A just proportion must be observed between both the Menstruum & Solvend, in order to produce the tertium quid, the something whose properties differ from those of both, which characterizes the Mixture."[117]

Kirwan's account of saturation was intended to be understood only in the second sense, in the context of combination. He distinguished between saturation and neutralization; the latter accorded with Cullen's account of saturation in mixture and was the indicator of satisfied affinities:

> "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.*"[118]

Concern to clarify the different status of various kinds of combinations and mixtures seems to have become more urgent alongside the pedagogical propagation of affinity theories. This is not to say that the differences between solution and combination were not noted prior to affinity theory, but I would argue that the prevalence of the doctrine of affinity provided a context in which the distinction became more crucial. The question of whether affinities were responsible for solution was important – if they were, then in most operations there were even more affinities competing than had been thought. In particular, the role of water in any of the operations that took place in "the humid way" which exhibited what Bergman called "free attractions" (see 4.1.1 below) would need to be reassessed.[119] If, on the other hand, solution was not a result of chemical affinities, it perhaps required some explanation and theory of its own.

3.2.2 **Modification: Combination as an Agent of Change**

As the previous section has indicated, chemical combination was predominantly characterised by a change in properties. This much seems to have been agreed by a majority of British chemists, although there were discrepancies over which specific situations resulted in combination and which did not. But it remained

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[117] Cullen 1766, Lecture 26.

[118] Kirwan 1783, 39.

[119] Bergman 1970, 16.

unclear how the properties were changed. Were they modified or ‘tempered’ or was the compound body possessed of entirely new properties? For those chemists who identified substances by their observable properties, could these be similarly used to indicate their constituents?

In what is often labelled the most influential and significant chemistry textbook of the 18th century (prior to the publication of Lavoisier’s *Traité*), Macquer included amongst the ‘fundamental truths’ of his affinity theory:

> “quand les substances s’unissent ensemble, elles perdent une partie de leurs propriétés, & que les composes qui resultant de leur union participent des propriétés de ces substances qui leur servent de principes.”[120]

This position has been called ‘principlist’ (or alternatively ‘principalist’) and Mi Gyung Kim has shown its prevalence amongst French chemists throughout the 18th century.[121] For British chemists though, Macquer’s proposition was never compelling. When Macquer reiterated his claim in his 1766 *Dictionnaire de Chimie* as part of the article on *Affinité,* the English translator James Keir included a condemnatory footnote:[122]

> “The rule mentioned in the text is so far from being general, that perhaps the reverse of it may be considered as a general rule; and a change of properties, and a production of new properties, may be considered as criterions, by which compound bodies, chemically combined, may be distinguished from bodies formed merely by mixture or apposition of integrant parts; in which latter compound bodies, the properties are intermediate betwixt the properties of the several component parts, and no new properties are produced.”[123]

Keir’s footnote suggests three possible positions on the relationship between properties of constituents and resulting compound. At opposite extremes were

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[120] Macquer 1749, 22.

[121] Kim 2003.

[122] Although Keir was clearly content to translate and even amend Macquer’s affinity theory, he was equally prepared, it seems, to jettison it when necessary. His daughter, in her posthumous edition of his life and letters, proudly reported that Keir’s successful business producing alkali in large quantities relied upon a reaction that contradicted the expectations of affinity theory. See Moilliet 1768, 75-6. Also, Hudson and Pugh 1985, Moilliet and Smith 1967. Keir never publicised his process, and it is not clear whether he was able to accommodate his process within his affinity theory, or whether it prompted a rejection of the theory as a whole.

[123] Footnote(s), Keir, in Macquer 1771, 25.

the stances that (a) the properties of the constituents were directly carried forward into the compound, or (b) that they bore no relation to the properties of the compound. The medium position (c) was that in some way the opposing properties of the constituents tempered each other, and the properties of the compound were intermediate to those of the constituents. Macquer clearly held to the first, and Keir, in the case of what Cullen would have called proper mixtures, preferred the second interpretation. Keir's theory also left room for Cullen's chemical solutions, stating that under these circumstances, the last position was appropriate

Cullen's stance, so far as chemical combination was concerned, was predominantly position (b). We saw his demonstration of the separation of nitrous acid from nitre by elective attraction in chapter 2. His comparison of the properties of constituents and compound showed that their properties were unrelated. I have been unable to find a British chemist of the 18th century who explicitly adopted Macquer's position (a). Perhaps they were more dedicated to giving priority to their empirical observations than their French counterparts, most of whom seem to have accepted Macquer's propositions without question.[124] The situation is not, however, without complications. Fordyce in 1765 declared without caveat that:

> "The properties of the Compound do not depend on the Properties of the Elements."[125]

There is a distinction to be made between difference and dependence. Macquer's stance (a), it must be remembered postulated that the properties of the ingredients were carried into the compound. Fordyce's statement purportedly falls under standpoint (b), but it intimates the existence of a further position. The most familiar form of phlogiston theory, after all, hinted at a form of principalism, in that those substances that were found to be inflammable were argued to contain phlogiston. There were, however, two ways of viewing this assumption: the first the most dogmatic Macquerian type of principalism, (position (a) above). The second was a compromise position that would

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[124] Duncan 1996, 194.

[125] Fordyce 1765, 3.

probably have been acceptable to Cullen, and indeed to many British chemists. According to this position (d), the properties of compound substances could be argued to depend on their ingredients, but in a somewhat less direct sense.

Black's work on fixed air accords to some extent with both positions (c) and (d). Its presence in combination apparently 'sweetened' the causticity of alkalis,[126] although the property of 'sweetness' was not ascribed to the substance itself. Under position (c), the fixed air might be assumed to 'temper' the causticity of the caustic alkalis. Black argued that when native alkalis were heated, driving off their fixed air,

> "the remarkable acrimony which we perceive in them after this process, was not supposed to proceed from any additional matter received from the fire, but seemed to be an essential property of the pure earth, depending upon an attraction for those several substances which it then became capable of corroding or dissolving; which attraction had been insensible as long as the air adhered to the earth, but discovered itself upon the separation."[127]

Black's explanation suggests that he subscribed to position (c), that the simpler, 'pure' alkalis were naturally caustic, possessed of strong affinities, but that their combination with fixed air tempered or even smothered these affinities. The concept of saturation seems to be important in this explanation, suggesting an idea of affinities that were occupied, or used up by the combination with fixed air, and consequently revived by its release. As Black continued:

> "Commonly, when we join two bodies together, their acrimony or attraction for other substances becomes immediately either less perceivable, or entirely insensible … A neutral salt, which is composed of an acid and alkali, does not possess the acrimony of its constituent parts. … the attraction both of the acid and alkali for these several substances, seems to be suspended till they are again separated from one another."[128]

The notion that each substance's affinities are 'suspended' in combination, and that this prevents them acting would thus explain the sweetening of alkalis combined with fixed air. Causticity was often regarded as the potential for strong chemical activity, similar to acidity but opposed in nature. As with

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[126] Black 1910.

[127] Ibid, 22-23.

[128] Ibid, 23.

acidity, this very activity was the consequence of strong affinities. As a substance was saturated, and its affinities were satisfied, so its activity inevitably decreased. The identification of chemical properties with affinities was made explicit by this type of explanation, where combination modified or tempered the affinities of a substance, and with it the chemical properties.

Black's explanation is heavily biased towards the theoretical. Taking a purely phenomenological view, the addition of fixed air to a caustic substance did apparently confer the property of 'mildness'. This position clearly approximates position (d) above, and Black seems to have regarded it as a sort of shorthand for the more theoretical explanation above. He explained that:

> "Crude lime was therefore considered as a peculiar acrid earth, rendered mild by its union with fixed air"[129]

This property of 'mildness' only arose when fixed air was combined with caustic alkalis or earths. As I have indicated, when Black first postulated the existence of fixed air, its presence in combination was indicated primarily by the property it apparently conferred. This property could be transferred from substance to substance as the fixed air was transferred by virtue of its affinities.

Similarly, phlogiston was seen as conferring the property of inflammability by its presence in compound substances, but was not necessarily thought of as inflammable itself. While phlogiston continued to have "never been got by itself",[130] its own properties would be mysterious, a matter for conjecture. Where early Stahlians, among them Geoffroy,[131] had defined phlogiston as the substance released on inflammation, later phlogistonists like Fordyce were more specific. For Fordyce, lecturing only a year before the *Méthode de Nomenclature Chimique* was published in France, the interaction between phlogiston and the air was crucial to any account of combustion. It had been assumed that phlogiston was present in any substance that would deflagrate with nitre. However, neither gold nor silver would deflagrate with nitre, implying that neither contained phlogiston. But there were other signifiers to be

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[129] Ibid.

[130] Cullen 1765, MS 1920, f 72v.

[131] Kim 2003; Smeaton 1971.

considered. Fordyce explained:

> "We have reason also for believing that phlogiston is contained in gold and silver, for if we dissolve them in an acid & apply another metal to them Copper for example to a solution of silver, the Copper will unite with the acid & precipitate the silver in its metallic form without extricating any inflammable air wch copper does if dissolved in an acid alone, so that it is probable phlogiston is contain'd in silver & gold, though they are not capable of deflagrating with Nitre; so that phlogiston may be contain'd in bodies that are not inflammable."[132]

Kirwan's decision to specifically identify inflammable air with phlogiston confused chemistry.[133] Substances that were not normally regarded as inflammable were nevertheless found to contain this phlogiston. The original *raison d'etre* of phlogiston had thus been prised from its chemical identity. Where the inflammability of a substance had originally indicated that phlogiston was present, phlogiston was now shown to exist in substances that were known or believed not to be inflammable. To confuse matters further, it was highly debatable under traditional Stahlian theory whether phlogiston itself could be inflammable. When combustion took place, the phlogiston was released into the atmosphere, eventually saturating the air so that it could absorb no more, and combustion would cease. The light and heat given off during combustion was evidence of the release of phlogiston, but did not necessarily imply that the phlogiston itself was burning. Kirwan's identification of phlogiston with a substance that was itself inflammable both contradicted traditional Stahlian understanding, and gave limited support to the principlist viewpoint. Nevertheless, it was clear that even if phlogiston was inflammable, it did not confer a similar inflammability on its compounds.

In defiance of Macquer, British chemists had typically accepted by this point that the properties of compound substances were in general not the same as the properties of the ingredients. Further, where early Stahlians had claimed position (d), the new identity of phlogiston denied even this sop to principlist ambitions. On the other hand, the principlist chemist's loss was the empirical

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[132] Fordyce 1786b, Lecture 45.

[133] Although Cavendish 1766, 145 had implied such an identification, it was not until Kirwan 1782 that such an identification was made explicit. Cavendish 1784, 140 states that in fact Cavendish believed that inflammable air was "phlogisticated water".

chemist's gain. Phlogiston had gained an observable as well as a material existence to add to its series of demonstrable affinities.

In Fordyce's 1786 lectures, he set out the properties of phlogiston for his students. Rather than mentioning the taste, colour, specific gravity, or other physical marks of phlogiston, he presented a series of affinities. Thus,

> "Phlogiston decomposes almost all the neutral Salts, attracting the Acids stronger than the alk. It unites therefore with the Acid & detaches the alk. It has no Effect as far as we know on oils, or Alkali, or Sulphur. … It unites with the Calces of the Metals and gives them their Metallic Form. It seems rather tho' to be inflammable Air that unites with the Metallic Calces & gives them their metallic Form, than pure Phlogiston."[134]

Clearly reluctant to identify inflammable air directly with phlogiston, Fordyce apparently believed it was a combination of phlogiston and something else. Stahlian tradition had held phlogiston responsible for metallic form but, for Fordyce, this was no longer the role of the pure phlogiston, but rather a property of inflammable air. Nevertheless, the semi-principlist position held: the metallic form was consequential upon the combination of a particular substance with the metal calx. In the same way as the addition of heat induced fluidity in solid bodies, the addition of phlogiston or inflammable air induced metallicity and the addition of fixed air to earths conferred mildness. So, while Macquer's position (a) above was almost universally agreed to be erroneous, many British chemists seem to have tacitly adopted position (d), albeit sometimes as a phenomenological shorthand for (c), which allowed that certain specific properties of compound substances could be generalised as being dependent in some unspecified way on their constituents.

3.2.3 **Mechanism: How does Combination take place?**

Geoffroy's 1718 paper covered only what were later called simple affinities; either combinations of two substances or displacements of one substance in combination by another. He did not discuss how affinities might behave when two compound substances were mixed together, and indeed there is little evidence that this was contemplated until some time in the middle of the 18th

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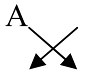
[134] Fordyce 1786a, Lecture 41.

century. Geoffroy's table implicitly posed the question of how combination affected affinities; were the affinities of blue vitriol simply a direct product of those of copper and vitriol, or was it possessed of its own unique affinities? Geoffroy's paper was contradictory. The 'law' of affinities hung upon the former assumption, but we have seen that certain of the substances included in Geoffroy's affinity table were thought to be compound. Section 1 of this chapter explored the notions of chemical elements and contextually contingent operational elements which coexisted in some affinity theories and formed part of attempts to understand complex combination. Such notions implied that affinity columns would be required for those compound substances, sulphur for example, that were able to act as elements in combining with other substances. On the other hand, when complex substances were mixed together a tidy synthesis was rare, most often resulting in a jumble of decompositions and recompositions that were almost impossible to untangle.

Cullen seems to have been the first chemist to systematise what he called 'double elective attractions', although it is unclear precisely when he formulated his ideas. Cullen applied this term to operations where two compound substances were mixed together, and the constituent substances of each separated under the influence of the competing affinities, and united instead with one of the constituent substances of the other. The earliest example of Cullen's system appears in a set of lecture notes of 1756-7.[135] He contrived diagrams which set out how the multiple affinities present in mixtures of complex substances determined the results of the mixture, an example of which is:



" {Spt Salis A B Aq Fortis
Corrosive Sublimate {
{Mercury C D Silver"[136]

This shows what happens when corrosive sublimate (itself composed of spirit of salt and mercury) is mixed with a solution of silver in aqua fortis. According to Geoffroy's table, the affinity of aqua fortis for mercury is stronger than its

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[135] Crosland cites an MS at Aberdeen University which has been dated 1756/7. See Crosland 1959 and Wightman 1955, Wightman 1956.

[136] Cullen 1757, f 40. Crosland has explained in detail Cullen's use of these diagrams, which were subject to subtle evolution during his teaching career. See Crosland 1959.

affinity for the silver with which it is initially combined. Similarly, the affinity of the spirit of salt for silver is stronger than its affinity for mercury. The substances are depicted as originally combined either side of the page, and the arrows show the affinities which are strongest in this particular combination.

Cullen asserted that there were four possible types of double elective attraction as set out in figure 3 (p. 185 below). He formulated a general rule covering such operations, (not discussed by Crosland) which is most clearly set out in a draft letter to Fordyce in 1759:

> "when on each side or in each mixt there is a substance that by itself would decompose the opposite mixt the Attraction between these substances in the opposite mixts must always be greater than the sum of the attractions on each side".[137]

In such situations, the substances would decompose and recombine afresh, and the results could be predicted by recourse to an affinity table. Cullen's third instance showed the decomposition of vitriolated tartar without the addition of heat. The combined attractions of the nitrous acid for the fixed alkali and the silver for the vitriolic acid were sufficiently powerful to overcome the affinity between the vitriolic acid and the fixed alkali, the very strongest affinity depicted in Geoffroy's table.[138] While in the other cases the results of such double combinations could be predicted, in such cases as this, they could only be ascertained by experiment.

Although the earliest set of extant lecture notes that includes Cullen's cross diagrams is dated 1757, it seems likely that he was using them some years earlier. A set of notes of Hadley's chemistry lectures dated 1758 includes similar diagrams of "double decompositions" and "double unions", although without any explanation or discussion.[139] As the diagrams do not appear in Hadley's own notes of his lectures, their presence in his student's notes is perhaps a further indication of the vitality of the 'black market' in chemistry lecture notes.

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[137] Cullen 1759a.

[138] This was one solution to the problem set by Stahl of decomposing vitriolated tartar 'in the palm of one's hand'. Further discussed in Chapter 4 below.

[139] Crellin 1969, 182-184.

The idea of complex combinations soon became both commonplace and influential. It proved useful in explaining why some combinations (or separations) could be helped along by the presence of other substances. Occasionally, however, where a double affinity was cited, this was not a double elective attraction. In 1787, William Austin sought to synthesis volatile alkali from light inflammable air and phlogisticated air.[140] The two airs simply would not combine on their own, but:

> "if phlogisticated and light inflammable air be presented to each other at the instant of their separation from solid or liquid substances, and before their particles have receded from each other, they readily combine and generate volatile alkali."[141]

Austin offered a number of examples, including the mixture of water and iron filings in the presence of phlogisticated air. In this operation the water was decomposed faster by the actions of two separate affinities, each acting on one of its elements, but only the water was decomposed.[142] Austin called this a double attraction, but it would probably not have been recognised by Cullen as a double elective attraction. This was really a case of two single affinities in action at the same time; double affinities, but not double elections. Similarly, Maehle shows how Will Falconer, another of Cullen's students, introduced a solution of salt of tartar impregnated with fixed air as a cure for urinary calculi, explaining its action as resulting from a "double attraction". Falconer's choice of term suggests that he too was aware of the fine distinction.[143]

Black adopted Cullen's diagrams, but also produced his own which used a system of circles divided in half.[144] These diagrams seem to have been used by Black from around the 1770s, although it seems they did not have the same pedagogical power of Cullen's 'dart' diagrams which developed a life of their own, to the extent of apparently being adapted by Bergman and included in his influential *Dissertation*. Josiah Wedgwood also had an idea of using coloured circular diagrams to show "Chemical affinities, compositions, decompositions

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[140] Austin 1788.

[141] Ibid, 380.

[142] Ibid, 383.

[143] Maehle 1999, 93-105.

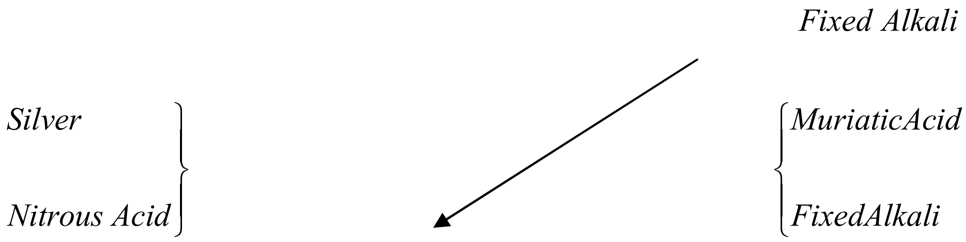
[144] Crosland 1959.

and recompositions etc. visible".[145]

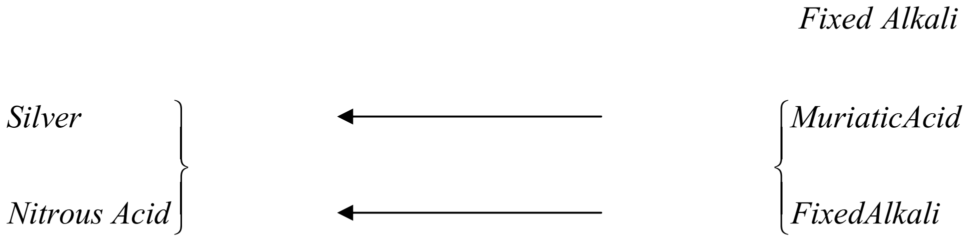
Kirwan used the distinction between single affinities and double affinities to draw conclusions about the relative affinities between substances. Knowing that a solution of silver in nitrous acid added to a mixture of fixed alkali and common salt, produced *luna cornea* (a combination of silver and muriatic acid), he argued:

> "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"[146]

A diagram (similar to Cullen's) helps to explain his reasoning:



If the fixed alkali that was mixed with the common salt (i.e. 'free') had a stronger affinity to 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 *luna cornea*, a double affinity must have been required to decompose the lunar nitre. In this case, the diagram would look like this:



Kirwan's claim that the affinity between nitrous acid and silver was greater than that between the fixed alkali and the nitrous acid contradicted many of the

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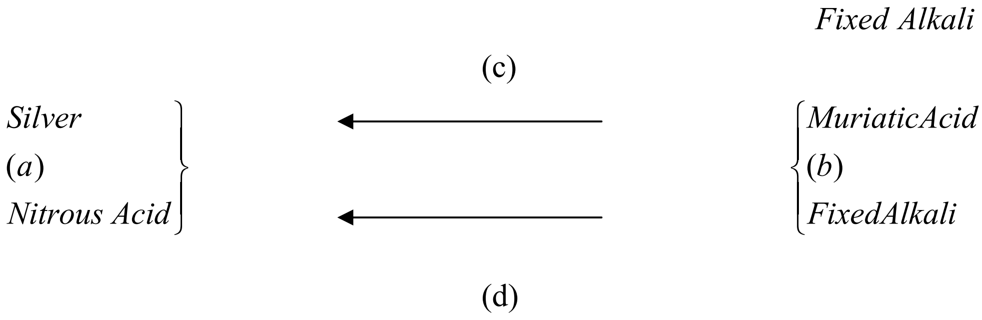
[145] Wedgwood, 1779. See Lowengard 2002.

[146] Kirwan 1783, 54.

affinity tables produced up to this point, from Geoffroy's to Bergman's. He also claimed that the muriatic acid had a greater affinity to silver than the nitrous acid had to fixed alkali. This too requires some explanation:



As we know that the double decomposition took place, (c) + (d) must be greater than (a) + (b). But we also know that (d) is less than (a). On this basis then, (c), the affinity between the muriatic 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. That this experiment was carried out to justify his laboriously quantified affinities does not detract from the importance of the mechanism itself. Cullen's system of double affinities was followed carefully, and although Kirwan did not offer the diagrammatic rationale that I have used, similar assumptions presumably underpinned his thinking. Kirwan's interpretation of his experiment 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. His use of competing double and single affinities in the same mixture of substances was innovative. This experiment was reported in a paper delivered to the Royal Society in which he expounded his new system of quantified affinities and explained a peculiar anomaly in his quantification. While his mechanism gave countenance to his quantifying system, it was a circular process and his system of quantification (discussed below), in its turn conferred authority on his mechanism.

Cullen's double elective attractions offered a way of systematising more complex affinities, together with a useful general rule. But his theory still assumed that only one substance could combine with one other and was thus not designed to deal with more complicated scenarios. Fordyce's theory took

Cullen's system and extended it to cover every possible eventuality.

Cullen's theory did not require any statement of an underlying ontology, considering such speculation, as we have seen, positively unhelpful. His students were instead taught how double elective attractions worked in terms of the macroscopic world. This, after all, was the only world that was truly relevant to the practice of chemistry. Fordyce was more content to overtly link his particulate ontology to his affinity theory. Although many historians have assumed that affinity theories always entailed a particulate ontology, it is rare that any British chemist was as unequivocal as Fordyce. Fordyce's particles were peculiarly chemical, being particles of different bodies, each possessed of its particular affinities; and as they combined they retained their chemical identity, although adopting a new "Sphere of Mechanical Action". In his 1765 *Elements of Agriculture* he provided diagrams to show how combination of particles worked (figure 4 on p. 186).[147] It seems likely that in this case, ontology was driven primarily by chemistry, and by his affinity theory in particular. This led to some interesting ideas. He opined, for example, that

> "One of the smallest integral particles of one body, may unite with only one of the smallest integral parts of another body so as to form a compound that will have an equal number of particles of each of its Elements; or one particle of one body may unite with two particles of another body, so that there would be only half the quantity of one that there was of the other."[148]

Another set of lecture notes, also dated 1786, includes a footnote:

> "We can easily conceive (therefore 'tis possible) that one of the smallest integrant parts of one body may unite with 2 of the smallest integrant Parts of another Body so as to form a compd. The Proportions of the number of ye smallest Integt Particles of one Body together yth ye smallest Integt Parts of another yt may unite, so as to form ye smallest integt Part we cannot well determine."[149]

Fordyce's theory seems to have been that when substances combined together, whatever the proportions of integrant particles that combined to form one

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[147] Fordyce 1765, Notes to plate 3rd.

[148] Fordyce 1786b, f 71.

[149] Fordyce 1786a, Note 6, lecture 5.

particle of the compound, they could only combine in this proportion in one stage. Were we in the business of whiggish precursor-spotting (which of course we are not) this might suggest an early law of definite proportions. In general, presumably for the sake of simplicity, and for the lack of any evidence to the contrary, Fordyce's lectures assumed a 1:1 proportion. He did, however, envisage more complex combinations in different stages. Thus, two elements combined together to form a new compound substance. In Fordyce's scheme the resultant compound could itself become an element in a further combination:

> "a compound may unite with one of its Elements so as to form a different Compound: as for example Mercury unites with Muriatic Acid so as to form Corrosive sublimate, & corrosive sublimate is capable of combining with the Solvend (mercury) so as to form Calomel; so that altho' Muriatic acid appears to combine in two proportions with Mercury yet it does not."[150]

His affinity theory thus included a carefully worked out mechanism of combination, envisaging specific substances as composed of particular ratios of particles in combination. Under his scheme:

> "Vitriolic acid may unite with phlogiston in one proportion so as to form volatile vitriolic acid, but if it is united with a greater quantity of phlogiston it forms sulphur."[151]

Sadly Fordyce did not expand any further on his system. It is clear that in a single stage of any chemical operation he envisaged combination only in one proportion (whatever that proportion might be). However, his compound substance could in turn behave as an element and combine with more of one of its elements to produce a further compound with the same elements, but in different proportions.

Saunders envisaged a different kind of mechanism. Referring specifically to the different substances produced by the combinations of vitriolic acid and phlogiston, Saunders's chemistry syllabus states that where ordinary combination produced 'volatile acid of sulphur', when the vitriolic acid

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[150] Fordyce 1786b, f 73.

[151] Ibid.

combined “more intimately” with phlogiston, sulphur was produced.[152] Fordyce, remember, specified that a two stage process, increasing the proportion of phlogiston in combination, produced sulphur. Saunders apparently believed that the phlogiston was combined in a different way in volatile vitriolic acid and sulphur. “More intimately” is not the same as “in greater proportion” and its seems likely that the difference in the observable physical characters of the two substances might have prompted Saunders’s choice. Volatile vitriolic acid is, unsurprisingly, volatile and spirituous, while sulphur is unquestionably solid. These differing states of aggregation of the substances produced by the union of phlogiston and vitriolic acid perhaps led to a belief that the particles of the volatile substance were more loosely held together than those in the solid.

Fordyce’s and Saunders’s affinity theories both offered explanations for the two different substances apparently produced from combinations of vitriolic acid and phlogiston. We can learn two useful things from the a comparison of their components:

Firstly, the fact that both set forth their explanations in terms of their affinity theories suggests that these had become important explanatory tools in their chemistry. As both were former students of Cullen, perhaps this should not be a surprise. As Cullen’s students were trained and taught to use affinity theory, so it became their natural reaction to explain new phenomena in terms of affinity.[153] Thus my first point indicates a similarity of attitude.

Secondly, both explanations shed light on their ideas of the physical mechanism by which affinities operated, they emphasise that a clear difference lay between their imagined mechanisms. This is an example of Cullen’s students formulating their own components to fill in the lacunae in their affinity theories. Fordyce and Saunders added their own theoretical components to flesh out the mechanisms of their affinity theories, to try to accommodate anomalies that Cullen’s teaching had not covered.

In this comparison between explanations of a single phenomenon we see clear evidence of the paradox of similarity and difference that characterised the

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[152] Saunders n.d. [1766?], 2.

[153] On the importance of training to scientific explanation, see Galison and Assmus 1989.

doctrine of affinity, as well as an illustration of the limitations of pedagogical influence.

The components set out in this section have emphasised the importance of Cullen's teaching in fleshing out Geoffroy's affinity theory to allow its application to complex combinations. Cullen's pedagogical endeavours began the attempts to clarify the doubtful parts of the doctrine of affinity. At the same time though, they have similarly emphasised that even Cullen's theory was incomplete. Sometimes such incompleteness was deliberate, a result of his pedagogical strategy, while sometimes it was an accident of history. Sometimes it may have simply been the result of poor note taking. However they arose, in the face of these lacunae Cullen's students and other affinity theorists formulated new components or amended old ones in accordance with their observations.

3.3 Concepts of Order

The previous two sections examined components of affinity theories that dealt with substances and the effects of affinity on them. The following discussion is in contrast more concerned with the affinities themselves, the powers that obtained between the objects of chemistry.

The production and use of affinity tables and indeed affinity theories as a whole, hung upon a conception of order. Initially, affinities were only susceptible to a relational ordering, as they were apparently not subject to any method of measurement. For later chemists, accurate measurement of affinities became a desideratum, prompted by their desire to predict the results of more complex combinations. Towards the end of the century, Nicholson listed what he perceived to be the most likely bases for future accurate measurement or ordering of affinities:

> "The time required to effect any change of combination, the correspondent change of temperature, of specific gravity, of consistency, fluidity, or elasticity, and the relative quantities of principles required to produce the most perfect saturation"[154]

This gives just a hint of the variety of empirical evidence that could be invoked

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[154] Nicholson 1795, 164.

to justify the ordering of affinities. As the action of affinities produced change, so any or all of these changes could be seen to signify the strength of the affinity in operation. The first sub-section examines methods and techniques of ordering affinities. In the absence of any clarification by Geoffroy, a variety of methods were adopted for ascertaining and comparing the relative strength of affinities. Such components were urgently required, both for the future expansion and extension of affinity tables, and for the correct understanding of those that had already been created.

The other two sub-sections are case studies of new components formulated by Fordyce and Kirwan that were intended to solve the most significant problem of the doctrine; the universal comparability of all affinities. Both offered different solutions, Fordyce by the deduction of new general rules governing compound affinities, and Kirwan through his experimental quantification of affinities. These case studies emphasise the continuing importance of affinity in chemistry and offer evidence of the prevailing expectation that improvements to the discipline would come from improvements to affinity theories. They also illustrate by their very disparity the methodological and conceptual differences that lay between affinity theories in spite of their similarities.

3.3.1 **Relativity: The Methodology of Order**

Geoffroy's law generalised the behaviour of different substances when mixed together. The affinity table brought all these observed relations together and ordered them. The law thus implied how the 'rapports' compared in the affinity table were ordered. If substance C be added to a compound substance AB, if the rapport of C for either A or B is greater than that between A and B then it would unite with the chosen partner, the other would be expelled from combination and either BC or AC would be formed. For each experiment, there were three possible results:

$AB + C = AC + B$

$AB + C = BC + A$

$AB + C = AB + C$

For each such experiment, two sets of triplet relations could be produced, intepreting it in two possible ways. So, for example, $AB + C = AC + B$

showed:

A	C
C	A
B	B

although it did not provide any method of ascertaining the relative affinities of A and C for B – more experiments would be required for that. Bergman's *Dissertation* included a section explaining how he determined the affinities shown in his huge table from a careful examination of displacement reactions. His system required a disconcerting number of experiments to be carried out. As he explained:

> "Let us suppose only a series of five terms, a, b, c, d, and e, to be examined with respect to A, twenty different experiments are requisite, of which each involves several others: a series of ten terms requires ninety experiments".[155]

Geoffroy had promised in his original paper[156] to publish the experiments on which his table was founded, but the promised explication never appeared, and this left the details of how the rapports had been established unknown. Six of the columns in his affinity table were triplets, which suggests that his experiments were broadly along the lines set out above. Nevertheless, most of his columns compared the affinities of more than three substances, and his methods for pulling his assumed triplets together were unknown. Lacking experimental and methodological information, the orders set out in Geoffroy's columns became the subject of disagreements. In his own notes for his earliest lectures, Cullen complained:

> "It is a pity Geoffroy has not given the Expts as I am sometimes at a loss."[157]

Cullen cited the "possible fallacy of the experiments" as a potential cause of the

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[155] Bergman 1970, 68.

[156] Geoffroy 1719, 212.

[157] Cullen n.d. [1749-56?] Although this fragment is undated, it is likely that it dated from between 1749 and 1756. It is in Cullen's own hand and appears to be a set of notes for his own use when lecturing. He was still presenting his students with Geoffroy's table, and there is no mention of double elective attractions. We know that he was presenting his students with his own affinity table by 1757. See Cullen n.d. [1757/8].

table being “erroneous and defective”.[158] The most immediate problem faced by the chemist wishing to extend his table was methodological. Which processes and operations would show affinities most clearly? For Lewis, writing in 1753, affinity was closely linked to precipitation. There were two models of precipitation reaction:

> "one, where the substance superadded unites with the menstruum, and occasions that before dissolved to be thrown down; the other, in which it unites with the dissolved body, and falls along with it to the bottom."[159]

Before the orders of precipitation could be delineated in the tables, they had first to be established. Lewis took up this challenge in his investigation of the properties of platina, where he endeavoured to determine the affinities of the new metal.[160] As part of his investigations he carefully noted the results of adding other metals to a solution of platina in aqua regia. This was not a Newtonian demonstration of successive displacements, but rather five separate tests in which zinc, iron, copper, and mercury precipitated the platina from its solution, and gold did not. Each test indicated the relative affinities of aqua regia to the two metals. The quotation above hints here at another layer of classification that usefully limited the interpretation of precipitations. Lewis’s combined bodies (AB) were divided into menstruum and ‘dissolved body’, and while the substance C might be able to take the place of either in combination, in fact very few substances could behave as both menstruum and solvend in any single context. If, for example, A was an acid, and B were an alkali, if C were another alkali, although it might be able to replace B in this combination, by its very nature it would not be able to replace A. So, in fact there would only be a single intepretative triplet to be gleaned from this operation, showing the affinities of B and C for A. Although another triplet could be offered showing the relative affinities of A and B for C, as both B and C were alkalis, this would fulfil no useful purpose.

Dossie adopted a similar taxonomic complication to the idea of displacement as

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[158] Cullen 1765, MS 1921.

[159] Lewis 1753, xxii.

[160] Lewis 1754, Lewis 1757a, Lewis 1757b.

an indication of affinity.[161] He asserted (in rather tortuous terms) that:

> "When any two bodies of a different genus are combined, and a third of the same genus with either of them is added under the circumstances proper for their commenstruation, such third will not for the most part commenstruate with them, so as to become an additional element to the compound; but if it be of a superior or higher degree of attraction than that in the compound which is of its own genus, it will commenstruate with the other of the different genus from itself, notwithstanding the state of combination in which this was before with that of its own."[162]

Dossie's affinity theory thus implied that, when forming a column of an affinity table, all the substances below the header row must be of the same genus (and a different genus from the header substance). As an example of this he recounted the familiar (although expanded) series of precipitations from spirit of nitre, listing silver, copper, iron, chalk, volatile alkaline salt and fixt alkaline salt, explaining that:

> "This is an example with regard to the alkaline bodies."[163]

The affinities of substances were, in Dossie's theory, fixed in the specific context of their classification. His further division of substances into species allowed him to assert, for example that:

> "oil of vitriol … is of the highest order of attraction in the series of the acid genus".[164]

Dossie's affinity table was therefore a list or series of the orders of affinity of acids "with respect to each other in relation to alkalies"[165] and of "alkaline salts, earths and metals with respect to each other in relation to acids".[166]

Lewis also carried out experiments showing how platina behaved in combination with various other metals. Thus he claimed that:

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[161] Dossie 1759. Some care should be taken in the use of the word 'affinity' in reference to Dossie's textbook, as he retained the more ancient usage wherein affinity denoted similarity, Thus, his taxonomy of genera and species was dependent upon the affinity of substances "or sameness of qualities".

[162] "Commenstruation" was a word coined by Dossie to signify "this power in bodies, of combining with each other in consequence of their specific attractions." Dossie 1759, 8.

[163] Dossie 1759, 18.

[164] Ibid, 27.

[165] Ibid, 275.

[166] Ibid.

> "Mercury is supposed to have a greater affinity with lead than any other metallic body, gold and silver excepted. In this experiment, it had a greater affinity for platina than lead, since it retained most of the platina, after the lead, which was in much larger proportion, had been thrown out."[167]

This particular experiment, which had mixed lead and platina together and then added the mixture to heated quicksilver accorded with the model of single affinity. In the publication of his investigations into platina as part of the *Commercicum Philosophico-Technicum*, Lewis presented its affinities in columnar form. Rather than a single long column of affinities, he offered fifteen separate sets of triplets, drawn from his 1754 experiments. Thus, for the experiment with lead and mercury, the triplet was as follows:

> "Mercury:
> Platina:
> Lead."[168]

In the case of combinations of metals (which could produce either alloys or amalgams) the menstruum/solvend distinction was meaningless, so another possible interpretation of the experiment might have formed part of a new affinity column for platina:

Platina

Mercury

Lead

Lewis never proceeded beyond his series of triplet affinity columns for platina, perhaps because the number of operations required to produce a single coherent column was more than he was prepared to carry out. His triplets were nevertheless adopted by chemists with alacrity, although no one seems to have attempted to turn them into a single column. Warltire simply added Lewis's triplets to Geoffroy's table as separate individual columns.[169] Saunders also added Lewis's triplets to the table he offered in his Syllabus.[170]

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[167] Lewis 1754, 677.

[168] Ibid, 377.

[169] Warltire 1769b.

[170] Saunders n.d. [1766?].

Lewis's affinity theory included an interesting distinction between the 'strength' of an acid and its affinities. While the order of the strength of substances seems to have corresponded with the order of affinity to a certain extent, Lewis pointed out that this was by no means a universal parallel:

> "The vitriolic is the strongest of all the acids ... The nitrous acid is next in strength to the vitriolic. ... It is remarkable of this [marine] acid, that though so much weaker than the two foregoing as to be easily expelled by either from alcaline salts and earths, it nevertheless dislodges them from metallic substances; with which it has a much greater AFFINITY than any other acid."[171]

The 'weakness' of marine acid, as shown by its relative inactivity in comparison with the other acids, was proven by its displacement from combinations, but nevertheless it still had so great an affinity with metals as to displace the 'stronger' acids from combination with them. Fordyce drew on similar phenomena to argue that readiness to unite was not a measure of affinity:

> "The strongest attractions do not always take place most readily. Nitrous Acid unites with Mercury readily; Muriatic Acid unites with it with great Difficulty yet the Muriat: Acid attracts Merc stronger than ye Nitrous Acid."[172]

This neat contrast between the fact that marine acid was only with difficulty able to dissolve metals (and thus to combine with them) and its ability to displace the other 'stronger' acids from combination with metals, was also cited towards the end of the century by Nicholson. In 1777 Wenzel, a German chemist, had attempted to assign numerical values to affinities on the assumption that the affinity between two substances was inversely proportional to the time taken for one to dissolve the other.[173] Nicholson disparaged this attempt to measure strength of affinity by speed of combination, explaining:

> "Yet from the true test of superior affinity, namely, the decomposing of compounds already formed, the attraction of the marine acid, slow as its effects are, often proves stronger than that of the nitrous, from which it separates many metallic

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[171] Lewis 1753, 10.

[172] Fordyce 1786a, Lecture 9.

[173] Wenzel 1777. See also Duncan 1996.

> basis."[174]

Displacement reactions along these lines were for many the accepted method for ascertaining relative affinities. Nevertheless, strength of affinity was often thought to be manifested in other properties that were more observable, if not more measurable.

Elliot linked the change in certain sensible properties on combination with the strength of affinity. He explained that oil of vitriol and fixed vegetable alkali had the strongest tastes of all their classes. But in combination, as vitriolated tartar, both substances lost all almost all their taste. He argued that the loss of taste was proportional to the strength of affinity between them:

> "if the substance has no attractive force remaining, it can have no taste."[175]

It does not seem likely that Elliot formed his orders of affinities on the basis of changes in taste of the constituents; his hypothesis emanated from his ontological commitments, although it was presented as an empirical generalisation. The gradual loss of taste as affinities grew stronger was related to the 'activity' of the substance, its ability to affect others by means of affinity. Similar assumptions seem to underlie Kirwan's claim, emanating from his phlogiston theory, that colour was linked to strength of affinity.[176] Both Elliot's and Kirwan's components also hint at some kind of notion of 'satisfying' affinities, of some form of saturation.

A further position is evident in a 1784 letter from Watt to De Luc, published in the *Philosophical Transactions*. This suggests that Watt's notion of affinity incorporated the much older notion of kinship between elements:

> "It appears to me very probable, that fixed air contains a greater quantity of phlogiston than phlogisticated air does, because it has a greater specific gravity, and because it has more affinity with

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[174] Nicholson 1795, 161.

[175] Elliot 1782, 107-108. Elliot's familiarity with the taste of so many substances serves to confirm the conjectures of historians that his 'insanity' towards the end of his life was most likely to have been a consequence of his close contact with dangerous substances. See, for example Manning 1993, Partington and McKie 1960.

[176] Scheele 1780.

> water."[177]

The greater affinity of fixed air with water was caused by the possession of a larger proportion of their common constituent, phlogiston. This type of assumption would have been regarded as old fashioned in Watt's time, and indeed was one of the reasons why Cullen rejected the word 'affinity' in favour of elective attraction. Watt, it should be remembered, was an instrument maker, and perhaps an auto-didact in the matter of his chemistry. Macquer had included in his affinity theory a statement that:

> "it may be laid down as a general rule that all similar substances have an Affinity with each other, and are consequently disposed to unite; as water with water, earth with earth, &c."[178]

For most British chemists, this was a proposition to be ignored, but Watt's use of similar reasoning reminds us that much of his chemistry was probably learned from such textbooks as Macquer's.

Aside from the classic model of displacement of substances, the guide to strength of affinity most commonly recruited by the chemist was the heat required to separate combined substances. In 1749 Cullen claimed in a lecture that:

> "The union of Aquafortis & Pot Ashes in Saltpetre is so strong, that if the Saltpetre is put into a crucible and kept from immediate contact with the Coals, it will bear a great force of fire without having its parts disjoined."[179]

Again Cullen refers to his most important demonstration, the combination of aqua fortis and pot ash to make saltpetre. He suggested that the affinity between these two bodies might be judged by the amount of heat which the compound would resist without decomposition. Although Cullen differentiated between the attraction which caused bodies to unite, and elective attraction, which caused them to separate, he did assert that both were instances of the same "general power". As the same force was responsible for both the combination and the adhesion, it was undoubtedly feasible that the 'force of fire' required to

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[177] Watt 1784.

[178] Macquer 1764, 12.

[179] Cullen 1749, f 17.

separate two combined bodies would be at least proportional to the force of attraction required to hold them together. Although Cullen seems to have used displacements as a starting point for his expanded affinity tables, *in extremis* he was clearly prepared to turn to more equivocal evidence offered by operations to separate by fire. This was a common enough strategem as can be seen from Elliot's *Elements* which explained, with regard to the metallic and earthy salts,

> "From most of the two latter kinds, the acids may be expelled by heat. But in those with alcaline bases this does not happen, or not so easily, by reason that their principles are held together by stronger attractions"[180]

Many British chemists similarly assumed that the more heat required for a separation, the stronger the attraction. Black suggested that fixed air combined with magnesia

> "with considerable force, since a strong fire is necessary to separate it … and the strongest is not sufficient to expel it entirely from fixed alkalis"[181]

There is an interesting difference between the concepts of affinities determined by displacement and affinities determined by fire. While the first can only afford a relative measurement, the latter is, potentially at least, a measurable property. The first asserts no more than that the affinity AB is greater or less than the affinity BC, but the second is capable of assigning a quantity (presumably of heat required) to the affinity AB, and of quantifying the difference between the affinities AB and BC.

The notion of ordering affinity tables based on how difficult it was to separate substances in combination emanated from the 'law' of affinity. It also offered the *desideratum* of quantifiable affinities based on physical measurements, rather than the relative affinities of the qualitative displacement reactions. This in turn would solve the most intractable problem of the doctrine: how to use tables to predict the results of the more elaborate combinations.

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[180] Elliot 1782, 22.

[181] Black 1910, 22.

3.3.2 **George Fordyce's "On Compound Elective Attractions"**

Nicholson in 1795 was painfully conscious of the limitations of tables of single affinities. They were useful, and encompassed a great deal of important chemical information, but

> "it must be remarked … that these results merely indicate that the powers are greater or less than each other; but how much greater or less is not determined, either absolutely or relatively."[182]

He took a gloomy view of the possibility of using affinity tables to predict complex reactions:

> "a table of simple attractions can be of no use to determine the effects of double elective attraction, unless the absolute power of the attractions be expressed by number instead of their order merely."[183]

But Nicholson was writing in 1795, with the benefit of a great deal of experience, and in the midst of a degree of theoretical disorder, if not a revolution. Some 36 years earlier the youthful Fordyce composed an optimistic attempt to place what he called 'compound affinities' on an *a priori* basis. Fordyce, presumably encouraged by Cullen's generalisation of all potential combinations of four substances down to only four different cases, attempted to discover rules that would enable him to predict the results of combinations of complex substances from an affinity table. That his attempt was unsuccessful is irrelevant; what is of interest is firstly, the fact that he made it at all, and secondly, the way in which he tried to emulate Cullen's methodology. The first emphasises once more the foundational status of affinity in chemistry, as well as the expectation, presumably derived from Cullen's teaching, that the best possible opportunities for the improvement of the discipline lay in a better understanding of affinity. The second offers a useful example of the potential for misunderstanding and misconception in the gap between pedagogue and student.

In 1759, Fordyce, having just left Edinburgh, was in London, waiting to travel to Leyden to study anatomy. Some of this time was spent drafting a paper "On

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[182] Nicholson 1795, 160.

[183] Ibid, 161.

Compound Elective Attractions" to be sent to the Royal Society. Before he presented it however, he sent a copy of it to Cullen, asking for his opinion.[184] The paper, together with the series of letters that ensued set out Fordyce's proposed system in alarming detail.[185]

Fordyce began his paper with diagrams showing double elective attractions. These were similar diagrams to those taught by Cullen (see figure 3 p. 185), although in a different order. A full transcript of the paper appears at Appendix I.

Fordyce adopted a rather cryptic notations to his diagrams, labelling the four substances 1m, 2m, 1s and 2s. These labels are a consequence of his division of all substances to be combined into menstrua and solvends. This division appears to be Fordyce's own innovation. Wherever it came from, Fordyce clung to it throughout his career, later including it in his own chemistry lectures.[186] It bore some resemblance to Dossie's genera although Fordyce's classification was, like his operationally specific elements, peculiar to each individual operation, where Dossie's emanated from an overall taxonomy of the substances. It did allow him to argue that one menstruum was 'stronger' than the other, according to their position in the affinity table, and similarly with the solvends.

To take his first instance (a mixture of nitrous and vitriolic acids with vegetable fixed alkali and silver), in Geoffroy's column for metallic substances the acid of vitriol appeared higher than nitrous acid, so it was the 'strongest' of the two. In the column for fixed alkalis, it appeared higher than nitrous acid, so again it was strongest. Thus Fordyce categorised the vitriolic acid as 1m (signifying the strongest menstruum) and the nitrous as 2m (signifying the weakest). In a similar comparison of the columns for vitriolic acid and nitrous acid, the vegetable fixt alkali appears in both as the 'strongest' solvend, so it was given the label 1s and the silver 2s. The second instance worked in a similar fashion.

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[184] Fordyce 1759-1774, September 21, 1759.

[185] Fordyce's draft paper itself has never previously been mentioned by historians, presumably having been believed to be lost. I have, however, located it, also in the archives of the Glasgow University Library, and what follows is the first detailed examination of Fordyce's system to be carried out. Fordyce 1759.

[186] See e.g. Fordyce 1786a, Fordyce 1765.

In the third and fourth instances, the notation was rather more complicated. Taking the fourth as an example: examining Geoffroy's column for muriatic acid, silver appeared above mercury, so silver on this account should be labelled 1s. But in the column for nitrous acid, mercury appears above silver, so it too had a right to the label 1s. From the metallic substances column it appeared that the muriatic acid is the strongest of the two menstrua, so it was labelled 1m and the nitrous 2m. The silver was thus the strongest solvend so far as the strongest menstruum was concerned and was labelled 1s to 1m. Likewise, the mercury, the strongest solvend to the weakest menstruum, was labelled 1s to 2m.

Both instances were, according to Fordyce, cases where "one menstruum attracts the one solvend strongest and the other menstruum the other".[187] Fordyce generalised further, comparing the affinities between the substances using his generalised labels, opposing the affinities tending to separate and recombine the substances with the affinities favouring the status quo. His rather tortuous reasoning can be seen in full in Appendix I. It led him to draw the conclusions:

> "as these powers can't be defined by numbers a priori we can never say whether the first or second instance will take place. In the third instance and likewise the fourth … the stronger powers being on one side this attraction must always take place which is confirmed by all the experiments yet made … therefore we may conclude a priori & posteriori that the 3rd & 4th instances always take place Q.E.D."[188]

Like Cullen, Fordyce claimed that two of the four generalised instances were predictable from the affinity table, while the other two, his instances 1 and 2, were not.

In the case of instance 1, the equation was balanced as follows:

$1m \rightarrow 1s + 2m \rightarrow 2s$ in favour of the status quo

against

$1m \rightarrow 2s + 2m \rightarrow 1s$ in favour of change.

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[187] Fordyce 1759 f 4.

[188] Ibid, f 5-7.

The strongest affinity added to the weakest affinity was opposed to the two middle affinities. This type of comparison was later used by Kirwan in his attempt to set forth a methodology for predicting complex affinities. Without being able to define the affinities numerically, Fordyce was unable to work out *a priori* whether the chemical change would take place. This was the same dilemma later recognised by Nicholson.

In order to solve this problem, Fordyce drew on his own experimental evidence (a grand total of nine different cases were listed) to argue that in all cases, the sum of the medium affinities was greater than the sum of the strongest and weakest affinities.[189] From this he drew a corollary:

> "The difference between the strongest menstruum attraction to the strongest solvend and the same menstruum attraction to the weakest solvend is less than the difference betwixt the weakest menstruum attraction to the strongest solvend and the same menstruum's attraction to the weakest solvend."[190]

Something very odd happens to Fordyce's pseudo-algebra during a quite excruciating set of comparisons which attempts to prove this statement.[191] He apparently believed that he had shown that the difference between affinities got larger towards the lower end of the scale. Affinity tables, as Weininger has pointed out, 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."[192]

Fordyce's paper illustrates the fact that, to achieve full predictive power, the differences between affinities, envisaged perhaps as the difference between cells in a column, needed to be known. The table needed, in effect, to develop a second dimension. Fordyce was tentatively trying to achieve this two dimensionality by finding a way of reading the table horizontally or at least in

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[189] He did specify that this was only true when dealing with acids and their solvends "for there are some cases in which acids are not the menstruums where 1m → 1s is greater alone than 1m → 2s + 2m → 1s". See Fordyce 1759 note 1.

[190] Fordyce 1759, f 9.

[191] At the stage where he 'subtracts' 1m+2s from his equation – there is no way (that I am familiar with) that this can be done. He seems to have some trouble differentiating between his affinities (shown in the form a → b) with a simple statement of relative strength, which is what his labels are. The two types of item cannot be added or subtracted as they are entirely different concepts.

[192] Weininger 1998, 6.

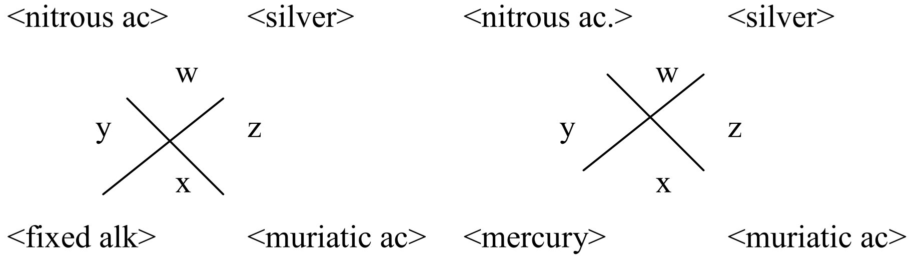
finding some cross-columnar relation between the spaces between the substances. Underlying this endeavour was a conviction (discussed more fully in the next chapter) that affinities existed in discrete quanta.

Glasgow University Library hold two drafts by Cullen of letters to Fordyce in response to his projected paper. Fordyce in turn responded twice to Cullen's objections. The arguments between the two become more repetitive and progressively more opaque. For considerations of space (and sanity) I consider here only Cullen's draft initial response to Fordyce's paper. It is clear from certain crossed out statements on one draft that Cullen found the paper frustrating. He said:

> "After studying it with all the attention possible I must tell you that ~~I do not understand it. I must say so of it as a whole and I could mention many particulars that must be unintelligible to every body~~ … it is very difficult to be understood."[193]

In response, he set out the way he dealt with the matter in his lectures. He pointed out that his four generalised cases were the same as Fordyce's (although his instances 3 and 4 were Fordyce's 1 and 2) and here outlined his general law. He then set out the latest version of his own diagrams, which no longer took the form of the dart diagrams he was using in 1757.[194] He described them instead in terms which emphasised the attractions that he supposed to exist between the different substances:

> "Let there be two Rods Intersecting one another and moveable on a common axis in the point of Intersection. At the extremities of each let there be placed substances that have an attraction for each of the substances on the extremities immediately contiguous to them & let the attractions be expressed by the letters w, x, y, z …



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[193] Cullen 1759a, f 1.

[194] Discussed in Crosland 1959.

> $y>x$ & $z>w$ by table $\qquad$ $y>x$ & $z>w$ by table
> Ergo $y+z>x+w$ $\qquad$ Ergo $y+z>x+w$"[195]

These new diagrams allowed Cullen to produce relational formulae similar to those attempted by Fordyce, but undoubtedly simpler. His intention was to distinguish predictable combinations. In the case of Fordyce's second instance (see Appendix I), Cullen argued that his general rule applied and the substances would be separated and recombined. However, as he said, "this instance is always convertible with Instance 1st which happens to be stronger".[196] Thus:

> "Instance 2 however takes place always when the general conditions of opposite attractions being given there is however no attraction between the two others as in the case of soap & the mixts that decompose it."[197]

He offered another scenario in which the second instance would take place, when the two separated substances are volatile or made volatile by heat, in which case they would escape from the mixture without combining. This still left as problematic the situation epitomised in Fordyce's Instance 1, in which the result of the balance between the affinities could not be predicted from the affinity table. Although in most cases like this, as Fordyce claimed, the decomposition did occur, the results could still only be known a posteriori, as Cullen explained:

> "This last we judge to be the case from a general experience but that it must be so a priori I cannot, nor have you I think at all ~~explained~~ demonstrated."[198]

Fordyce's attempt to prove his corollary using his algebraic reasoning also got short shrift as Cullen pointed out that the assumption of a difference between affinities of *a* did not assist him in evaluating the magnitude of *a*. Finally, he exhorted:

> "If you still think your essay worthy of the public I must beg of you to have the composition mended in every part. I would have you set out with the use & importance of the doctrine of Elective Attractions the state of it hitherto & a clear enunciation of what

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[195] Cullen 1759a, f 3.

[196] Ibid, f4.

[197] Ibid.

[198] Ibid, f 5.

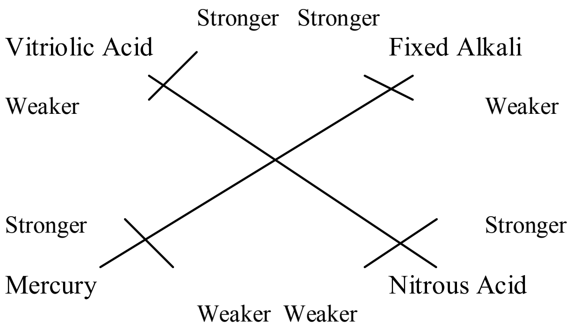
> you further propose in your Essay. … At best it is an abstract consideration that few are willing to enter into & there are at the same time so very few chemists that at best you are to expect few readers & in the present state of your Essay none at all. I would also have you support the dryness of the subject by a number of facts & if possible new ones. This is the appearance I would wish you to make & depend upon it it will be the most successfull."[199]

An interesting comparison can be made between this exchange and Fordyce's 1765 lectures in which he included a new kind of diagram that suggests that his theory now consisted of a mixture of his 1759 ideas, and Cullen's, taken from his response. He explained it as follows:

> "We then form a Diagram by drawg two Lines to intersect each other in ye middle, & write ye Menstruums at ye ends of one of ye lines, & ye solvends at ye other; we then draw shorter Lines at ye ends of these former so as to interset ym nearly at right angles. We are next to consult a Table of Elective Attractions & examine ye difft degrees of attractn wch these Elemts bear to each other; we begin for example with ye vitriolic acid & examine whether its attractn is strongest to ye fix'd alkali or to ye mercury, we find it has most to ye alkali; we therefore write stronger on one of ye cross line next ye alkali, weaker on that wch is next to Mercury. … In this manner we proceed till we have completed our Diagram"[200]

Fordyce's diagram looks like this; adapting Cullen's cross diagrams as set out in his 1759 letter, he continued to pursue his line of comparing each and every affinity that might be supposed to exist in the mixture:

"



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[199] Ibid, f 7.

[200] Fordyce 1765, f 61.

> Vitriolic Acid unites with ye mercury formg Turpeth Mineral
>
> Nitrous Acid unites with ye fixed fossil alkali formg Cubic Nitre".[201]

Cullen's earlier criticisms of Fordyce's ideas had been (probably rightly) harsh, but Fordyce did not give up on the idea of a generalised rule that would enable the prediction of all compound affinities. It is interesting to note here that although Fordyce happily appropriated Cullen's cross diagrams, amended for his own purposes, Cullen's 'law' of compound affinities made no appearance in Fordyce's teaching. Instead, he offered his own general law, that where the two weaker affinities coincide, then that axis of reaction would never occur. This conformed with the original corollary of 1759, and applied to all the four instances that Fordyce had presented there. Thus by 1765 he was able to generalise the previous four instances to just a single one, accompanied by his new rule.

For both Cullen and Fordyce, affinity theory formed a useful and important part of chemistry, and a technique for applying the table to more complex cases was an important part of their theories. It was apparent that in many cases such affinities were underdetermined by the theory. While the affinity table could be used to predict the results of certain combinations of complex substances, its one-dimensional form limited its application; and both Fordyce and Cullen appreciated the need to rectify this. One of Fordyce's 1760 letters in response to Cullen's criticism appears to be the first instance yet known of the conjectural (as Duncan calls it) allotment of numbers to signify the relative strength of affinities. The figures were selected to reflect the empirically justified relations between affinities, but as they were intended to exhibit a single set of relations there was no implication that these were the 'measure' of affinities. In his letter to Cullen he offered three sets of conjectural figures applicable to a particular combination of substances under the increasing application of heat (see 4.1.1 below). This type of conjectural quantification of affinities became more familiar towards the latter end of the century, with both Fourcroy and Guyton de

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[201] Ibid, f 60.

Morveau in France producing figures for a range of affinities.[202] These chemists assigned notional numbers to affinities on the basis of the series set out in the affinity tables. They were not, properly speaking, quantifications, but it was hoped that they would provide *a priori* indications of the results of complex operations. Crosland has suggested that Black was responsible for the first use of numbers to denote relative affinities (contradicting Wheeler and Partington, who had given the honour to Elliot).[203] But the MS that contains Black's single use of figures postdates Fordyce's usage by a full ten years and therefore it seems that the laurels are due to Fordyce.

Fordyce clearly believed that quantification of affinities was fervently to be desired, and that it would benefit the status of chemistry itself. He explained his thinking in another letter to Cullen:

> "I think it would be of use to introduce sometimes mathematical reasoning into chymistry where it will admit of it as by that means some curious propositions might be found out and it would give it more of the air of a science."[204]

However, neither he nor Cullen seem to have pursued the idea of empirically justified quantification, or even a full system of conjectural quantification. Instead, they both envisaged further inductive generalisation to elicit a law (or laws) of comparison between the affinities in the table, imposing relationships between columns, and perhaps between vertical cells within a column. Fordyce's nine experiments that he marshalled to prove his contentions were judged by Cullen to be insufficient, but not inappropriate, and Cullen suggested that such an induction (presumably on a larger scale) might eventually prove to be of use. Sadly there is no evidence to tell us what Cullen might have thought of Fordyce's 1765 rule, but as it made no appearance in Fordyce's lectures of the 1780s it was presumably proved to be as underdetermined as his original theory.

Over twenty years after the exchange of letters set out here, a new relation between experiment and affinity theory was set forth. In contrast to Fordyce's

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[202] Duncan 1996, 198-9.

[203] Crosland 1959, 83.

[204] Fordyce 1759-1774, letter 3.

purely theoretical algebra and his equally theoretical conjectural quantification of affinities this attempted to experimentally measure affinities. Although affinities were not observable, their effects were, and this endeavour hung on the identification of an observable measure that could reasonably be assumed to be proportional to the affinities acting.

3.3.3 **Quantification: Richard Kirwan's Saturation Proportions**

In his 1766 course, Cullen pointed out a contradiction between saturation proportions and affinity. During a lecture on 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:"[205]

There was no correlation between the saturation quantity of an alkali by an acid 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 sulphur) 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 *ad hoc* measurement typifies the difference between observation and experiment. While Cullen did quote some measurments, his language, mixing figures with relations, suggests that this is a phenomenon he has noticed in the course of performing other operations rather than experiments carried out specifically in order to ascertain the quantities of each acid and alkali that combine together. Such a lack of interest in quantification perhaps places Cullen very firmly in his time, indicating the limitations of his chemistry. On

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[205] Cullen 1766, Lecture 51.

the other hand of course, we must remember the pedagogical context – statements of exact quantities would probably be both inappropriate and unnecessary in a lecture environment. Cullen's discipline was primarily qualitative; the chemist manipulated the natural inclinations of bodies to produce new substances with particular properties or qualities. From this perspective, perhaps there was no clear use for measurement.

In contrast, Kirwan pursued the idea of saturation proportions as an indicator of affinity through much of his life. In 1782, he was awarded the Copley Medal by the Royal Society for his work on the potential for measurement of affinities through the comparison of saturation quantities. Three papers were published in the *Philosophical Transactions* from 1781-3 setting out his experiments and calculations,[206] and he continued to experiment and amend his figures for many years.[207] His work has been seen by some historians as an essential move towards Richter's law of reciprocal proportions, and eventually to Daltonian atomism.[208] However, the details of his theorising have so far been neglected.[209]

Although by his third paper Kirwan was using saturation proportions as measures of affinities, this was not his original intent. This had been to measure the specific gravities of two substances and compare them with the specific gravity of their compound. He found that in most cases there was a difference between the specific gravity expected of the compound substance (being the sum of the specific gravities of the ingredients) which he called the 'mathematical specific gravity', and the specific gravity of the compound as found by 'actual experiment'.[210] Often, he argued, the specific gravity of the compound "is greater without any diminution of the lighter ingredient".[211] He went on to assert that:

> "This increase of density must then arise from a closer union of

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[206] Kirwan 1781, Kirwan 1782, Kirwan 1783.

[207] Kirwan 1790.

[208] E.g. Kim 2003, Bergman 1970, Introduction and Guerlac 1968.

[209] Althugh, Scott 1979 does explore his work in some depth.

[210] Kirwan 1781, 8.

[211] Ibid, 8-9.

> 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."[212]

The idea that one of the actions of affinity was to increase the density of the compound substance was itself not particularly novel. In 1765 the same notion had formed an important part of Cullen's speculative theory of heat, fire and phlogiston.[213] Cullen had produced tables showing the combinations of substances that produced heat and cold.[214] 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).

Kirwan was later to argue that this same 'condensation', the difference between the mathematical specific gravity and the actual, experimentally determined specific gravity might provide a measure of affinity. There is no indication in Cullen's account of his hypothesis that he considered measurement of affinity as potentially viable. Even in his explanation of the generation of heat in chemical combination, Cullen appeared uninterested in attempting to measure the temperatures of the mixtures, or to quantify the amount of heat produced. We have already had cause to note this qualitative bias to Cullen's philosophy, and this confirms it further.

Kirwan's friend Elliot also gave some thought to the relationship between the density of substances, combined and uncombined, and their affinities. In his 1780 *Philosophical Observations* he argued that in a combination of oil of vitriol and water:

> "the phlogiston of the water will therefore be laid hold of by the acid, and that still retaining the water, a close and intimate connection, or strong attraction, or cohesion will take place between the particles of the acid and those of the water, so that they will be drawn into lesser dimensions."[215]

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[212] Ibid, 9.

[213] Cullen 1765, MS 1920. See Taylor 2006.

[214] Some of his observations were published in Cullen 1756.

[215] Elliot 1780, 142.

The lack of quantified justification for Elliot's assertion suggests that it was, for him, a matter of simple logic. For Kirwan too, the assumption seems to have been intuitive. He began his experiments on combination expecting that measurement of the 'condensation' of the ingredients being combined would provide a measure of the affinity between them. Kirwan believed that from Priestley's discovery of 'marine acid air' he would be able to ascertain the quantity of pure acid present in spirit of salt of any specific gravity. From this, he hoped to discover the quantity of such pure or 'real' acid contained in any of the common acids, and thus the amount combining in any salt. His hypothesis depended on an assumption 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."[216]

Kirwan's first few experiments ascertained the specific gravity of the 'pure' marine acid when combined with various quantities of water. He proceeded to work out the correct quantities and specific gravities of spirit of salt that would saturate a known amount of vegetable fixed alkali.[217] With a little further calculation he was able assign proportions to the quantities of acid, fixed alkali and water in 100 gr of the resulting salt. Assuming that this amount of alkali would be saturated by a similar quantity of 'real acid', he applied these figures to combinations of alkali with nitrous acid and vitriolic acid. After all these experiments and calculations, he concluded firstly that:

> "fixed vegetable alkalies take up an equal quantity of the three mineral acids, and probably of all pure acids … it should therefore seem, that alkalies 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

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[216] Kirwan 1781, 10.

[217] Kirwan's explanations of how he came to his figures is confusing, apparently relying on an assumption that the difference between the specific gravities of the mixture and the heavier ingredient was equivalent to the volume of that ingredient, and similarly that the difference between the specific gravities of the lighter ingredient and the mixture was equivalent to the volume of that ingredient. The accuracy of his mathematics being nevertheless irrelevant for this study, I have assumed that he, at least, knew what he was doing.

> the vegetable alkali."[218]

This conclusion is not entirely surprising when it is borne in mind that it was a fundamental 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. Nicholson later cited this tautological assumption as one of the methodological problems that he perceived in Kirwan's theory.[219]

He produced tables comparing the mathematical specific gravity of his dilute acids with their actual specific gravities. By subtracting the former from the latter, he produced a figure for 'accrued specific gravity', i.e. the increase in density of the dilute acid due to the affinity between the pure acid and the water from which he derived figures for the affinities of the acid for the water and the water for the acid. This data led him to claim that:

> "the attraction, …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."[220]

It would seem that Kirwan had some speculative notions about how affinities were operating in the dilute acids, and these influenced the way he drew up the columns for affinities in each table. He apparently believed that the affinities between acid and water were not quantitatively reciprocal, but that 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 clearly present in Kirwan's thinking at this point. He concluded the first paper by asserting:

> "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

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[218] Kirwan 1781, 33.

[219] Nicholson 1795, 163.

[220] Kirwan 1781, 33-34. Kirwan's argument here is confusing as his statement does not seem to accurately represent the data in his table for nitrous acid. Nor is it clear where the figures that he included in his tables for the affinities between the acid and the water actually came from.

> 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."[221]

Assuming that at this point Kirwan was still pursuing his idea that affinity was proportional to the accrued density of the combined substances, he seems to have been saying that as there was a maximum density, there was a maximum affinity. If a third substance be added, 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 separating combined substances by affinity, the operation rarely proceeded to completion.

Kirwan only produced tables showing the the affinities of nitrous and vitriolic acids for water using this method. He stated at the start of the first paper that he had been 'undeceived' about the relationship between accrued density and affinity.[222] It is unclear at what point he decided that his idea was erroneous; perhaps it was the results of these tables that had led to his rejection of the idea. He claimed in his third paper that he had been led "unexpectedly"[223] to his new theory of the relationship between affinities and proportions. The rhetoric of gentlemanly natural philosophy is here intruding on Kirwan's tale – he presented his new laws as a truly empirical discovery, his experiments having discredited his own assumptions about affinity. Presumably, his new discoveries should thus be regarded as correspondingly more valuable to the scientific community. In any event, he moved apparently seamlessly into his new method of quantifying affinities on the basis of the proportion of each substance in combination. This adopted the same practical methodology as he had been using throughout to ascertain the proportions of water and acid in acids of various specific gravities.

Kirwan's second paper, read to the Royal Society nearly a year and a half after

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[221] Kirwan 1781, 34.

[222] Kirwan 1781, 9.

[223] ibid, 38.

his first, followed similar methods to ascertain the combining proportions of the common alkalis with pure acids.[224] It also set out at some length Kirwan's conjectures concerning phlogiston, including his assertion that phlogiston in its free and uncombined state was in fact inflammable air.[225] As this paper was primarily concerned to rebut the anti-phlogistic claims of Lavoisier, there is no reference to affinities, and I shall therefore not discuss its contents here.

The third paper, read to the Royal Society later that same year, was concerned with the quantification of affinities through the comparison of the proportions of substances uniting in combination.[226] Following the same procedures, Kirwan calculated the quantities of the various acids that would combine with 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."[227]

Like Fordyce, Kirwan saw affinity theories as the basis for the discipline, but he admitted that problematic anomalies were coming to light. He echoed Bergman in proposing that these exceptions should be closely investigated, and that rules should be laid down that made allowances for "the action of these antagonist powers".[228] His quantified affinity theory was intended to solve these very problems.

Kirwan emphasised the difference between the law of simple affinity, operating between three substances in competition, and more complex cases like double

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[224] Kirwan 1782.

[225] Ibid, 195-6.

[226] Kirwan 1783.

[227] Ibid, 34.

[228] Ibid, 35.

decompositions. The latter, he asserted in a familiar lament, operated in many cases that seemed to be single attractions.[229] 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 then 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."[230]

As Fordyce had perceived, a method of predicting the results of complexes of competing affinities would assist with such difficulties, but such a method was as yet a desideratum. Kirwan's introduction of 'fire' into these combinations will be discussed further in the next chapter, but it is apparent from his example that one of the powers that disturbed the rules of affinity was the power of fire (and perhaps its affinities) to complicate any chemical operation. He argued that a resolution of this problem would lie with the quantification of affinities. He acknowledged the efforts of Guyton and Wenzel in this direction, but pointed out that Guyton's method could not be "generalized". Kirwan anticipated Nicholson's criticism of Wenzel's method, pointing out that his results contradicted certain "well known" affinities:

> "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."[231]

The "well known" affinities in this case were the affinities of the metals to spirit of nitre (by this time, something of an old chestnut) based on displacements. Kirwan resorted to similar tactics in his pro-phlogistic arguments, where he contrasted the affinities implied by Lavoisier's theory with the latter's affinities

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[229] Ibid, 36.

[230] Ibid.

[231] Ibid, 37.

of oxygen.[232] However, in this case Kirwan was on rather slippery ground. When Fordyce had sent his paper on compound affinities to Cullen, he included a new column for nitrous acid which Cullen incorporated into his own affinity table.[233] This column, which Fordyce claimed was based on his own experiments, assigned a greater affinity to tin than to lead, and a greater affinity to antimony than to copper.[234] It is true that Cullen was not entirely happy with the column (although he included it in his affinity table, he retained his original column and modified Fordyce's), but even in the modified version, antimony appears above copper, and the affinities of tin and lead for nitrous acid are adjudged to be equal. Fordyce's affinity table thus flatly contradicted Kirwan's statement. This discrepancy illustrates the general uncertainties that dogged the ordering of affinities, and that Kirwan's "well known" affinities were less certain than his rhetoric implied.

Kirwan's attack on Wenzel was not entirely consistent. According to his first paper, the eighteen days required for marine acid air to be absorbed by the water had led him to suspect that "the attraction between them was not very considerable."[235] Having refuted Wenzel's assumption that the time taken for dissolution reflected the strength of the affinity at work, it appears that Kirwan made similar assumptions. Inconsistency is, of course, no crime, but it does serve to demonstrate that many of the components that made up each individual's theory were the result of intuitive assumptions that explained empirical observations.

The key to Kirwan's theory were his new laws of affinity:

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

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[232] Kirwan 1968, 44.

[233] Fordyce 1759 The column is included with this MS as a neatly cut out strip of paper showing the affinities of nitrous acid.

[234] Fordyce 1759-1774 Fordyce gives no details of the experiments he carried out when formulating this column.

[235] Kirwan 1781,12.

> to each basis."[236]

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 was a man who 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:

$$1.\ \frac{\textit{Quantity acid}}{\textit{Quantity basis}} \approx \frac{1}{\textit{affinity basis to acid}}$$

$$2.\ \frac{\textit{Quantity basis}}{\textit{Quantity acid}} \approx \textit{affinity acid to basis}$$

It is clear that in fact the two affinities, base to 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. It 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 less 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 even more general terms, more acid meant less affinity, and more base, 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. Kirwan was particularly interested in ideas of differing capacities of bodies, most commonly for heat or fire, and perhaps this influenced his thoughts on the relationship of combining proportions to affinities. One of Nicholson's biting criticisms of Kirwan's theory was of his unexplained decision to embed this apparently arbitrary inequality therein:

> "the fundamental assertion, that the attraction of an acid to its

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[236] Kirwan 1783, 38.

> basis is proportionate to the quantity it demands for saturation, is so far from being founded upon any argument, that it is evidently nugatory. The attraction of an acid to its basis cannot but be the same as that of the basis to the acid; because action and re-action are equal."[237]

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.

Later in the 1783 paper, Kirwan expanded his quantitative rules, restating his conclusion drawn from his earlier investigations into specific gravity that:

> "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."[238]

As a particular quantity of an acid's affinity for a basis is satisfied by the addition of more and more basis, so its affinity for the remainder of the basis necessary for its saturation would decrease. At the same time, however "its affinity to the retained part is as its whole affinity"[239] This notion too is familiar, although in a less mathematically formal statement, from Kirwan's notes to Scheele's *Chemical Observations*.[240] 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.[241] Quantitative proportion was clearly inextricable from affinity in Kirwan's theory. A similar component appeared in William Keir's dissertation, *De Attractione Chemica* citing one of Geoffroy's experiments that showed that heat could extract only three ounces of vitriolic acid from five pounds of Alum although much more was known to be present.[242] Kirwan did not offer any information on the source of his convictions, although it seems to have been a

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[237] Nicholson 1795, 164.

[238] Kirwan 1783, 39.

[239] Ibid, 40.

[240] Scheele 1780.

[241] Ibid, 211.

[242] Duncan 1967, 152

phenomenon, as he said in his first paper, that “all chemists have observed”.

Kirwan intended his empirically determined figures for affinity to be applied to complex mixtures of substances. Like Fordyce, 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.”[243]

Cullen’s cross diagrams 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 still scope for two stage processes. Acknowledging an apparent inconsistency, where the quiescent affinities were 233 and the divellent merely 223 and yet decomposition had taken place, Kirwan argued firstly that he had been unable to replicate the anomalous experiment himself, and secondly that:

> “if it does succeed at all, the decomposition must arise from a large excess of acid in the alum, which acted upon and decomposed the common salt.”[244]

The excess of acid in the alum would act alone, by single elective affinity, to

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[243] Kirwan 1783, 40.

[244] ibid, 43.

decompose the common salt, in a process with a similar mechanism to that set out in section 3.2.3 above.

Kirwan continued his work on affinities in his *Elements of Mineralogy*.[245] Here, practical difficulties impinged on his work. As he complained,

> "we are … obliged to have recourse to the *dry* way, which is much more imperfect: for as they are all reduced by fire to a state of liquidity, they differ but little in specific gravity, and can difficultly be examined while in fusion, when cold they are all found so mixed that it is not possible to judge of their affinities by the way of preference and exclusion"[246]

He therefore proposed to assess the affinities between earths

> "as we do of that of water to salts, by the greater or the lesser quantity which one of them considered as a menstruum, can take up of another or what proportion of the one determines the fusion of another"[247]

In this way, Kirwan was able to produce a small affinity table showing the affinities between the different types of earth. In this case his table was of the traditional, qualitative type, with five columns showing the affinities of lime, magnesia, argil, silex and calx of iron. Much of his data was gleaned from the experiments of others (he quoted particularly the proportions observed by the German chemist Achard) and the resulting mixture of proportional measurements was probably insufficiently consistent to provide quantified affinities.

In spite of his receipt of the Copley Medal for his three papers, Kirwan's figures for affinities were not received with immediate acclaim. They were included in the second edition of Elliot's *Elements* and Fourcroy too apparently accepted them, including Kirwan's law in his 1800 list of ten laws of affinity.[248] Pearson also included them in his *Translation of the Table of Chemical Nomenclature*[249] alongside more conventional affinity tables. Pearson admitted that the tables

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[245] Kirwan 1784.

[246] Ibid, 12.

[247] Ibid.

[248] Elliot 1786, Duncan 1996, 195.

[249] Anon [George Pearson] 1799.

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:

> “I have long found these tables of such utility in both teaching and investigating the composition of substances, as to make me deeply lament that similar determinations had not been obtained of the chemical attractions of a much greater number of substances.”[250]

These examples were not followed by many. Fordyce was positively scathing in his lectures on the subject of Kirwan’s notion of real acid, calling it a ‘vulgar prejudice’.[251] 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.”[252]

Nicholson, as we have seen, preferred to include Guyton’s conjectural numerical affinities in his *Dictionary.*[253] He did explain Kirwan’s reasoning at length in the entry for *Attraction*, but it seems to have been included mainly in order that it might be refuted point by point. Nevertheless, he seems to have remained hopeful that with greater methodological care and experimental corroboration, future endeavours along similar lines might well 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.”[254]

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[250] Ibid, 122.

[251] Fordyce 1788, Vol 2, Lecture 36th, November 24th, 1788.

[252] Moilliet 1768, 83.

[253] Nicholson 1795.

[254] Ibid, 164.

Kirwan's notion of ascertaining combining proportions was apparently of interest to many, but his hypothesis that these figures could be used to quantify affinities was less convincing.[255] Not all his efforts were ignored, however. James Parkinson's *Chemical Pocket-Book* of 1800 adopted Kirwan's suggestion that the ordinary qualitative affinity tables might be more accurately labelled as 'tables of precipitations'. Kirwan had specifically advocated such a change in conceptualisation,[256] arguing that, particularly in the case of the affinities of acids to metals:

> "the common tables, which postpone metallic substances to all others, are in reality just; they only require a different denomination, being in fact tables of *precipitation* rather than of *affinity*, as far as they relate to metallic substances, expressing by their *order*, what metallic substances precipitate others from the different acids."[257]

Parkinson also adopted Kirwan's terminology of quiescent and divellent affinities, but he did not, however, choose to include Kirwan's quantified affinities in his work, preferring instead Pearson's lengthy "table of precipitations".[258]

3.4 Conclusion: Diversity and Affinity

This chapter has illustrated the surprising lack of consistency amongst affinity theories. But at the same time it has shown that a broad structure can be discerned amongst this diversity. Components were formulated in order to answer questions about how to utilise affinity theories. The classification of the miscellany of components into component-types illustrates that in spite of the differences between them, there was a tacit similarity of intent. Theories are, as any good historian of science knows, artificial constructs, artefacts of human ingenuity, and as such humanity is (in theory at least!) inextricable from hypothesis. The various components I have set down here were linked by the

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[255] Duncan 1996, 209-210.

[256] Kirwan's suggestion may have been partly prompted by a sight of Gellert's *Chemical Metallurgy* which was translated anonymously into English in 1776. See Gellert 1776. This included "A Table which shews how different bodies dissolve one another" (185) which looked like the conventional tables of affinity, but with the substances that were dissolved with most difficulty at the top of each column directly beneath the header substance, and those that dissolved with ease at the bottom.

[257] Kirwan 1783, 53.

[258] Parkinson 1800, 217-229.

commonality of purpose shared by their creators.

I have endeavoured also to trace within the pattern of diversity some of the links and connections of pedagogy. It is evident that while some components and even what might be called sub-components were passed whole and entire from pedagogue to student, other components were replaced by the student according to preference. Different students retained different components, and where they rejected Cullen's components, they did not always replace them with the same alternative. Cullen's students did not just unquestioningly adopt his theory wholesale; neither did they always follow his advice. Fordyce, in particular, seems to have adopted a magpie attitude, picking and choosing components and techniques from his master while at the same time ensuring that his original thoughts remain firmly embedded in his theory. The pedagogical pyramid thus reveals its own pattern of adoption and rejection.

Perhaps the most obvious point of similarity that has became evident through this chapter is the foundational status of affinity theories. They were believed to be important, and known to be useful. There was a widespread expectation that the future of chemistry would be founded on an improved understanding of affinities. This is a theme that is pursued further in the next chapter, which examines the 'supplementary' component types that were formulated to deal with a very particular set of problems, the effects of heat on affinities.

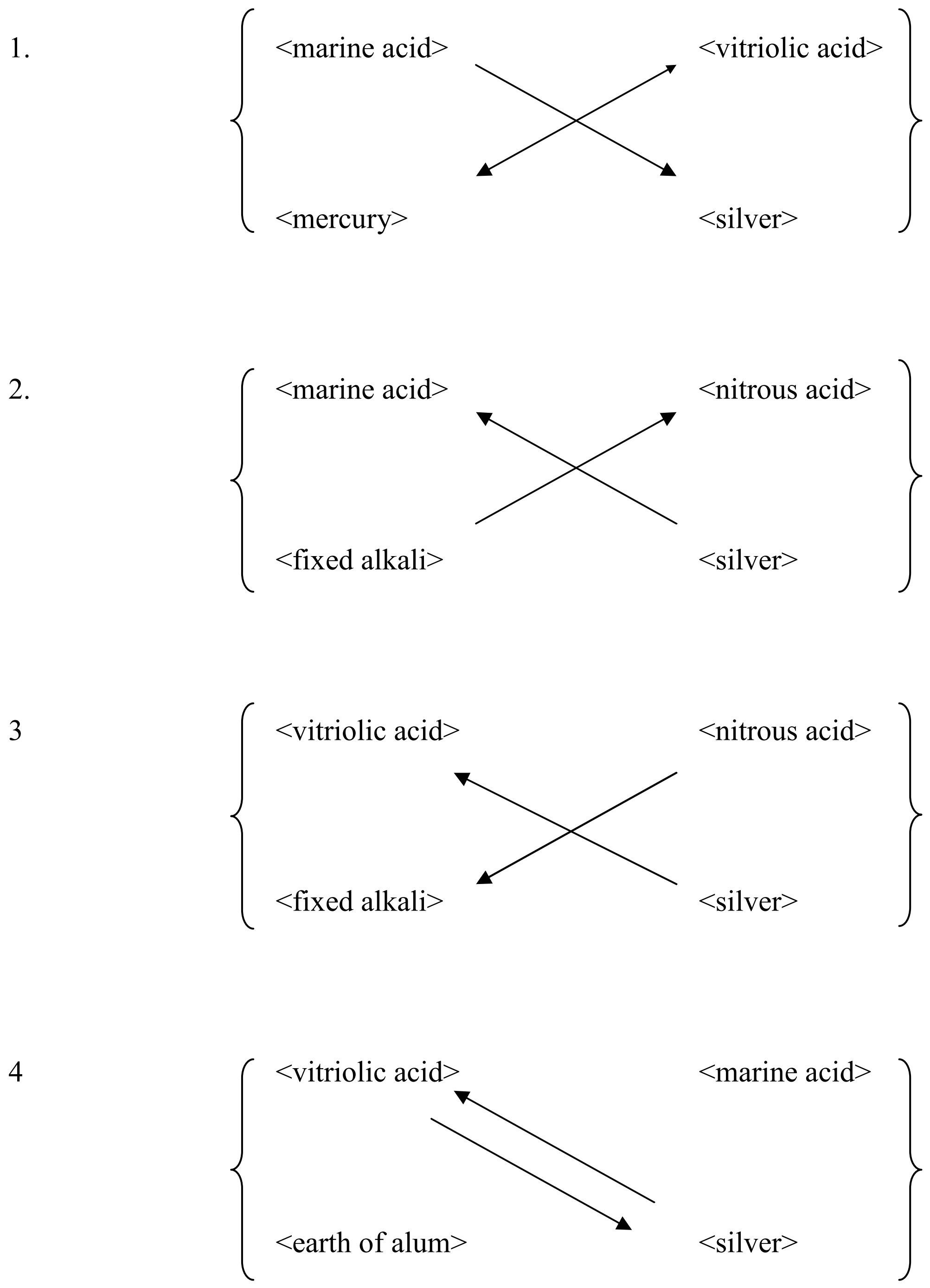

Figure 3: Diagrams of Double Elective Attraction from Cullen 1766, Lecture 23

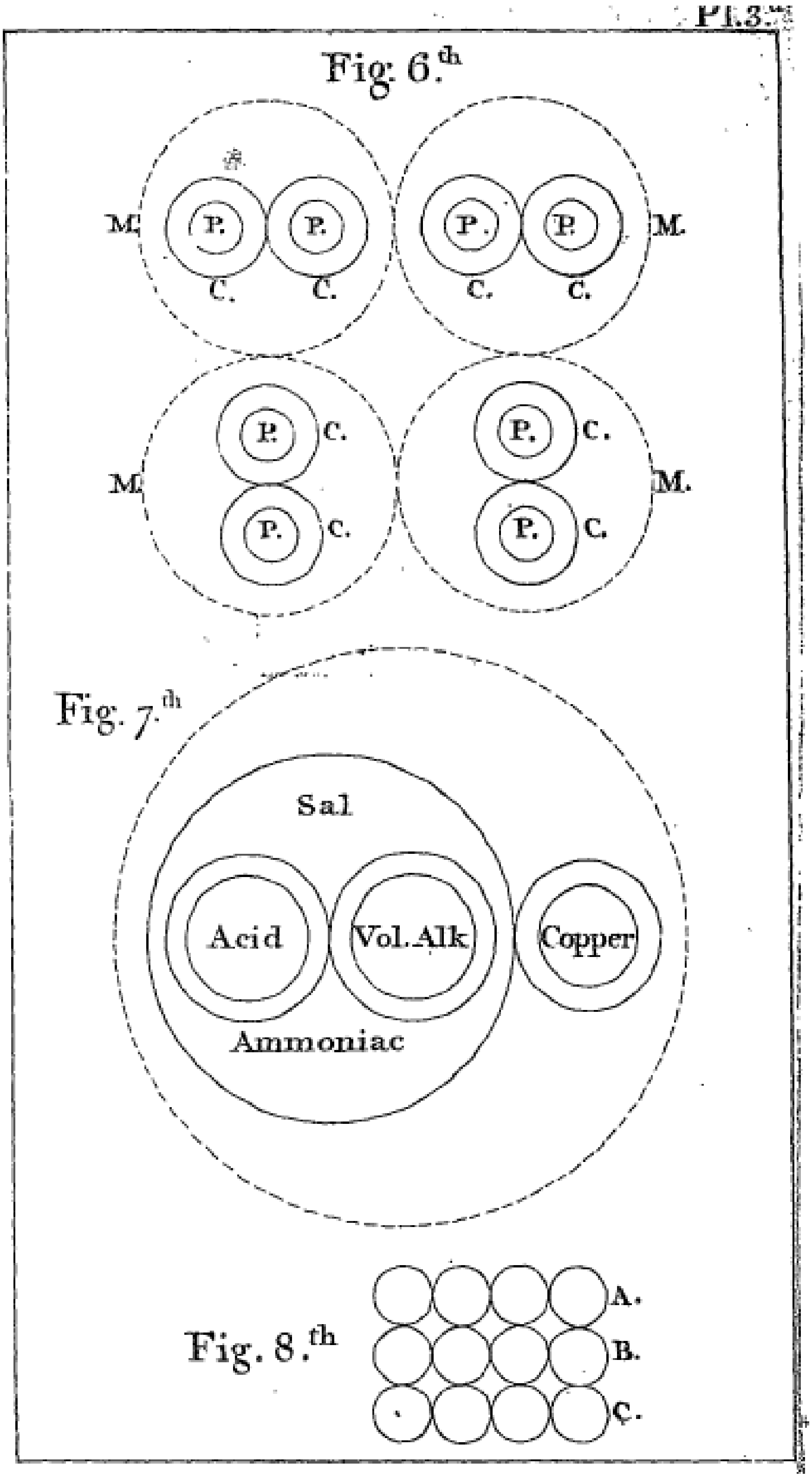

Figure 4: Diagrams of Chemical Combinations, Fordyce 1765, Plate 3rd

4. Heat: Work in Progress

This chapter explores another class of component-types. These were only gradually included in theories, prompted by a variety of factors, from a concern to preserve the utility of affinity theories, to developments that were, initially at least, external to the doctrine of affinity and, in many cases, outside chemistry itself.

Where the previous chapter drew predominantly on pedagogical sources, most of the components set out below are culled from advanced sources such as the pages of the *Philosophical Transactions*, private research papers, or polemical publications. These components, responses to new empirical and theoretical information, assumed the doctrine of affinity to be foundational to chemistry. In particular consequence of the pedagogical use to which affinity theories were put in Britain, new explanations were set forth in terms of the doctrine of affinity.[1] Affinity theories thus began to reflect and reinforce the invisible boundaries around the discipline. Examples of these 'supplementary' component-types can be found if we consider the place of heat in 18th century natural philosophy.

Geoffroy had not included any component dealing with heat in his 1718 affinity theory. Nevertheless, it had long been appreciated that heat affected chemical combination; indeed, the traditional agent of the chemist was fire. Nicknames like 'philosophers by fire', 'sooty empirics', even 'puffers',[2] emphasised their near-permanent station beside the furnace.[3] Operations like distillation and sublimation had been used for centuries to 'resolve' complex substances into their principles or constituents. In his efforts to separate and extract active 'essences' from complex natural bodies, fire, the "grand agent in the resolution of bodies",[4] was the chemist's friend.

I have already noted that Cullen's chemistry relied on the agencies of affinity

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[1] On the crucial relation between training and scientific practice, see Galison and Assmus 1989.

[2] Read 1995, 79.

[3] A recent work covering the 'history of chemistry from alchemy to the atomic age' was titled "Creations of Fire", presumably in homage to the earliest methods of chemistry. Cobb and Goldwhite 2001.

[4] Lewis 1753, 7.

and fire, but the continuing importance of heat to the practice of chemistry in the 18th century is also evident from the variety of furnaces available. Lewis listed five common types (the open fire, sand furnace, melting furnace, still, and athanor)[5] each designed to produce a particular range of temperatures. Cullen devoted four of his 1766 lectures to different types of furnace[6] and Black developed one to his own design.[7] The main method of controlling the intensity of heat was the choice of furnace employed, although this was being refined by technological improvements and theoretical advances. Lewis assimilated notes from Boerhaave's lectures in his *Course of Practical Chemistry* which converted 'degrees of fire' measured in numbers of coals of charcoal or the colour of the furnace into degrees of Fahrenheit's thermometer.[8] Nevertheless, imprecise phrases such as sand heat, red heat and melting fire, many of which were still in use at the end of the century, are indicative of just how blunt an instrument fire was.

Traditionally, heat could 'raise' substances, separating the volatile from the fixed, as in distillation and sublimation. This physical effect of expansion was well understood and was closely tied into affinity theory. I have already mentioned that Cullen insisted that for combination to take place one or both substances must be fluid, and some variant of this claim was included as a component of most affinity theories. This necessary fluidity was achieved by solution or fusion; the former often, and the latter always, requiring the application of heat. Thus recalcitrant substances that were reluctant to combine when cold could be induced to unite by the addition of heat. But by the 1760s it was becoming widely acknowledged that the presence or absence of heat also disrupted the way in which affinities acted. In chemical operations the addition (or removal) of heat seemed to change the affinities of bodies, and this in turn modified the outcome of combinations. The effects of heat on mixtures were predictable only through long experience, and subject to no known universal law. As Nicholson noted,

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[5] Ibid, 12.

[6] Cullen 1766, Lectures 40-43.

[7] One of Black's furnaces cost Joseph Priestley £3 13s 6d. Anderson 2005, 36.

[8] Lewis 1746, 5-6.

> "the variations of temperature, … tend greatly to disturb the effects of elective attraction. These causes render it difficult to point out an example of simple elective attraction, which may in strictness be reckoned as such."[9]

Although these effects were bewildering, chemists seem to have been generally sanguine about the possibilities of rationalising them. Indeed Nicholson airily predicted that:

> "doubtless, by separating their parts, it will not be difficult to explain the effect of heat upon the change produced in bodies by their elective attractions."[10]

In spite of his optimism, Nicholson seems to have eschewed any attempt to systematise the chemical effects of heat. There were, however, a few venturesome philosophers who did attempt to generalise and clarify these phenomena. They tried to preserve the status of their affinity theories as useful tools by adding new components that might enable them to predict the results of the conjunctions of heat and affinities.

Even if heat was not applied by the chemist, certain operations were apparently capable of producing perceptible heat or cold, e.g. the slaking of quicklime in water, which produced a great deal of heat.[11] Newton had speculated that this phenomenon was due to the speed with which the particles of each substance approached each other in consequence of their mutual attraction.[12] With Black's work on specific and latent heats[13] a material view of heat became predominant in natural philosophy.[14] Where such a material heat was postulated, it was often considered as a constituent of chemical combinations, capable of expulsion like any other substance. Black and Irvine's doctrines were often seen as endorsing the material ontology as heat capacities could be seen as the tendencies of heat to combine with ordinary matter. Perhaps heat's

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[9] Nicholson 1795, 158.

[10] Nicholson 1792, 75.

[11] This particular instance of the generation of heat was a common interest for chemists of both the 17th and 18th centuries, discussed and explained in various ways by Boyle, Hales, Lemery, Boerhaave amongst others. See Dyck 1967, chapters II and IV.

[12] Newton 1979, 377-378.

[13] On the history of specific and latent heats, see Scott 1981, Dyck 1967, Fox 1971, McKie and Heathcote 1935.

[14] Fox 1971, 19-20, McKie and Heathcote 1935, 137.

own affinities were responsible for its inclusion or expulsion from combinations?

The effects of heat needed to be examined, rationalised and codified, to be brought under control as affinities had been. Then chemists would be truly in control of matter. Rules were formulated attempting to codify the various roles of heat as part of chemical practice. Many of these rules were specifically designed for inclusion in affinity theories, as new ‘supplemental’ components. The unpredictable effects of heat threatened the doctrine of affinity by casting doubt on the consistency of affinities and it was thus vital for the continuation of the doctrine that these effects be brought to order.

It appears that the weight of the anomalies that were mounting between theories of heat and affinity prompted chemists to place an even greater reliance on the latter. Theories were extended on the assumption that they were a solid foundation even as the phenomena of heat eroded that very assumption. The following examples of new components and component-types illustrate how affinity theories increased in both explanatory power and heuristic scope. The addition of these components to affinity theories reflected the disciplinary development of chemistry, and the growing opinion that heat was a chemical problem.

I do not here intend to retread ground that has been thoroughly trodden by others,[15] but to pick out only those ideas on heat of particular relevance to affinity theories. I begin by unpacking some of the components that attempted to rationalise the paradoxical effects of heat in apparently promoting both combination and separation. This highlights the preservative efforts made to ensure that affinity theories were able to account for these inconvenient anomalies. The second section sets out some of the ways in which chemists tried to account for the chemical generation of heat or cold with their affinity theories. The third examines ideas that a material heat might perhaps be possessed of its own set of affinities. The latter two sections demonstrate how new ideas on heat were drawn into affinity theories to the extent that such ideas were influenced in their turn by their role in such affinity theories. In particular

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[15] See particularly Dyck 1967, Fox 1971, Gregory 1950, McKie and Heathcote 1935.

they illustrate how such ideas were dispersed from the pedagogical context to the research context, and back again, and the concomitant effects of such translations.

4.1 The Paradox of Heat: Promoting Combination and Separation

Traditional operations like distillation, evaporation, sublimation, even crystallisation, all employed heat to separate mixed or combined substances. Mechanical philosophers had conceptualised these separations as being due to their differing volatilities. Chemical and pharmaceutical works listed the orders in which different substances would 'come over' in a distillation.[16] However, it was unclear how far these 'analysed' substances had been present in the original substance.[17] By the late 17th century, doubt was setting in. Boyle had emphasised the uncertainty inherent in the use of fire as an instrument of separation,[18] and in 1753 Lewis warned:

> "… by the action of a burning heat, the principles of vegetables are not barely separated, but altered, transposed, and combined into new forms."[19]

While there was little doubt that fire often did assist in the separation of substances, it also promoted chemical union. In such operations the jumble of resolutions and combinations taking place was far from clear. Even as Lewis was writing, Cullen was teaching his students that there was a second, more precise, agent available to the chemist to assist with combination and separation. As Cullen's two agents of chemistry, affinity and heat were inextricable from the discipline, although heat, it seems, had become the junior partner of the enterprise.[20] Affinities could be manipulated in order to separate or combine substances, and were subject to rules, and to coherent generalisation. But the role of heat remained problematic. Cullen explained:

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[16] See, for example, Coxe 1674, and Boyle 1693.

[17] On the French transition from a tradition of separation by destructive distillation to solvent analysis, see Holmes 1971.

[18] Boyle 1661, 48-75.

[19] Lewis 1753, 9.

[20] As Taylor 2006 makes clear.

> "The power of Heat may probably increase the Power of Attraction between bodies that are separate & lessen the attraction between those that are combined. We may hence see how dangerous it is to draw general Principles till experiments have been made on all the different bodies in all their different Circumstances."[21]

Sometimes heat separated substances, while at others it encouraged combination; it seemed that experience was the only true guide. Cullen advocated caution, but made no attempt to generalise these powers and similarly Lewis made no attempt to rationalise the effects of heat. For some of their successors, though, it seems that this position became untenable.

As the doctrine of affinity became more firmly entrenched as the foundation of chemistry, "confessedly the basis of the science",[22] the need to protect it became pressing. New components were formulated that attempted to deal with the contradictory phenomena that threatened the doctrine. In a sense they were *ad hoc* hypotheses, added to protect the hard core of affinity theory. Assuming such an identification suggests that for many chemists, affinity had assumed the status of a research programme. Whether or not the Lakatosian model is appropriate here does not form part of my argument, but it does perhaps offer us a useful lens through which to view these 'supplementary' components.

4.1.1 **Destroyer of Affinity**

By the 18th century, it was becoming clear that it was preferable to avoid the use of heat in chemical operations where possible. Heat was not only unreliable and inconsistent in its effects, but it was difficult to manipulate with safety, and the furnace was an expensive devourer of fuel. Geoffroy's second paper on affinity had drawn attention to a question posed by Stahl to Neumann: how to separate vitriolic acid from fixed alkali (combined as vitriolated tartar) in the palm of the hand (that is, in a heat no more than that of the human body).[23] Leaving aside the doubtful wisdom of performing chemical operations using one's hand as crucible, this demonstrates the utility of affinity theories in suggesting new, safer and perhaps cheaper ways to perform operations traditionally requiring

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[21] Cullen 1765.

[22] Thomson 1830, 157.

[23] Geoffroy 1720, 28.

heat. The affinity between vitriolic acid and fixed alkali was believed to be amongst the strongest known, so no separation could be envisaged by the addition of a third substance. The application of heat appeared to be the only option. Geoffroy solved the riddle by proposing a number of different operations, all of which were based on the action of affinity.[24] The strong affinity between vitriolic acid and Geoffroy's sulphur principle (phlogiston) was sufficient, he claimed, to expel the fixed alkali from its combination without the need for heat.

Separation by fire was thus contrasted with separation by affinity. But there was no theoretical contradiction here. Affinities only had the power to separate by preferential combination. Few chemists would cavil at the assumption that heat reduced or destroyed affinities. This was an obvious conclusion to draw from the observation that fire apparently separated combined substances. Accordingly, little effort was expended on components that formalised this particular effect of heat. Fordyce's theory provides a rare exception, and it is on his efforts to quantify the destruction of affinities by heat that this section concentrates.

Fordyce's philosophical investigations included a considerable number of experiments on the effects of heat. In one paper, investigating an apparent loss of weight in heated or melted bodies, he speculated:

> "heat certainly diminishes the attractions of cohesion, chemistry, magnetism and electricity; if it should also turn out, that it also diminishes the attraction of gravitation, I should not hesitate to consider heat as the quality of diminution of attraction, which would in that case account for all its effects."[25]

Fordyce did not doubt the potential importance of his investigations, although his paper did not reach any conclusion about whether heat did in fact diminish gravitational attraction. His notion that 'diminution of attraction' might offer a 'universal mark' of heat, was not pursued any further publicly, although in 1786

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[24] Geoffroy's solutions in fact departed somewhat from the criteria of Stahl's original problem, in failing to actually separate out vitriolic acid and fixed alkali, one or both of which required to be united with another substance in consequence of the elective attraction which would divide them. The solution was also given in a letter from Stahl's son to Boulduc. See Partington, 1970, 2, 704.

[25] Fordyce 1785, 364.

he informed his students unambiguously that "heat diminishes and destroys all attractions".[26] Perhaps the most important implication of this rule was that:

> "We may separate two Substances then by destroying the attraction between them by means of Heat."[27]

Referring to the destruction of affinities by heat, Fordyce was keen to ensure that this was not confused with the use of heat to separate mechanically mixed substances:

> "It is not merely that one is volatile & the other fix'd, because they would not separate if they be chemically combined from that Cause; but the attraction must be destroy'd between them."[28]

The conjunction between heat and affinity occupied Fordyce's mind throughout his career. In his unpublished paper on compound elective attractions (see 3.3.2 above and Appendix 1) he included a short discussion on how the addition of heat might be incorporated into his algebraic scheme. To recap, Fordyce had shown (to his satisfaction, at least) that in cases where it was not immediately clear which way a double affinity would act, the weight of affinities would favour the sum of the medium affinities, rather than the sum of the strongest and the weakest. There was, however, an important caveat; this reasoning was sound in "a moderate degree of heat"[29] but:

> "on the other hand in a very great degree of heat and by distillation the other combination may often if not always happen"[30]

This was explained by the fact that the same degree of heat varied particular affinities to differing degrees. Warltire too noted this phenomenon, although he had no notion how it might be generalised.[31] Bergman's affinity table offered one solution, famously differentiating between affinities subsisting with and without the application of heat.[32] It has rarely been appreciated by historians

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[26] Fordyce 1786a, 9th Lecture.

[27] Ibid.

[28] Ibid.

[29] Fordyce 1759, f 8.

[30] Ibid.

[31] Warltire 1769b, 25.

[32] Bergman 1970.

that Bergman's division of his table into two halves was preceded by similar divisions in a number of pedagogical tables. A set of Cullen's lectures dating from 1757/8 include an affinity table divided into two halves, one "of fluids and solids" and the other "of fusion fluxed metals".[33] Black too divided his table into "Metals with respect to one another", "Relation Bodies have to water" and "elective attractions in consequence of heat", and similarly divided his diagrams of double elective attractions.[34] A syllabus produced in 1770 by Benjamin Rush, one of Black's students who had carried his influence to the United States of America,[35] shows that he too adopted this division in his own lectures. Bergman's innovation followed a clear pedagogical trend.

Bergman stated that he considered the "genuine" or "free attractions" to be those "which take place when bodies are left to themselves", that is, without heat.[36] But while his table showed that the orders of affinities changed when heat was applied, it still covered only single affinities. The old problem, the one-dimensionality of affinity tables, meant that changes could not be compared across columns, and complex mixtures remained impenetrable.

The youthful Fordyce seems to have been optimistic that his new system of compound affinities could accommodate the effects of heat. His algebraic explanation implied that he envisaged the diminution as taking place from one set level of affinity to another similarly set level. The addition of heat meant that:

> "1m → 1s be diminished to 2m → 1s as we suppose, 1m → 2s will be likewise diminished to 2m → 2s and consequently in greater proportion than 1m → 1s."[37]

As the sum of the two medium affinities (2m → 1s and 1m → 2s) was greater than that of the strongest and weakest (1m → 1s and 2m → 2s), the difference between the strongest and the medium affinities would, Fordyce assumed, be

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[33] Cullen 1757, f 98.

[34] Black 1966, 162-164. See Duncan 1996, 129.

[35] From 1799 Rush lectured in Philadelphia – "the first professor of chemistry in America." Partington 1989, 94.

[36] Bergman 1970, 16.

[37] Fordyce 1759 Note f 2.

less than that between the medium and the weakest. He assumed that heat reduced the strongest affinity to the level of the medium when cold, while the latter were reduced to the level of the weakest. Hence his claim that the heat would reduce the medium affinities far more than the strongest.

As it seems that even Cullen found this confusing, Fordyce clarified his thinking in a letter.[38] He assigned numbers to the affinities between four substances, vitriolic acid, nitrous acid, fixt alkali and calcareous earth. The affinity of the vitriolic acid to the fixt alkali he supposed to be 20, to the calcareous earth 16, the affinity of the nitrous acid to the fixt alkali was similarly 16, and from these figures he assigned a figure for the affinity between the nitrous acid and the calcareous earth of 11.[39] According to his theory, the vitriolic acid would normally unite with the calcareous earth, and the nitrous acid to the fixt alkali (the two medium affinities). However:

> “by heat the vitriolic acids attraction to the fixt Alkali be diminished to 16 then its attraction to the calcareous earth must be 11 (*because it is reduced to the state of the nitrous acid in cold*). The Nitrous acids attraction to the fixt alkali must now be likewise 11 … and the Nitrous acids attraction to the Calcareous earth less than 6, suppose 5 reduce them again and they will stand
>
> | | | |
> |---|---|---|
> | Vitriolic acids | → fixt Alkali | 11 |
> | | → Calcareous earth | 5 |
> | Nitrous acids | → fixt Alkali | 5 |
> | | → Calcareous Earth | 0”[40] |

There were only a small number of affinities available in this system (five, including the state where no affinity subsisted at all), and at each stage each one dropped to the level below. As more heat was applied, this diminution of affinities increased stepwise and would eventually lead, in “a very great heat” to a reversal of the expected result.

By Fordyce’s reasoning, affinity was discontinuous, reducing in set quanta as heat was applied. His “very great heat” corresponded to two stages of such

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[38] Fordyce 1759-1774, undated letter [1759].

[39] He assigned this figure on the basis of his rule that the medium affinities must be stronger than the sum of the strongest and the weakest. Thus this last affinity must be less than 12.

[40] Fordyce 1759-1774 [1759], f 3. (my emphasis).

reduction, upon which the affinity of the vitriolic acid for the fixt alkali would outweigh the sum of the two medium affinities, and the combinations would change accordingly. Fordyce triumphantly reported that his reasoning was proved correct by experiment. When the four substances were mixed without heat, they combined as his theory predicted. But on distilling this mixture, the fixed alkali united with the vitriolic acid. The nitrous acid and calcareous earth had no affinity when hot (as his figures had shown), so the earth was precipitated and the nitrous acid distilled off.[41]

Fordyce's quantum theory of heat and affinity thus endeavoured to explain the phenomenon of reversible affinities. He persisted with similar ideas throughout his pedagogical career although by 1788 they had been slightly amended. As before, he adopted conjectural figures for affinities of the type recently propounded by both Fourcroy and Guyton.[42] He used these figures to explain the different results of combining calx muriata (muriatic acid and lime) and mild volatile alkali (ammonia and gas) in the cold and with heat (figure 5, p. 246). In the cold, the affinities dictated that a double decomposition would produce chalk and sal ammoniac and, as before, the heat reversed the combinations. This time, the reduction in affinity due to the addition of heat was a flat rate reduction of an apparently arbitrary 12, applied to all the competing affinities alike.[43] this was presumably an *a posteriori* quantification on the basis of his observations. This time, the heat was assumed to affect all the affinities to the same degree.

Most of Fordyce's contemporaries included a component in their affinity theories stating that the application of heat destroyed or reduced affinities. Some adopted elaborate explanations, but only Fordyce, so far as I am aware, made any attempt to quantify (however vaguely) just how much effect the application of heat had. It is impossible to know whether he regarded his conjectural figures as anything more than a pedagogical tool, although the fact

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[41] Ibid, f 4.

[42] See Morveau 1786, *Affinité,* Fourcroy 1788, II, 308-324. Fourcroy's figures bear no resemblance to Fordyce's. Fordyce did adopt the same figure as Guyton for the highest affinity, but all the others differ slightly. It seems likely that he was making use of his own conjectural figures. In his 1788 lectures, a parenthetical note refers to a table, possibly of numerical affinities, but this is missing.

[43] Fordyce 1788 Lecture 46th, 8th December 1788.

that he included similar figures in his 1759 paper would suggest that he considered this method to be the most appropriate of those then available. His formulation held out the hopeful possibility that the effects of heat and temperature on affinities might be subject to a tidy mathematical formulation. Such a possibility would, however, be dependent upon the successful quantification of what Bergman had called ‘free affinities’, and perhaps this is why this line of enquiry was not pursued any further, either by Fordyce or by his students.

For most, the opposition of heat to affinities was unproblematic on its own; The expansion of bodies by heat was a physical phenomenon, and although it might overlap with certain operations involving affinities, it did not confound the theory. For practical purposes, a better understanding of the extent to which heat changed affinities was a desideratum, but this was at least partially fulfilled by Bergman’s affinity table. There was no pressing need for the formulation of components to explain how or why heat could destroy affinities. This was not, however, the case with those effects of heat that apparently encouraged or promoted combination.

4.1.2 **Increasing Affinity**

Nicholson concurred with Fordyce’s deduction that heat reduced all attractions, including chemical attractions, adding, however, that:

> “though its operation in producing the fluid state is so favourable to combination, as to render the observation of this last effect difficult.”[44]

Most chemists assumed that heat acted to promote separation, but it was also undeniable that it also acted to promote combination, as, for example, when heat was required before some metals could dissolve in acids. That heat acted in such a contradictory fashion, both destroying affinities and encouraging them, made affinity theories seem somewhat precarious.

My examination of various attempts to rationalise the ability of heat to apparently advance chemical combination highlights two main strands of thought:

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[44] Nicholson 1795, 381.

For many, as for Nicholson, the action of heat physically rarefied substances, putting them into a state more adapted for affinities to act. The perspective could be inverted - some argued that heat removed obstructions that prevented the affinities acting freely. These views were effectively two sides of the same coin; the application of heat was not seen as increasing affinities (much as Bergman had not regarded it as reducing them), but rather as allowing them to act freely.

Others believed that the application of heat changed the very mode of combination in some way. As we shall see, this view was often adopted by those who subscribed to the doctrines of specific and latent heat.

This is not a mutually exclusive classification; these strands were often intermingled. Nevertheless, they do enable me to impose some order over the rather haphazard components that endeavoured to rationalise this effect of heat. This section explores these two themes in the order mentioned above. The examples cited demonstrate surprising similarities and discrepancies entirely independent of the two main themes. They indicate how new and complex components were added to affinity theories and how new tools, such as the doctrines of specific and latent heat, were embraced and manipulated to assist in the endeavour.

Natural philosophers had long recognised that the application of heat rarefied homogeneous substances, expanding them and changing their physical form. While this phenomenon could be harnessed to separate mixed substances, the state of aggregation of substances was agreed by most chemists to be of vital importance to the operation of affinities. In this way, the two powers of heat to assist with combination and separation could be reconciled as manifestations of a single power.

Cullen was perhaps the first to explicitly introduce the state of aggregation as a factor into affinity theory. He insisted that for the affinity between two substances to act, their particles needed to be able to mingle closely, to be contiguous. This was only possible if one or both substances were in a fluid state. He offered an example that Austin (3.2.3 above) would recognise:

> "I take a small quantity of Alkali & Crude sal ammoniac each

> being first well dried these two substances are quite inodorous & remain so when mixed till by addition of a little water the salt is dissolved & emits a strong volatile fume."[45]

Fluidity, for Cullen, could be attained either at atmospheric temperature, by solution, or with the addition of heat.[46] Accordingly, Cullen classified all the chemical operations under the headers of fusion and solution. In later years, he became aware of a third state in which affinities could act, that of the 'elastic fluid'. By 1766, all of the chemical operations introduced by Cullen to his students were classed as solution, fusion or exhalation.[47] 'Solution' covered the processes of fermentation, precipitation, digestion, maceration, circulation, putrefaction and deliquescence; 'Fusion' covered congelation, eliquation, vitrification and de-calcination; and 'Exhalation' included calcination, cementation, evaporation, crystallisation and distillation.[48]

The role of heat in many chemical operations was thus to induce fluidity (or elasticity, although this was only paid lip-service by Cullen) on one or both of the substances to be combined, in order for their affinities to act. Lewis offered a particularly interesting example of this phenomenon:

> "if steel heated to whiteness, be taken out of the furnace, and applied to a roll of sulphur; the sulphur, instantly liquefying, occasions the steel to melt with it; hence the chalybs cum sulphure of the shops."[49]

In this case, the sulphur and steel, both solid, would not combine if simply placed in juxtaposition. But when the sulphur was melted by the heat of the steel (such heat being insufficient to melt the steel itself), its affinity for the steel was enabled to act, thus dissolving the steel as a solvend.

Kirwan also adopted Cullen's specification that bodies must be at their loosest degree of aggregation in order to allow affinities to act, claiming that:

> "bodies, which refuse to unite to each other chymically when

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[45] Cullen 1757, f 37. The 'strong volatile fume' was the volatile alkali that would have been released as the fixed alkali combined with the marine acid.

[46] Ibid, f 38.

[47] Cullen 1766, Lecture 24.

[48] Ibid, Lectures 24-39.

[49] Lewis 1753, 30.

> they are most minutely divided, as when both are in a vaporous or aerial state, or when both are in a liquid state, may be judged, in the first case, to have none; or in the second case, to have at best a very small affinity to each other."[50]

For Kirwan, the easiest way to encourage substances to combine was to ensure that one or both of them were in their elastic state. In contrast, Austin explained his failure to synthesise volatile alkali from inflammable and phlogisticated airs by reference to their gaseous state:

> "when they are not in an aëriform state their attraction to each other is greater, on account of the proximity of their parts; it is then superior to their attraction to fire, and therefore they combine; but when their particles have receded from each other, as in the aëriform state, their attraction to each other is so diminished by the distance of their parts, and keeps them in a separate state."[51]

From Austin's point of view then, fluidity provided the optimum conditions for combination; particles of gases did not intermingle close enough for their affinities to act. Fordyce, lecturing in 1786, added an apparently teleological dimension to Cullen's law of fluidity, asserting that:

> "Substances will not act on one another in a solid form, excepting after they have united they become fluid. Two solids that are capable of forming a fluid compound will unite. Substances will act on one another in the form of vapour."[52]

Nicholson's *Dictionary* includes a fuller explanation of this phenomenon that drew on a mechanical view of matter. In the case of two solids, the affinities could only act where the particles of the two actually came into close contact. If the freezing point of the compound produced by the two substances was lower than the temperature at which the operation was carried out, "the fluid particles being at liberty to arrange themselves according to the law of their attractions, the process will go on". [53] This unusual phenomenon thus formed an exception to Cullen's rule that fluidity was necessary in one or both bodies to be combined.

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[50] Kirwan 1783, 35.

[51] Austin 1788, 382.

[52] Fordyce 1786a.

[53] Nicholson 1795, 136.

In 1782, Kirwan explained that the reason that phlogiston (in its aerial form as inflammable air) and respirable air required heat to induce them to unite was due to the comparative densities of the two substances. The affinity between these two airs was believed to be strong, although at low heats they were capable of remaining in close conjunction for a long period of time without uniting at all. Watt (borrowing from Priestley) claimed the airs required to be "set in motion by external heat" before they would combine.[54] According to Kirwan's theory though, without heat, there was little difference between the densities of the two airs, and thus insufficient "points of contact"[55] between the two to enable the affinities to act.[56] The problem was not that two airs were too rarefied for their affinity to take effect; it was that their densities were too similar. Heat rarefied the respirable air more than it did the inflammable air, allowing the particles to mingle more intimately.[57] In combustion or other processes in which the inflammable air/phlogiston emerged from combination in what he called its 'nascent state' the two substances combined with ease. This notion, and even the phrase, 'nascent state', originated with Priestley,[58] and was adopted by Watt as well as Kirwan to describe substances that lacked their full complement of specific fire. When the phlogiston was in this state there was clearly sufficient difference between its density and that of the respirable air to enable them to combine.

The components set out above endeavoured to explain how the application of heat promoted the action of affinities by changing the physical state of bodies. Some conceptualised this effect differently, arguing that the heat removed obstructions to the affinities, enabling them to act with more ease. Fordyce's 1788 lectures postulated an 'obstruction' that acted in the same way as air resistance 'obstructed' gravitational attraction. As air resistance prevented a feather and a guinea falling to earth at the same rate, so too the hypothetical

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[54] Watt 1784, 335.

[55] Kirwan 1782, 201.

[56] Kirwan's ideas here sit a little oddly with his assertion cited above that aeriform substances that would not combine were unable to combine at all.

[57] Ibid.

[58] Priestley 1781 2, 77 and 112-128.

‘obstruction’ reduced the effects of certain affinities.[59] He explained:

> “heat removes some obstruction which prevents chemical attraction taking place but what that obstruction is we don’t know most probable it is viscidity or the attraction of cohesion.”[60]

Fordyce made a clear distinction between the ease of combination and strength of affinity. In some cases, even where there was a strong affinity between substances, external circumstances could prevent these affinities from acting. The distinction was emphasised by an experiment, although this took place without the application of heat. Fordyce showed that when muriatic acid was mixed with mercury, no combination took place, but if nitrous acid was then added, the mercury was dissolved. Once dissolved, the mercury combined with the muriatic acid. Therefore the mercury’s affinity for muriatic acid was stronger than for nitrous acid “although the nitrous acid unites more readily.”[61]

Fordyce’s affinity theory retained a consistency that many of his contemporaries’ theories lacked, with regard to heat at least. For him there was no paradox. While heat destroyed affinities, it augmented their ‘readiness to unite’. Nicholson claimed that the term ‘avidity’ was in “common use among chemists” as denoting “that modification of the attractive powers which conduces most to their speedy exertion.”[62] The word ‘avidity’ certainly crops up in some chemical works, most commonly in Bergman’s *Dissertation*, although I have found none that assign it a particular sense distinct from the action of affinity, and indeed some apparently equate the two.[63] Nevertheless, Nicholson’s attempt to coin a particular term for the ease of union suggests that the distinction was routinely drawn, with the concomitant effect of refining and clarifying notions of affinity.

A slightly different point of view is evident in the theory of William Higgins,

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[59] Fordyce 1788, Lecture 12th, October 21st 1788.

[60] Ibid.

[61] Ibid. This demonstration is perhaps derived from a comment included in Macquer’s *Dictionary* as an illustration of the distinction between ease of combination and strength of union that “Mercury … unites much more easily with nitrous acid than with the marine, but yet it adheres much more strongly to the latter than to the former.” Macquer 1771, *Affinity*, 24.

[62] Nicholson 1795, 188-189.

[63] E.g. Keir 1789, 108, Bergman 1970, 108.

for whom heat was able to compensate for weak affinities, suggesting that he viewed the effects of each as similar in kind. He speculated on the difference between the products of the combustion of light inflammable air and dephlogisticated air when ignited by electric spark as opposed to more "languid" combustion. Priestley had asserted that these two airs invariably combined to produce nitrous acid. Higgins agreed that he too had produced nitrous acid when the airs were inflamed by electric spark, but that when he burned the inflammable air slowly in an atmosphere of dephlogisticated air, no such acid was produced. He explained that:

> "the intense heat produced … by the general and instantaneous inflammation of both airs, together with that of the electric spark, promotes an union between a portion of the dephlogisticated air and the phlogistic, which is always present in the purest respirable air. Whereas the languid combustion in the former experiment is insufficient to cause such an union."[64]

In the first case intense heat was sufficient to promote a naturally rather weak affinity. In the second operation, the heat involved was far less intense, and was insufficient to compensate for this weaker affinity.

There were other situations where substances formed different compounds when combined at different temperatures that were not susceptible to a similar explanation. In these cases the heat applied had apparently resulted in a different mode of combination. Macquer claimed that there were different modes of union between mercury and sulphur:

> "If these two substances be only rubbed together in a gentle heat, or even without any heat, they will contract an union, tho' but an incomplete one. This combination takes the form of a black powder, which has procured it the name of *Aethiops Mineral*.
>
> If a more intimate and perfect union be desired, this compound must be exposed to a stronger heat; and then a red ponderous substance will be sublimed, appearing like a mass of shining needles: this is the combination desired, and is called *Cinabar*."[65]

There is a hint of Fordyce's distinction between ease of combination and

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[64] Higgins 1960, 6-7. Page numbers refer to the page numbers of the reprinted *Comparative View*, that is Higgins's original page numbering rather than to the page numbers of the "William Higgins" part of the book.

[65] Macquer 1764, 82.

strength of affinity here. But the distinction between 'incomplete' and 'perfect' modes of combination also recalls Cullen's between solution and proper mixture. Mercury, as the only metal fluid at normal temperatures, was traditionally a special case in chemistry. It might perhaps be supposed to be capable of solution as well as chemical combination ("more intimate and perfect union"), the latter requiring the application of heat.

Elliot adopted a subtly different explanation of the formation of cinnabar and aethiops mineral in a list of exceptional cases to his affinity theory. To create cinnabar, he specified, the sulphur and mercury "must be raised in vapour".[66] Elliot thus explained the binary combination by reference to the state of aggregation rather than the heat applied. Clearly the one was contingent upon the other, but the terms of Elliot's explanation imply that it was the *state* of the constituents that was the proximate cause of the two different modes of combination.

The question of how different substances could be produced from the same constituents became more urgent during the debates that exercised chemists' minds so considerably towards the end of the century. By this time there was a new explanatory tool available which many chemists seized with alacrity. During the last quarter of the century, two alternative theories of heat capacity and latent heat circulated in Britain: Black's theory, which distinguished between heat capacity (or specific heat) and the latent heat produced or absorbed on change of state, and the theory of William Irvine. Irvine, formerly one of Black's students and his eventual successor at Glasgow, postulated that change of state was correlated with a change in heat capacity. As heat was absorbed by a substance, its heat capacity increased, this process being "synchronous, … neither cause nor effect of each other".[67] Kirwan, thought to have been the author of the first table of specific heats[68] (in Magellan's *Essai sur la Nouvelle Théorie du Feu Élémentaire, et de la Chaleur des Corps*[69]) and

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[66] Elliot 1786, 120.

[67] William Irvine Jr, quoted in Dyck 1967, 186.

[68] McKie and Heathcote 1935, 43, 109.

[69] Magellan 1780.

to have first coined the term,[70] had early assimilated the notion into his affinity theory, and refined the component still further.[71]

I referred above to Kirwan's 1782 explanation of the fact that heat was required to initiate combination between inflammable and respirable airs. Kirwan's theory, as we have already seen, required each substance to have different densities so that they could mix sufficiently to combine. Either heat could be added to the system to create the necessary disparity in density or:

> "when they do unite, it is because one of them has not its whole quantity of specific fire."[72]

Cavendish's synthesis of water from inflammable and dephlogisticated air prompted Kirwan to subtly revise his thinking. In 1784 he claimed that while water was formed when these airs were exposed to a red heat, in a lesser heat they combined to form fixed air.[73] He explained that phlogiston had a stronger affinity to dephlogisticated air than to any other substance and that when they united by inflammation this was "in circumstances the most favourable to the closest and most intimate union".[74] These favourable circumstances included the fact that "both, in the act of inflammation, are rarefied to the highest degree"[75] and that

> "both give out their specific fire, the great obstacle to their union, it being by the inflammation converted into sensible heat."[76]

For Kirwan, the quantity of specific fire possessed by substances made a great difference to their combinations. Substances in possession of either more or less than their appropriate quantity of specific fire, behaved almost as if they were different substances. Whether they were free, combined or in their nascent

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[70] Scott 1981.

[71] Crawford 1779.

[72] Kirwan 1968, 43. Kirwan used the phrase 'specific heat' in two quite different senses. While in the one sense he was clearly referring to the capacity for heat of different substances as compared with each other or with water, in another, looser sense, he referred simply to all the heat that was apparently held within a substance in consequence of this capacity. The 'specific fire' he refers to in the quotation above is intended for the latter sense.

[73] Kirwan 1784, 167-8.

[74] Ibid, 167.

[75] Ibid.

[76] Ibid.

state affected their chemical combinations. In addition, when a combination would result in a reduction in bulk (usually, but not always, on change of state), their excess of specific fire was an obstacle to their union. He had cited this notion in 1782 as an additional reason why inflammable airs only united "difficultly and slowly" without heat.[77] According to his (rather confusing) thinking, to effect the 'closest and most intimate' combination as water, rarefaction of both substances and the expulsion of their specific fire was essential. Of course the rarefaction would involve the addition of more specific fire, presumably increasing the impediment, but Kirwan seems to have envisaged a two stage process. The rarefaction of the airs was necessary to increase the affinity between them sufficient to overcome the 'great obstacle' of the specific fire that they must lose in combination.

As before, he observed that fixed air was produced from respirable air and inflammable air in "common cases of combustion" when the latter was emerging from a compound state at the moment of combination. In this state it lacked the appropriate quantity of specific fire, and

> "being denser and less divided, unites less intimately with the dephlogisticated part of common air, consequently expels less of its specific fire, and therefore forms less dense compounds, *viz*. fixed and phlogisticated airs."[78]

There are two points here. Firstly, the phlogiston/inflammable air in its nascent state, unites 'less intimately' with the dephlogisticated air. Secondly, in consequence of this different mode of combination, it gives out less specific fire, and forms a less dense compound.

Kirwan's early idea that a difference was necessary between the densities of the two airs for their successful combination had apparently been discarded by 1784. By this time the marked disparity between the densities of the two substances was responsible for a 'less intimate' union. This was prompted by a crucial change in the empirical information from which he drew his argument. Where he had previously based his theory on the apparent failure of the two airs to combine when both were rarefied, Cavendish's experiments had indicated

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[77] Kirwan 1782, 201.

[78] Kirwan 1784, 167.

that they combined to produce water. By 1784, the primary difference between the combination which produced fixed air, and the combination of the same substances that produced water lay in the amount of heat present in the constituent substances, as a proportion of their heat capacities. This version of Kirwan's affinity theory thus distinguished between substances in their free, combined and *nascent* states. This was perhaps the most advanced expression of the long held belief amongst chemists that physical state of aggregation influenced the operation of chemical affinities.

This section concludes with an examination of William Higgins' attempt to accommodate the effects of heat into his complex affinity theory. Higgins's efforts, while recalling a number of the components cited above, give another example of an attempt to quantify the effects of heat. His theory was articulated in the context of his defence of the anti-phlogistic doctrine. One of Kirwan's specific objections to Lavoisier's column showing the affinities of the oxygen principle[79] was that as charcoal appeared above the 'inflammable principle' in the column, charcoal should decompose water:

> "at least in a boiling heat, which is full sufficient to communicate as much specific heat to the inflammable part of water as is necessary to its aerial form : yet water has not yet been decomposed in that manner; whereas water and iron will produce inflammable air in the temperature of the atmosphere, though iron has in his system less affinity to the oxigenous principle"[80]

Kirwan's invocation of heat here is something of a red herring; perhaps he was trying to dispose of any objection that heat distorted affinities from the outset. But Higgins responded by introducing a further influencing factor. He argued that although charcoal might appear to have little "aggregate attraction" (defined as "that power which solid or less condensed bodies have of counteracting chemical union"),[81] being easily broken up, this was due to its hollow texture. Once pulverised into powder, the particles of charcoal cohered with a greater force than might be expected, but in addition to this

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[79] Lavoisier 1785, 535.

[80] Kirwan 1968, 44.

[81] Higgins 1960, 16.

> "I think the ultimate particles of charcoal are surrounded with some repelling fluid, which defends them from the action of air and water; and the same may be said with respect to spirit of wine, ether, and oil: for they all have greater affinity to dephlogisticated air than phosphorus, which combines with it in the common temperature of the atmosphere."[82]

The mysterious fluid introduced in this rather *ad hoc* component of Higgins' theory obstructed the action of affinity, recalling once more the distinction between affinity and Nicholson's 'avidity'. He offered further examples:

> "Pure calcareous earth, perfectly dried, will not attract marine acid air; and yet water, to which it has less affinity, will condense it, and enable it to unite to this. Light inflammable air and dephlogisticated air will not combine in their ordinary state but by the help of the fire, either the electric, or a common spark; yet they both will unite very readily when one or both are partially condensed."[83]

Higgins's point that partial 'condensation' through combination was often required for affinities to act to their full capacity sounds similar to the nascent state of his phlogistonist antagonist. He also suggested that heat capacity might be involved, arguing that the attraction of fire to matter counteracted the affinities between other substances (thus, like Fordyce, explaining the power of heat to separate), but also speculated that some other power also interfered.

Higgins's theory provided for a power that counteracted affinity, in the "aggregate attraction" within solid and (presumably) liquid bodies. Higgins was convinced that this power acted against affinity so that affinities of solid substances were restricted or tempered. Where Cullen's theory cited the inability of particles to approach sufficiently closely as the cause of the restriction, Higgins postulated an oppositional power. Like Kirwan's quiescent affinities, the aggregate attraction might be seen as the affinity of a substance for itself.

> "let us suppose charcoal to attract dephlogisticated air with the force of ten, and contrary powers, which I shall call the aggregate attraction, to resist this with the force of eleven. Let us likewise suppose iron to attract dephlogisticated air with the force of

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[82] Ibid, 12.

[83] Ibid.

> seven, and its aggregate attraction to counteract this with the force of six and seven-eights. It would require greater heat to unite the two former than the two latter, though they have by far the greater affinity to one another. But when once the scale is cast in favour of the former, the rapidity of their union ought to be greater than that of the latter; which is really the case."[84]

Thus heat promoted affinity simply by overcoming the aggregate attraction. Higgins' equations setting off the relative strengths of attractions against each other recall Fordyce's explanations of how the application of heat could reverse a complex reaction. While in Fordyce's system the heat was subtracted from the affinities, Higgins only subtracted it from the aggregate attractions, thus retaining a distinction between the effects of heat and affinity. Unusually, he saw the strength of the affinity between charcoal and dephlogisticated air as evidenced by the speed with which the combination took place once the obstacle to their union had been overcome. Higgins did not specify that the fire had to actually change the physical state of the substances to fully overcome the aggregation attraction. It does not seem that this was his intention, as he made no attempt to link it to the idea of latent heat. He did briefly speculate that 'heat capacity' might be connected with the phenomena, but did not pursue this notion any further.

Most of the problems highlighted by Higgins were the result of a certain confusion about which phenomena were most appropriately taken to exhibit the true affinities of substances. Anomalies arose out of attempts to factor in both heat and state of aggregation. The amount of heat required to institute a process was sometimes taken to indicate affinity, but this was not a reliable indicator of the order of affinities. Higgins believed that the correct indications of affinity should be clarified, distinguishing ease of combination from affinity:

> "the attractive forces of bodies are not to be estimated by the facility of compounding, but rather by the difficulty of decompounding them again."[85]

Unfortunately, his own theory was far from consistent in this 'ordering' component, as can be seen from his apparent belief that speed of combination

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[84] Ibid, 16-17.

[85] Ibid, 16.

was also indicative of strength of affinity.

This comparison of a range of efforts to account for the apparently paradoxical effects of heat has demonstrated once more the variety to be found amongst the components of affinity theories. Nevertheless, certain features did recur in somewhat disparate contexts. For example, both Fordyce and Higgins attempted to quantify the effects of heat on affinities, although each adopted a rather different stance. It is also clear that most chemists tried to protect their theories by demarcating the physical effects of heat from the chemical effects of affinity. This last is perhaps one facet of a general trend that sought to refine the understanding of affinity beyond the 'tendency to combine' of Geoffroy. As is common in such endeavours to define the unknown, it seems to have progressed primarily along negative lines, by setting out those phenomena that were not admitted to be evidence of the 'free affinities'.

What becomes strikingly clear from the components cited above is the rather precarious nature of a large proportion of them. This is nowhere more apparent than in Kirwan's rapid reformulation of his ideas of how the physical state of matter affected combination when confronted by Cavendish's synthesis of water. Many of the new components were similarly formulated to deal specifically with new experimental observations, and sometimes these were built on shaky foundations. Most chemists were reluctant to allow doubt to be cast on their affinity theories. This would certainly seem to be a case of Lakatosian theory preservation in action. Much of the energy expended by the various theorists, although resulting in quite varied components, was expended in a common cause, the preservation of the doctrine of affinity against falsification by the anomalies that beset it.

4.2 Chemical Generation of Heat and Cold

Where the previous section explored components that were formulated for the most part in a spirit of theory preservation, this section demonstrates the encroachment of affinity theory into the traditionally physical domain of heat. These components testify to a growing confidence in the doctrine of affinity, a belief in its supremacy in the hierarchy of causality.

The phenomena of chemically generated heat had been familiar for centuries.

Mixtures of acids and alkalis generated heat, as did quick-lime and water. Attempts to comprehend how heat (and cold) could be generated in this way occasioned perhaps the most intimate and complex conjunction of affinity theories with heat theories.

The question of whether heat consisted of matter or motion remained open throughout the 18th century, and although the material view was in the ascendant by the end of the century, few were inclined to commit themselves wholeheartedly.[86] Dyck provides a useful classification of heat theories into the dynamic, the material and the "dynamic-fire particle".[87] All three kinds of ontology were invoked to explain the chemical generation of heat. I have adopted Dyck's classification as an organising principle for this section. I first set out components that drew on a vibratory theory of heat, then those that assumed an material heat whose oscillations caused the sensation of heat (Dyck's "dynamic fire particle") and finally the components that relied on a material view of heat. Although the dynamic theories tend to be more prevalent during the first half of the century, while the material view dominated towards the end, it will be noted that this section does not describe a neat chronological trend. The advent of the doctrines of latent and specific heat in the second half of the century were taken by many chemists (but not all) to confirm the material nature of heat. As neither Black nor Irvine published their ideas, they were initially disseminated in a pedagogical context. For the majority of those chemists who adopted a material view of heat the Irvinist view of specific heat, as disseminated by Crawford, provided a lead. This section highlights the difficulties inherent in translation from pedagogical to research contexts and back again.

4.2.1 **Dynamic Heat**

The production of sensible heat when certain substances were mixed together had been explained in terms of vibrations consequent upon chemical attractions long before Geoffroy's paper conferred law-like status on affinities. Mechanical philosophers had explained the production of heat in chemical

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[86] E.g. Nicholson 1795, 381.

[87] Dyck 1967, 8.

operations by referring to mysterious powers that obtained between the particles of different substances. When substances were mixed together, they were assumed to be mechanically attacking each other, tearing into each other with great force, in some cases modifying their particulate figures, and setting up the vibration that was sensible heat.[88] This was a mechanical understanding of heat, applied in the context of a largely mechanical understanding of matter. The cause of the conflict was the postulated attraction (or sometimes repulsion) between two qualitatively different substances. Something similar to this theory was adopted by Isaac Milner, Jacksonian Professor of Natural Philosophy at Cambridge University. Milner carefully considered the three prevailing versions of heat (which conform neatly to Dyck's classification), eventually settling upon a dynamic theory:

> " Heat consists in a vibrating motion of the parts of bodies, and Fire is a body heated so hot as to emit light copiously."[89]

For Milner, an "intestine motion" amongst the particles of substances was responsible for the sensation of heat.[90] He also attempted to use his dynamic theory to explain Black's doctrine of latent heat as a consequence of the rearrangements of the particles of bodies on change of state.

Black himself, famous for propounding the doctrines of specific and latent heat that so many regarded as evidence for a material heat[91] might perhaps be expected to have adopted the material view himself. In fact, he seems to have been extremely cautious when it came to his pedagogy. In 1767 he taught his students:

> "The heat that is produced in Slacking lime may be owing to the sudden transition of the water from a fluid to a Solid State; It may happen like many oy^{r} Mixtures, from the Bodys uniting so greedily together."[92]

Black offered two possible explanations of the phenomenon; the first, referring

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[88] Ibid, 13-39.

[89] Milner 1784, f 23v-24r. See also Coleby 1954, 244-245.

[90] Ibid, f 27r.

[91] Encyclopaedia Britannica 1778-1780, 3, *Heat,* 3559.

[92] Black 1966, 64.

to the transition from fluid to solid, suggested physical contraction of matter, and perhaps implied the release of latent heat. The alternative suggestion evoked a similar image to Milner's of substances uniting ferociously together, with the heat presumably produced by something similar to friction. Black gave no indication of which explanation he preferred.

Although Black did not publish his work on heat, the anonymous *Enquiry into the General Effects of Heat and Mixture,*[93] believed to be taken from his chemistry lectures, did include his ideas to some extent. The first part, constituting the majority of the work, dealt with the changes effected by heat on matter in general. The new doctrines were only brought to bear on the physical effects of heat while inflammability was referred to a fairly traditional version of phlogiston theory. The second part, covering the "Theory of Mixture" referred only briefly to the heat produced as a result of mixture. Aside from an early distinction between the "quantity of heat"[94] present in a particular substance and the intensity of heat measured by the thermometer, in this part of the *Enquiry* heat was described in dynamic terms drawn directly from Newton. So far as pedagogy was concerned, it does not seem that Black considered his new concepts as being explicitly relevant for chemistry.

The theories of specific and latent heat did not, then, entail a material ontology of heat. For the most part, those who held to a dynamic view found Irvine's theory to be more congenial. Milner scolded those chemists (like Cavendish) who spoke of latent heat, but refused to commit themselves to a material view:

> "several speak in this way of the existence of heat in a latent state, & of its emersion again into a sensible state, who yet do not chuse to affirm openly that heat is Matter. … they intrench themselves in cautious expressions.
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> … In a word, heat must either be matter, or it must depend upon a certain disposition of matter; and I think the notion of a latent disposition of matter is hardly intelligible."[95]

The three chemists discussed in this section who specifically denied the

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[93] Anon [Joseph Black?] 1770.

[94] Ibid, 21.

[95] Milner 1784, f 97.

existence of a material heat, Cavendish, Milner and Fordyce, all held slightly different points of view. Fordyce rather glossed over the chemical production of heat in his lectures:

> "… there is generally either Heat or Cold takes place in Chymical combination, as for instance uniting Oil of Vitriol & Water together it produced heat. … Now when heat or Cold is produced it is always a Chymical combination; for no heat or cold is produced in Mechanical Mixture."[96]

Other than noting that the production of heat (or cold) might be taken as a sign of chemical combination, Fordyce made no further attempt to generalise. His attitude might best be described as agnostic, reluctant to subscribe to either a material or a vibratory view of heat. Nicholson took a similar view:

> "since effects are proportioned to their causes, we may speak of the quantities of heat in bodies, without deciding whether they be quantities of motion or quantities of matter; the relation of those quantities to each other, and not their peculiar nature, being the chief object of our research."[97]

On the other hand, Fordyce's agnosticism was apparently rather more strict in the pedagogical context than in a research environment. In a paper read to the Royal Society only a year later, he concluded from an examination of the effect of heat on different substances painted with black paint, that heat was a 'quality' (although he remained cautious about definitely ascribing it to vibration) rather than a substance.[98]

The pedagogical context, it would seem, required a greater degree of certainty than did the *Philosophical Transactions*. Perhaps these pedagogical decisions also reflected the disciplinary identity that was being forged in chemistry. The chemical generation of heat blurred the lines between mechanical and chemical effects, and any in-depth discussion of it in the lecture hall might have served to similarly blur the disciplinary boundaries.

Where Black was apparently reluctant to apply his own doctrines of latent and specific heat to the chemical generation of heat by mixture, there were others

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[96] Fordyce 1786b, f 67-68.

[97] Nicholson 1795, 372.

[98] Fordyce 1787, 316.

who were not so cautious. Although the majority of these theorists assumed a material heat, this was by no means necessary to a chemical understanding of latent heat. Cavendish, as McCormmach has shown, was committed to the view that heat resulted from vibrations of the particles of ordinary matter. Cavendish's unpublished treatise on heat dating from the 1780s, attributed the heat and cold generated by chemical mixture to the vibrations of matter consequent upon the action of chemical affinity, although he was unable to avoid ambiguous language:

> "It seems a natural consequence of this theory that the mixture of two substances which have a chymical affinity should commonly be attended by an alteration of sensible heat; for as the arrangement of the particles must be alterd thereby, the quantity of latent heat can hardly fail of being alterd; & moreover it is very possible that the quantity of active heat necessary to produce a given sensible heat, may also be alterd; both of which causes will produce an alteration in the quantity of total heat necessary to produce a given sensible heat."[99]

In spite of Cavendish's thoroughly mechanical theory of heat, he still referred to the 'quantity' of latent heat and active heat. Cavendish's latent heat was, however, a mathematical entity derived from his principle of conserved vis viva. He also suspected (although as he considered it to be too hypothetical he only included it in a footnote), that in most chemical combinations heat and not cold would be likely to be generated. His mathematical explanation of this is complex, but broadly it seems to suggest that cold would only tend to be generated in mixtures where one of the substances was changed from a solid to a fluid state, or from either of those to an elastic.[100] This hypothesis implies that while heat could only be produced in cases of chemical combination, cold would be more likely to be produced in solutions. This echoed a hypothesis that had been set out by Cullen in the 1750s, although Cullen had coupled his conclusions to a quite different ontology.

4.2.2 Dynamic Fire Particle

Cullen's only published work on chemistry was a short paper on the generation

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[99] Cavendish, "Heat", in McCormmach 2004, 183.

[100] Ibid.

of cold by evaporation published in the *Essays and Observations* in 1756.[101] This paper was not explanatory, but simply set out his experimental discovery that the evaporation of volatile liquids on the bulb of a thermometer drove its temperature down. Another report given to the Literary Society in the College of Glasgow some time during the 1750s set out further experiments on which mixtures of substances generated heat, and which generated cold.[102] His paper presented tables showing each type of mixture, and concluded that heat was always generated on proper mixture (chemical combination), while cold was invariably generated on solution.

Some years later Cullen included a lengthy digression in his 1765 chemistry lectures that set out a complex and detailed theory of heat and combustion.[103] The inclusion of this highly speculative theory in his lectures is something of an anomaly. In most extant sets of lecture notes Cullen avoided speculation. Although the theory is glimpsed in other sets of notes, the 1765 version appears to be the most detailed and comprehensive.[104]

His theory sought to explain most of the phenomena of heat, whether physical, chemical or physiological by reference to the motion of an aetherial matter of heat. Briefly, the 'condensation' of matter that occurred during proper mixture expelled a proportion of the aether and its accumulation and consequent oscillation caused the sensation of heat. The amount of heat produced during the combination would thus be related to the proportions of the substances mixed. The production of heat by mixture was thus a mechanical consequence of the affinities between substances. Cullen's theory set a clear division between chemical combination and other forms of mixture and implied (as Cavendish was to assert a little later) that in all cases of chemical union heat must necessarily be produced.

Cullen also argued that combustion was merely a special case of the generation of heat by chemical combination. Although all inflammable substances

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[101] Cullen 1756.

[102] Donovan 1976, 221.

[103] Cullen 1765 MS1920. Also Taylor 2006.

[104] Christie has drawn on an earlier version of the theory in Christie 1983.

contained one constituent in common, the hypothesised phlogiston, this was not the elementary substance that was normally envisaged. Cullen's phlogiston was compound, a union of an acid and mephitic air.[105]

> "Now if this be allowed what is become of the Chymical Principle of Inflammation, - There is no such Body The <phlogiston> consists of 2 component parts neither of which are of themselves Inflammables"[106]

Cullen's elaboration of his phlogiston theory testified to the authority of affinity in his chemistry:

> "To me indeed Inflammation seems to depend on the decomposition of this Compound by the Common Air, which attracts the Mephitic Air."[107]

If the mephitic air must be attracted by common air for decomposition to take place, then common air was required for inflammation. As the two airs united, the affinity between them resulted in a condensation of their bulk. This was the proximate cause of the generation of heat:

> "From the whole I think we may conclude that the Inflammability of bodies is owing to the Resolution of a Compound, for which we shall return the name of a Phlogiston consisting of an yd[108] and Mephitic Air, and that this resolution is effected by the Elective Attraction of the Common Air, … that the Heat generated under Inflammation is to be attributed to the new Combination that takes place, and that therefore after all we are to refer this to the generation of heat by Combination."[109]

This incarnation of Cullen's heat theory differs from that cited by Christie, which was drawn from earlier lectures in which Cullen had explained affinity as

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[105] For Cullen at this time, there were only two different airs in the armoury: ordinary atmospheric air and Black's 'fixed air', which he called 'mephitic'. This was prior to the explosion of airs that began with the work of Cavendish and Priestley later in the 1760s.

[106] Cullen 1765, MS 1920 f74v . This MS is not foliated and as the course is not divided into individual lectures it is difficult to cite references. In order to provide a full citation I have counted pages from the first page of the notes "On Fire". These occupy the final quarter of the bound volume, and most pages are separated by a blank sheet. These too I have included in the pagination. The notes begin on f. 1r.

[107] Cullen 1765, MS 1920 f74v.

[108] This appears to be an unusual abbreviation of the word 'acid'. More familiar is the use of the 'y' shaped rune thorn (þ) for the phoneme 'th' resulting in abbreviations 'y^{t}', 'y^{n}', 'y^{y}' and the more mundane 'y^{e}'. It is possible that this was simply a phonetic extension of this usage.

[109] Cullen 1765, MS 1920 f80r.

the consequence of varying densities of the aether.[110] By 1765, Cullen no longer attempted to explain affinity in terms of the aether but, on the contrary, explained the behaviour of the aether as a consequence of affinity.

Cullen's theory, although adopting a very different ontology of heat from that of Cavendish, both implied and drew on the same two generalisations, the first chemical and the second physical. The first, that chemical combination always produced heat while solution produced cold, and the second that condensation of bulk produced heat, while rarefaction produced cold. The fact that the one entailed the other in both Cullen's and Cavendish's theories, and indeed the theories of many chemists who nevertheless adopted quite varying ontologies of heat emphasises the fact that most of these components were based on observation. Ontologies undoubtedly influenced the precise form each component took, but nevertheless each was grounded upon similar generalisations of empirical observations. Similarly, Black's and Irvine's doctrines of specific and latent heat offered formalised explanations of the very same observations that for many implied that heat was a material substance. After all, how reasonable was it to expect those who encountered their ideas to take the copious references to 'quantities of heat' anything but literally?

4.2.3 **Material Heat**

For many, the work of Irvine and Black (and, many would argue, their language) confirmed that heat was a material substance.[111] However, the failure of either to publish led to a certain amount of confusion about their doctrines. Milner complained that:

> "As Dr Black the Inventor of this Theory has no where printed his Ideas on this subject, one is left to collect them from what he is said to have delivered At his lectures, or from the Conversation & publications of his pupils or followers, who are very numerous."[112]

Both Black's and Irvine's ideas were initially disseminated in a pedagogical context. In spite of their didactic roles, neither made any effort to extend their

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[110] Christie 1983.

[111] E.g.. Encyclopaedia Britannica, 2nd ed., s.v. "Heat".

[112] Milner 1784, f 60v – 61r.

ideas to deal explicitly with the chemical generation of heat. It was, as Milner noted, their students, with their sets of lecture notes, and their recollections of their masters' theories, who were responsible for pushing versions of their theories out to the wider world. For most chemists access to Irvine's ideas came through the publication of Crawford's *Experiments and Observations upon Animal Heat*, which was received with great interest by his fellow chemists.[113] It seems likely that it was this work, together with the *Enquiry into the General Effects of Heat & Mixture* that prompted British chemists to draw on the new concepts to explain the production of heat or cold by chemical reactions.[114] Under Crawford's system,

> "the capacities of bodies for receiving heat, are considered as proportionable to the quantities of absolute heat which they contain, when the quantities of matter are equal, and the temperatures are the same"[115]

'Absolute heat' denoted the quantity of heat contained in a substance. So long as the quantity of matter remained the same, and no external heat was added, the only way in which sensible heat could be produced from a substance was by a change in heat capacity. In spite of Crawford's routine use of the phrases 'quantity of heat', and 'capacity for receiving heat', his commitment to a material view of heat was somewhat tentative:

> "my sole motive for adopting this language, was, because it appeared to be more simple and natural, and more consonant to the facts which had been established by experiment. At the same time, I am persuaded, it will be found to be a very difficult matter to reconcile many of the phenomena with the supposition that heat is a quality."[116]

Crawford compared the absolute heats of a variety of bodies, drawing the conclusion that the addition of phlogiston to any substance reduced its heat capacity, while its removal increased it. In respiration therefore, where (to simplify matters) atmospheric air was converted to fixed air and sensible heat by the addition of phlogiston, this was because the addition of the phlogiston to

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[113] Crawford 1779.

[114] Dyck 1967, ch. VI.

[115] Crawford 1779, 97.

[116] Ibid, 115-116.

the dephlogisticated air reduced its heat capacity sufficiently to expel a proportion of its absolute heat. The heat of combustion arose from the addition of phlogiston to the air which produced a reduction in the heat capacity that vastly outweighed the increase produced in the fuel.[117] Crawford also claimed that where the combination of certain substances produced heat, the reverse separation would invariably produce cold.

Any chemical operation was a complex system linking heat capacities, saturation quantities of phlogiston, quantities of matter and sensible heat in a web of influence. Where the product of the heat capacity and "quantity of matter" of one substance in a system fell by more than the equivalent product of the other substance rose, sensible heat was expelled from the system. This was essentially what Crawford believed happened in combustion, and he was able to account for some of the circumstances of particular combustions:

> "In the inflammation of alcohol and sulphur, a very great proportion of the fire which is detached from the air, is imbibed by the aqueous and sulphureous vapour; and, therefore, alcohol and sulphur burn with a pale and weak flame. On the other hand, those inflammable bodies which produce little vapour, or which produce a vapour that is capable of absorbing but little heat, as pit-coal, oil, wax, phosphorus, burn with a strong and vivid flame."[118]

Combustion was only one chemical process amongst many others which also involved the transfer of phlogiston, and a consequent change in heat capacities. Crawford used an analogy to explain the apparent opposition of phlogiston and heat:

> "in consequence of the addition of phlogiston, a portion of the fire will be detached, in the same manner as the nitrous acid is detached, by the vitriolic, from an earth or alkali; and therefore respiration and combustion will be truly chymical processes."[119]

This is interesting for two reasons. Firstly, it implied that in some sense phlogiston and heat belonged to the same class of substances, and thus could displace each other in combination, as acids did. Secondly, it suggested that the

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[117] Ibid, 91-95.

[118] Ibid, 109.

[119] Ibid, 116.

expulsion of heat by phlogiston occurred in a similar fashion to the model of single affinity. This notion, of heat behaving as it if had its own affinities to matter, is explored further in next section.

By the time Crawford produced his second edition, published in 1788,[120] doubts as to the existence of phlogiston were creeping in (although Crawford was for the most part unconvinced by the anti-phlogiston arguments), and the work was amended substantially. Nevertheless, his explanation of the chemical generation of heat remained substantially the same, focused on the comparative heat capacities of reactants and products.

Cleghorn's *De Igne*, produced in the same year as Crawford's first edition, cited Irvine as having shown by experiment that heat was not 'generated' in chemical processes, but simply 'separated'. He also, however, incorporated a nod to Cullen's heat theory:

> "for a given temperature and quantity, a mixture of water and vitriolic acid contained a smaller quantity of fire than did these fluids separately. Also the bulk of the mixture is less: when therefore water and vitriolic acid are mixed with one another, fire arises from both causes; this likewise occurs in other mixtures and for the same reasons."[121]

For Cleghorn, both the change in bulk on chemical combination and the change in heat capacity caused the generation of heat. It is interesting to note that he regarded these as two different, separate causes of the generation of heat. The change in heat capacity was not, for Cleghorn at least, necessarily linked to the physical change in bulk.

Kirwan's views were similar to Crawford's, and it is clear that he was very interested in Crawford's work. His correspondence with Guyton de Morveau between 1782 and 1785 abounds with Guyton's enquiries about the forthcoming second edition and both men were apparently eager to hear Crawford's revised views.[122] Nevertheless, in his 1783 discussion of affinities, Kirwan avowedly relied on "the doctrine of Dr Black",

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[120] Crawford 1788.

[121] McKie and Heathcote 1958, 39.

[122] Guyton de Morveau and Kirwan 1994, See letters 2, 4, 12 and 13.

> “viz. that solids absorb heat during their solution. Both the heat and cold, produced in different solutions, seem to me to depend on the same principle. If the menstruum gives out only *so much* of its fire as the solvend can absorb, or *less*, then cold is produced; but if it gives out *more*, of its specific fire than the solvend can absorb, this surplus heat becomes sensible”[123]

Kirwan envisaged a transfer of “specific fire” during solution from menstruum to solvend, as the (usually) solid substance was dissolved in a fluid, becoming effectively fluid itself. The action of affinities normally prompted this transfer, and as different substances in different states had different capacities for heat (the Irvinist view) sensible heat was generated when a menstruum gave up more heat than the solvend could absorb. As in Crawford’s system, heat was transferred according to the various capacities, states and proportions of the substances involved. It is interesting to note, however, that Kirwan (remembered primarily as the defender of phlogiston) did not specifically refer to the transfer of phlogiston between substances as the agent of change of heat capacities, but tied his ideas much more tightly to his affinity theory than had Crawford.

While sometimes the action of affinities produced heat or cold through this juggling of heat, sometimes the capacities were balanced in such a way as to prevent affinities from acting as expected. Kirwan utilised these ideas to explain certain anomalies in his affinity theory. His quantified affinities indicated that all the mineral acids had the same affinity to fixed vegetable alkali. This ran counter to two of the most familiar reactions, by which vitriolic acid decomposed both nitre and salt of sylvius (marine acid combined with fixed vegetable alkali). On the other hand, it had recently been shown that nitrous and marine acids could decompose vitriolated tartar (fixed vegetable alkali combined with vitriolic acid), from which Kirwan deduced that compound attractions were at play in all these operations.[124] 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,

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[123] Kirwan 1783, 50.

[124] Ibid, 44.

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.

Kirwan had already suggested that the apparently anomalous ability of some acids to decompose the vegetable alkali salts arose from their different heat capacities.[125] From the above experiment 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 this 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."[126]

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 priority over another; its observed affinity for the alkali was stronger. The experiment showed that in a situation where the nitrous acid had been vastly in excess of the vitriolic acid, the amount of fire 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.[127] Like Crawford, Kirwan claimed that chemists had to take account of the relative proportions of each substance in any operation. As they had to balance the total amount of heat possessed by each substance with their total capacities for heat, such proportions had a significant effect on the results of the operation.

Kirwan's thinking rested in part on a distinction between the physical processes

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[125] Ibid.

[126] Ibid, 46-47.

[127] Ibid, 44-45.

of solution and more enduring chemical combination that Cullen might have appreciated. While solution involved a physical change in one of the substances involved, it did not necessarily entail chemical combination. Kirwan differentiated carefully between the quantity of fire transferred between substances, and the addition of heat by the operator. This he called ‘foreign heat’. Considering the failure of either nitrous or marine acids to decompose selenite (vitriolic acid combined with calcareous earth), he explained,

> “it is dissolved by neither without the assistance of heat, and then the solution is performed by a foreign heat, and not by that which these acids give out when they act without the assistance of heat.”[128]

Although the application of heat could promote the solution of the selenite, this was simply a physical change; it did not initiate the transfer of specific fire from the free to the combined acids that was required for chemical decomposition. It is clear that Kirwan saw two interacting but distinct processes – physical change, often caused by the transfer of heat, and chemical change caused by affinities which in turn could prompt changes of state and consequent exchange of specific fire. Physical states of aggregation, themselves dependent on the amount of specific fire present, could also prevent or promote affinities. Kirwan did not draw on quantified heat capacities in this component of his affinity theory, and indeed seemed more concerned with what Crawford would have termed ‘absolute heat’ which was also dependent on proportions. He treated his heat as a material substance, suggesting at one point that in operations where changes of state occurred, fire was transferred as part of a double decomposition.[129]

Kirwan’s presentation of this component of his affinity theory perhaps does his theory a disservice. It is included in his paper not as part of a consistent, predictive theory, but rather in order to explain deviations from his quantified affinities. This gives the unfortunate impression that it was formulated solely in order to preserve Kirwan’s innovative quantification component. We should hesitate to accept this assessment. Kirwan’s interest in the chemical effects of

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[128] Ibid, 49.

[129] Kirwan 1783, 36.

heat, and specifically in the doctrines of Irvine and Black, was of long standing (as is evident from his early measurement of specific heats), and it seems likely that some form of this component had been included his affinity theory for some time. It was, however, presented as part of a paper that was intended to set forth Kirwan's new method of quantifying affinities, and as such any lengthy disquisition of this component would have served to distract attention from the main thrust of his argument. His consequent introduction of it only when necessary lent it an unfortunately ad hoc character. This perhaps emphasises the difference between a pedagogical presentation which, although selective as we have seen, might be expected to give equal weight to each component of a theory, and more research presentations which were intended to put across a very particular point in a persuasive manner.

Elliot, whose ideas are discussed in more detail in the next section, was unequivocal in his explanation of the generation of heat or cold:

> "When water is mixed with oil of vitriol, a great degree of heat is produced. The capacity of the mixture becomes less than the sum of the capacities of the ingredients before mixture; of course the fire which they contained must occasion the temperature of the mixture to be higher."[130]

A simple mathematical relation was sufficient, Elliot implies, to give *a priori* notice of those combinations that would produce heat and those that would produce cold. This is, of course, a vast simplification of the Irvinist basis of Crawford's and Kirwan's components. Elliot's component appeared in a pedagogical work explicitly intended to instruct the novice in the theory underlying chemical practice, and as such his priorities were different from those of either Crawford or Kirwan.[131] His causal hierarchy was strikingly similar to that adopted by Cullen in his own explanation of the generation of heat. He offered a more generalised explanation of the phenomena, with the specific case of phlogiston, and its (possible) effect in reducing heat capacity, subordinated to his theory of affinity, which was responsible for the changes in

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[130] Elliot 1786, 82.

[131] Ibid, vi.

capacity that in turn caused the generation of heat.[132] Thus the translation to pedagogical context ironed-out difference and elided variation to produce a component not clearly distinguishable from many of those that we have looked at, yet far from identical with any of them.

Irvine's and Black's doctrines were initially disseminated in the pedagogical context, but were translated into the research context by their students and extended to cover the chemical generation of heat, an area barely touched upon by the original theories. From this process of translation, confusion and misrepresentation abounded, such that Kirwan, for example, could misrepresent Black's doctrine as above. Crawford's theory, combined perhaps with Kirwan's, was then generalised and simplified for re-presentation in the pedagogical context by Elliot. Elliot's elision of many of the details of Crawford's theory in his much more generalised component offers an interesting example of the process of generalisation as these researches were translated for the pedagogical context. This process was perhaps taken to the extreme in the production of reference works like James Parkinson's *Chemical Pocketbook*, which in 1800 claimed that in all combinations consequent upon affinity, a change in temperature occurred immediately upon the union of the two bodies.[133] Parkinson listed this as one of his 'general principles or laws' of affinity and offered an explanation much like Elliot's, with the temperature change the consquence of changing heat capacities. Perhaps more importantly though, heat capacities were themselves the measure of the affinities between heat and ordinary matter.

4.3 Affinities of Heat

For those who did adopt a material heat, one of the consequences was the possibility that it might be possessed of its own set of characteristic affinities for ordinary matter. However, whether these affinities were of the same type as chemical affinities and could be determined by similar methodology, remained open questions. As I have demonstrated, affinities could be ordered on the basis of the speed of combination, ease of combination, the ease of separation,

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[132] Ibid, 83.

[133] Parkinson 1800, 2.

precipitation orders, or relative quantities. A correspondence between the affinities of heat and ordinary matter would presumably require a similar correspondence between the conceptualisations of affinity orders.

Heat capacity, or specific heat, common to both Black's and Irvine's theories, was a substance-specific quality, that many saw as being a measure of the affinities of heat for ordinary substances (or vice versa). Even the agnostic Nicholson let slip that if heat was a substance, then

> "the table of comparative heats or capacities may perhaps indicate the affinities of this substance, … better than any other table."[134]

Thus Nicholson, who removed the column for 'matter of heat' from Bergman's affinity table, remained firmly ensconced on his fence.[135]

On the other hand, it was Black's doctrine of latent heat that lent itself most easily to the concept of heat *in combination* with matter, with the usual consequence of loss of characteristic properties on all sides. I have, however, been unable to discover any chemist who suggested that the affinities of a material heat might be proportional to latent heats. Although the qualitative conceptualisation might seem to be analogous to chemical affinity, it does not seem that any chemist maintained that they were truly comparable. Black's own position is not entirely clear. In the posthumously published lectures edited by Robison, he expressly disavowed any notion that heat combined chemically with other matter:

> "Heat is … supposed to be somehow contained or lodged in the pores of bodies, and we endeavour to account for the changes of sensible appearance, such as increase of bulk, or fusion, or vaporisation &c. by shewing some resemblance between those appearances, and those which occur in chemical unions or mixtures.
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> Many have been the speculations and views of ingenious men about this union of bodies with heat. … This will please the imagination, but does not advance our knowledge. I therefore

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[134] Nicholson 1795, 165.

[135] Ibid.

> avoid such speculations …"[136]

At least in his posthumous incarnation, Black took a puritan attitude to the question.[137] On the other hand, he apparently expressed a preference for Cleghorn's ontology as set out in his inaugural dissertation.[138] Cleghorn speculated at length on the ontology of heat, concluding that heat or fire consisted of a self repulsive elastic fluid (hence the movement of heat until an equilibrium of temperature was attained), that was attracted by ordinary matter.[139] He cited in support an experiment of Black's (after Fahrenheit as reported by Boerhaave)[140] mixing equal masses of mercury and water at different temperatures, and similar experiments with water and lead, tin and glass:

> "It must therefore be concluded that there is in bodies a force attracting fire and that this is different in different bodies."[141]

What Black termed heat capacity was thus explained by Cleghorn in terms of an attraction of bodies for the matter of fire, or heat. When a number of bodies were apparently at the same temperature according to the measurement of the thermometer, they contained different quantities of fire, in each case proportional to "the power by which they attract fire and inversely [in proportion] to the repulsive power of the particles of fire."[142]

Cleghorn also explained the apparent generation or absorption of heat:

> "since fire is distributed among bodies directly as their attraction and inversely as the repulsion between the particles of fire, if in any body the former is diminished or the latter increased, fire will flow from that body until the equilibrium be again restored; heat is then said to be generated."[143]

This would seem to explain his view, noted above, that both the change in heat

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[136] Black 1803, 193.

[137] Fox 1971, 24-25.

[138] McKie and Heathcote 1958, 28.

[139] This bears a striking similarity to Henry Cavendish's 1771 hypothesised electrical fluid which was composed of mutually repelling particles which attracted common matter. See McCormmach 2004, 66.

[140] McKie and Heathcote 1935, 13-14.

[141] Ibid, 21.

[142] Ibid.

[143] Ibid, 23.

capacity and the change in bulk on chemical combination were responsible for the generation of heat. In the case of a reduction in bulk (Cullen's condensation), the repulsion between the particles of fire increased and heat was generated. Although Cleghorn explained both Black's latent heat and Irvine's theory of change of state in his dissertation, his avowed preference was for Irvine's ideas.[144] According to Cleghorn's version of Irvinism, a change of state resulted in a change in a substance's "disposition towards fire", and the consequent absorption or generation of heat.

Cleghorn made it clear, like Fordyce, that different types of attraction were destructive to each other.[145] Thus, on the application of heat, any subsisting attractions (presumably including chemical affinities) would be diminished. He opposed the attraction between fire and matter with the attraction within homogeneous substances that accounted for their aggregation. The increase in the attraction for heat when substances were rarefied was thus explained by the opposition of this 'attraction of cohesion' to the repulsion between the particles of fire.[146]

It is unclear from Cleghorn's dissertation how he conceptualised the attraction between heat and matter. Although he hypothesised freely on the ontology of heat, he was less concerned to distinguish between the attractions between heat and matter and chemical affinity. As with affinity, attractions were particular to each substance, and resulted in some type of union of heat and matter. But Cleghorn did not claim that heat was chemically combined with matter. Rather, he described how it was drawn to it, and held to it. Words like 'squeezed', and 'compressed'[147] seem to imply a sort of sponge metaphor.

Heat affinities were not invariably identified with heat capacities. The earliest specific reference to heat as being subject to affinities is by Erasmus Darwin. Endeavouring to explain the varying expansion of bodies on the addition of heat, Darwin argued that

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[144] Ibid, 27-28.

[145] McKie and Heathcote 1958, 25.

[146] Ibid, 29.

[147] Ibid, 33.

> "some bodies have a greater affinity to heat, that is, acquire it sooner and retain it longer than others."[148]

Darwin thus hypothesized that ordinary matter had an affinity for heat. He did not imply that such affinities might inhere in the heat itself. Rates of absorption and transmission of heat were at this time commonly related to the density of matter, and Darwin tried to develop this idea to fit his own observations. The affinities of different substances to heat were

> "in ratio of their specific gravities and their powers of refraction, reflexion, or absorption of light; or at least in some ratio much greater than that of their specific gravities alone."[149]

His discussion was almost entirely focused on the physical effects of heat, although he returned to the 'affinities' of matter for heat towards the end of the paper. He clarified his thoughts by separating out the two contributory powers of this 'affinity' into "the power of retaining heat" and "the quickness of acquiring heat". [150] Thus,

> "if (the power of expansion by heat being equal) the power of retaining heat be in a greater ratio than the specific gravities; then during the time of cooling after being sufficiently heated, there will be an instant, when the heavier body will become the lighter, and swim upon the other. … if the quickness of acquiring heat be in a greater proportion than their specific gravities … then, during the time of their acquiring heat, there will be an instant, when the body that was heavier when cold , will now become the lighter."

Darwin's concern was the physical behaviour of two dissimilar bodies when heated together rather than their chemical behaviour. These bodies were not undergoing chemical change, but his notion of varied affinities for heat suggests that he drew an analogy from chemical affinity.

As we have seen throughout this chapter, we can draw no distinct line between Irvinist and 'Blackist' theories. This is probably a consequence of the rather piecemeal process of interpretive dissemination of Black's and Irvine's ideas. Many chemists segued seamlessly from ideas that changing heat capacities

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[148] Darwin 1757, 243.

[149] Ibid.

[150] Ibid, 246-7.

caused changes of state to notions of heat in combination. As such, there is no correlation between those who espoused Black's theory and those who ascribed affinities to heat. Irvine's son provides an example of this confusion with a later attempt to describe his father's account of specific heat:

> "If then we suppose that any substance were totally deprived of caloric, yet retained its power of receiving or combining with it; it appears reasonable to say, that a certain quantity of caloric applied to this body, would raise its temperature by a number of degrees proportional to its capacity."[151]

His perception of his father's ideas, like many chemists', incorporated something akin to the combination of matter with heat. It is probable that Irvine himself would have accepted this view; indeed McKie and Heathcote tell us that both Black and Irvine referred to affinity when discussing what came to be known as 'heat capacity'.[152]

We have seen that Crawford was more adventurous than Black and Irvine in applying the theory of heat capacity to chemical processes, but he too was not beyond a Black-style evasion on more hypothetical matters. He pointedly declined to speculate on the ontology of heat, but then reminded his readers that

> "if we adopt the opinion, that heat is a distinct substance, or an element *sui generis*, the phenomena will be found to admit of a simple and obvious interpretation, and to be perfectly agreeable to the analogy of nature."[153]

The habit of speculation died hard with Crawford, it would seem. He was prepared, in a tentative fashion, to take one step that Cleghorn had disdained:

> "I may add, in the last place, that, if fire be considered as an element, which is capable of uniting chymically with bodies, a table may be formed, exhibiting the respective attractions of phlogiston and fire."[154]

An affinity column for phlogiston was not particularly novel. Crawford ordered much of his column on the basis of conventional displacements (although comparing the heat required to accomplish each). The bases of the inflammable

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[151] Irvine 1805, 51-52.

[152] McKie and Heathcote 1935, 32.

[153] Crawford 1779, 116.

[154] Ibid, 117.

bodies though, were arranged "according to the degrees of heat which are necessary to their inflammation."[155] This contrasts with the heat capacities on which he based his suggested column for fire.

> "Fire should be placed at the head of the second column; and if the attractions of bodies to this principle, be proportionable to the quantities of it, which they are found to contain, when the quantities of matter are equal; under fire should stand dephlogisticated and atmospherical air – the vapour of the nitrous acid, and probably of some other fluids – arterial blood, water &c."[156]

In spite of the purportedly quantifiable basis of this latter column, Crawford's description was conspicuously vague, and this acts as a reminder that it was written before Kirwan produced the first table of specific heats (many of which were derived from Crawford's experiments).[157] It is notable that in the heavily amended (and partly dephlogisticated) second edition of his work, he objected to suggestions that 'elementary fire' was a substance that could combine chemically with ordinary matter.[158] He still allowed that fire was attracted to ordinary matter, but it was something more than a chemical combination:

> "Fire will be considered as a principle, … The mode of its union with bodies, will resemble that particular species of chemical union, wherein the elements are combined by the joint forces of pressure and of attraction. Of this kind is the combination of fixed air and water; for fixed air is retained in water partly by its attraction to that fluid, and partly by the pressure of the external air"[159]

We have already seen an example of hurried amendment of a component in the light of new empirical information in Kirwan's response to Cavendish's synthesis of water. It was, perhaps, an inevitable consequence of the innovative nature of components such as this that they were subject to endemic uncertainty and prone to radical modification. Fire was still, however, envisaged as having affinities for ordinary matter, and indeed as uniting with it in some way that was

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[155] Ibid.

[156] Ibid, 118.

[157] McKie and Heathcote 1935, 109 fn.

[158] Crawford 1788, 372

[159] Ibid, 436.

analogous to solution, in particular because it apparently retained its distinguishing properties in such combination. Crawford still suggested that a table could be produced, but now it should show "the comparative quantities of fire contained in all known bodies".[160] Although inflammable air now appeared at the head of the table, the list of substances exactly replicated that earlier suggested as an affinity column.

Bergman took a more robust view than Crawford, introducing a column for "matter of heat" into his affinity tables in the second edition of his *Dissertation*. He devised this column on the basis of observations of the flow of heat from the mercury in a thermometer when placed in an evacuated air pump. He apparently understood these phenomena as proceeding from the successive attraction of heat by these different substances in a fashion a little like capillary action.[161] When water was placed on the bulb of an open thermometer and the air pump evacuated, the heat capacity of the rarefied air increased, drawing heat from the water. The water in turn attracted heat from the glass of the thermometer, and this finally drew heat from the mercury which contracted as a result and fell in the glass. The attraction of air for heat was thus presumed to be stronger than for water, the attraction of heat for glass was weaker and for mercury weaker still. Bergman believed that specific heats were a product of the particular attraction of a body for heat, and what he called the external and internal surfaces. These corresponded generally to the internal and external surface areas of bodies, the porous structure of which he compared to a sponge. As bodies changed state, their internal surface area changed accordingly (the greater the bulk, the larger the internal surfaces). Thus physical state and attraction combined produced specific heat.[162]

There is an enlightening corollary to Bergman's decision. The post-Lavoisierian Pearson amended and extended Bergman's table to take account of the new chemistry.[163] He reissued his translation of the *Nomenclature*

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[160] Ibid, 437-8.

[161] Bergman 1970, 240-248.

[162] Ibid, 237-139.

[163] Possibly the largest affinity table ever produced at 62 columns in both the wet and dry ways. Anon [George Pearson] 1799, Table III.

alongside his new tables which were "from *Bergman,* with alterations and additions".[164] Pearson adopted Bergman's matter of heat column, renaming it 'calorific' and adding at the bottom the "bases of all the gases", presumably in consequence of Lavoisier's theory. Pearson's tables were picked up and used in chemical reference works such as Nisbet's *General Dictionary of Chemistry*[165] and Parkinson's *Chemical Pocketbook.*[166]

In the latter work, Parkinson claimed that caloric combined chemically with matter according to its affinity for each particular substance.[167] The "combined caloric" was explicitly equated with Black's latent heat, while heat capacity was proportional to the affinities between caloric and matter. Pearson's dephlogisticated version of Bergman's table appeared alongside this theory with a column for 'calorific' which was still predominantly based on Bergman's idiosyncratic method of ordering, rather than on the heat capacities that might be expected from Parkinson's theory.

This example clearly illustrates the crucial nature of the connection subsisting between theories and tables. When tables of affinity were abstracted from the particular theory that had governed their creation their practical value declined. It is possible that Parkinson himself was ignorant of the way in which the 'calorific' column had been set out, but in any event, a hopeful chemist assuming that the orders of affinities shown in this table for caloric represented the various heat capacities of the substances shown would be sadly disappointed.

We have seen (see 3.3.3 above) that Kirwan's affinity theory explained many of his unexpected chemical results by reference to "a sort of double decomposition"[168] involving the transfer of 'fire' from one substance to another. Although this implies that Kirwan envisaged something like the classic elective

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[164] Ibid.

[165] Nisbet 1805.

[166] Parkinson 1800, 6.

[167] Parkinson was scrupulous in presenting alternative views from the material view of heat as well. His personal preference can, however, be ascertained by the fact that the four pages devoted to the caloric theory was 'balanced' by an account of Rumford, Davy and Beddoes's arguments in favour of vibratory heat occupying barely a single page.

[168] Kirwan 1783, 36.

model of affinity, other texts suggest otherwise. In many cases, it seems that the role of heat in chemical processes was not to combine with other matters, changing their properties, but to simply encourage affinities to operate: this was a reversion to the more traditional understanding:

> "it is remarkable, that bodies capable of an aerial form receive the latent heat necessary for that form, much more readily from a body that parts with its specific heat than by the mere application of sensible heat."[169]

Earlier works had implied a similar distinction between the heat held within bodies and sensible heat (previously referred to as 'foreign heat'). He continued with an example:

> "so liver of sulphur will not give hepatic air by mere heat, though it will by the intervention of an acid, even the weakest. The reason of which seems to be this: the matter of heat has no particular affinity with any substance, as is evident from its passing indifferently from any hot body to a colder, of whatever sort or kind the bodies may be; but it is determined to unite with this or that body in a latent state, in greater or lesser quantity, in proportion to the greater or *lesser* capacity of these bodies to receive it."[170]

In spite of his use of the word 'unite', heat capacity for Richard Kirwan was not another word for affinity. The fact that heat was present in all substances in different proportions distinguished it from chemical affinity. This perhaps explains why so many chemists struggled with the assumption that heat capacity was a measure of the affinity of heat for matter. All substances were assumed to have some affinity for heat, which distributed itself between all the substances according to these affinities. Where chemical affinity was elective, heat affinities were equilibrial; the type of displacement that had always epitomised chemical affinity was not an appropriate model for the transfer of heat. He continued:

> "acids, uniting to the alkaline basis of liver of sulphur, expel the sulphur, and give it their heat *at the instant* that it has the capacity to receive it; whereas external sensible heat, acting alike on both the constituent parts of liver of sulphur, separates

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[169] Kirwan 1786, 147.

[170] Ibid, 147-8.

> neither."[171]

Although the proportional relations of heat and matter must have seemed similar to those quantified in his affinity theory, Kirwan believed they were different in kind. Heat influenced chemical operations, and there is some indication that he considered that it combined with ordinary matter, but it did not possess chemical affinity. Most importantly, it could not supplant more tangible bodies in combination. The sulphur in liver of sulphur could only be expelled by acids, at which point it absorbed their heat. The application of heat was unable to expel the alkali. The very fact that Kirwan felt the need to explain this point perhaps suggests that many of his contemporaries were making this very assumption.

It is certainly true that while many were reluctant to commit to the idea that even a material heat was capable of chemical combination, others (in particular Darwin's fellow members of the Lunar Society) were positively bullish. As early as 1784, Wedgwood speculated on the "chemical affinity or elective attraction [of heat] to water".[172] Nor does Watt appear to have differentiated between the affinity of heat for matter and chemical affinity, happily comparing the affinities of "dephlogisticated water" for phlogiston and latent heat in a letter to Black.[173]

Priestley too was amenable to the notion that the absorption of heat was identical with or at least analogous to chemical combination. He believed, like Cullen, that the mark of true chemical combination was the disparity between the properties of the constituents of a combination and those of the compound. Combinations of heat with matter were, in his view, entirely consistent with this principle. In the *Philosophical Transactions* paper in which he claimed the successful conversion of water into air, he explained:

> "The difficulty that strikes many persons the most forcibly, is the want of analogy between the conversion of water into air with any other known facts in philosophy or its nature. But admitting that this conversion is effected by the intimate union of what is

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[171] Ibid, 148.

[172] Wedgwood 1784, 383-4.

[173] Watt and Black 1970, 126.

> called the *principle of heat* with the water, it appears to me to be sufficiently analogous to other changes, or rather combinations of substances. Is not the acid of nitre, and also that of vitriol, a thing as unlike to air as water is, their properties being as remarkably different? And yet it is demonstrable, that the acid of nitre is convertible into the purest respirable air, and probably by the union of the same principle of heat."[174]

Elliot was perhaps the most adventurous of the chemists who assimilated Black and Irvine's notions into their affinity theories, although his writings were not entirely consistent. His *Elements* demonstrates the horns of his dilemma most clearly. Throughout the main part of the work, which as we have seen was pedagogical in tone, he adopted a simplified version of Crawford's theory to account for the physical and chemical effects of heat.[175] Changes of state were correlated with changes in heat capacity, and the generation and absorption of heat was caused by heat capacities changing on chemical combination. The implication, avoided by Crawford, was that it was chemical action that was responsible for these phenomena, affinity presumably envisaged as the driving force. As we have already seen, Elliot's re-presentation of Crawford's theory in general terms led to some interesting assumptions. When he came to the heat produced in combustion, he explained:

> "Let it be supposed that a great quantity of fire is contained in air, in a fixed, or latent state. In combustion, the phlogiston of the inflammable body is transferred to the air; the fire is set at liberty because it has a weaker attraction, and by uniting with the substances around, produces the great degree of heat observable on these occasions."[176]

The fire was not expelled because the various heat capacities of the bodies taking part in the process changed (Crawford's view), but because the phlogiston of the inflammable body was more strongly attracted to the air than was the fire. Phenomenologically speaking, this was pretty much the same as Crawford's theory that the addition of the phlogiston to the air reduced its heat capacity, but Elliot had translated this to a wholly chemical understanding, describing the process in terms of the model of single affinity. He had not

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[174] Priestley 1783, 428-9.

[175] Elliot 1786, ch VII.

[176] Ibid, 126.

mentioned a 'latent' state of heat prior to this introduction of the idea, and indeed made little further reference to it.

Elliot added a postscript to the first edition, and a number of Appendices to the second, which included his own exploratory speculations on heat.[177] Here he reflected on the ontology of heat, explicitly suggesting that it should be viewed as a *principle* rather than as an *agent*. His decision was based on analogy with the phenomena of affinity. Comparing the role of heat in promoting the mixture of water and cream of tartar, with the role of alkali in enabling the union of oil and water he suggested that fire could act as an "intermedium", attracted by both the water and the cream of tartar.[178] He unambiguously explained decomposition by heat in terms of the classic model of single affinity:

> "Is it not because one of the ingredients has a greater affinity to it [heat] than to the principle it is already united with? The fire or heat, in some cases, is attracted away by the neighbouring bodies on exposure to cold, and the body is again capable of uniting with the principle that was expelled by the heat, but in other cases this does not happen."[179]

Elliot's inclusion of heat in his cache of chemical principles was unqualified, even extending the analogy to predict its properties in combination. It will be remembered that Elliot's theory held that the stronger the affinity between two combined substances the less 'active' they became (3.3.1 above). He also applied this component to his understanding of heat, confirming its status as a chemical principle.

> "If the same quantity of *fire* be transferred from some bodies, to others, in a like succession, according to their capacities for containing *heat*, the activity of this principle is, in like manner, decreased. For *fire* to appear as *heat* therefore, must it not be *dissolved* in bodies, or combined with them in the form of *atmosphere*? And is not its activity more restrained, in proportion as bodies attract it more strongly?"[180]

Elliot's ideas, framed as an extended query that deliberately recalled Newton's

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[177] Ibid, 326-331.

[178] Ibid, 327.

[179] Ibid.

[180] Ibid, 328.

Queries were, like the latter, carefully demarcated from the didactic generalisations that constituted the major part of the work. His affinity theory related heat capacity directly to affinity, but also incorporated a relationship between the strength of affinity and the sensible heat. Crawford's theory had balanced quantities of matter with heat capacities and temperatures, and a comparison of this trinity with Elliot's emphasises the latter's more comprehensively chemical stance. But Elliot's speculations continued:

> "Yet I think that we must consider heat, or fire in *two different states*. When it is set free, it then manifests itself as heat … and different bodies have different capacities for containing it, the same as they have for containing moisture. … But when fire is *chemically combined* with bodies, it then, I think entirely loses its property of *heat*, even as water does that of *moisture* when combined in quicklime … It is then no longer sensible to the feeling … and of course is by no means discoverable by the methods of finding the capacities of bodies for containing disengaged fire, or *heat*. This difference is so very obvious, that I wonder it had not occurred to me before."[181]

It is indeed rather surprising that it hadn't occurred to him, as a similar idea had been set forward by his friend Priestley only a few years earlier. Elliot explained his thinking by reference to the deflagration of nitre with an inflammable body by means of an electric spark. In this case he was able to find no difference between the heat capacities of the mixture and the residue and air generated by the process. He was confident that no heat was absorbed from the surroundings, as this process would take far more time than did the deflagration itself. The large amount of heat generated must have come from the combination of the nitre and the inflammable body.

> "I account for it by *supposing* that the latter displaces the fire *chemically combined* in the acid (or dephlogisticated air) of the former; all of which (except perhaps what the inflammable body absorbes in lieu of its phlogiston) becomes then disengaged fire, or sensible *heat*."[182]

Elliot's heat theory cannot be correlated with Irvine's or Black's, or indeed any other. While it borrowed certain components from these conventions, his heat

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[181] Ibid, 329.

[182] Ibid, 330-331.

theory was entirely located within his affinity theory. Heat was material, behaving according to the rules set out in the components of his affinity theory. It could combine with matter according to its affinities, and once combined it was "by no means discoverable". Heat capacity in Elliot's theory only applied to sensible heat, and was no indication of the affinities of heat. These affinities were presumably discoverable through experiments that displaced it from combination as in the deflagration of nitre. His theory invoked a fixed, chemically combined heat that bore some resemblance to Black's latent heat – perhaps a latent heat of combination - but viewed through chemical rather than physical spectacles.

Over the last quarter of the 18th century there was much debate over whether heat was possessed of affinities, and if so, whether they were chemical affinities. As this account has shown, although many were happy to agree that heat was indeed possessed of affinities, very few agreed that they were chemical affinities. The consideration of these questions served an important purpose for chemists though, for in resolving them they clarified their own understandings of chemical affinity, and indeed of the way in which affinity acted.

4.4 Conclusion: Preservation, Assimilation and Refinement

This exploration of some of the components of affinity theory that were formulated to deal with the relationship between heat and affinities has further demonstrated the extent to which affinity theories varied; this much is clear. But perhaps more importantly, it has shed some light on how and why new components were formulated.

The first section set out a range of components that attempted to rationalise the varied effects of heat on substances, and on their affinities. These were for the most part intended to preserve the utility of theories in the face of admitted anomalies. This preservative spirit is evident in an appendix that Keir added to his translation of Macquer's Dictionary in which he explained and clarified the two affinity tables he had added:[183]

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[183] He included Geoffroy's table and Gellert's table of solubilities, neither of which had been included in Macquer's French original. Macquer 1771 , 887-888.

> "The affinities of bodies to each other, as they are laid down in the above Tables, … do not at all times take place; some of them requiring certain degrees of heat, dilution, and various other circumstances. Many instances do also occur in which the affinities of substances seem even to be changed by these different circumstances; and hence many exceptions have been found to the present Tables, some of which are real, and others only apparent. … instances might be adduced of the inaccuracies and defects of these Tables, and of the apparent variations from the general rules laid down in them; but as all chemical compositions and decompositions depend on the affinities of the substances employed, we cannot explain and correct these, without considering almost all the operations in Chemistry. Till other Tables more perfect be formed, these may be of considerable utility."[184]

Keir's commentary indicates both the importance of affinity theories to the discipline of chemistry, and the extent of the problems that beset them. Many of the components cited in this chapter were formulated in an attempt to find a solution to the problems that Keir so eloquently laid out. The effects of heat were thus ascribed to a variety of causes, none of which necessarily entailed that affinities were changed by the application of heat. The consistency of affinities formed one of the crucial tacit assumptions of the doctrine of affinity, so exceptions were unacceptable. Affinity tables and their associated theories were perceived as being too useful and too important to give up, and so chemists made strenuous efforts to rationalise and codify the effects of heat simply to try to save their theories.

On this view, the eagerness with which chemists were to assimilate the doctrines of specific and latent heat into their theories is unsurprising. The work of Black and Irvine on the interaction between heat and matter was quickly seized upon as offering an opportunity to explain the chemical generation of heat. Earlier explanations had drawn on the sort of notions now abjured by chemists like the strife between opposing bodies, or rather naïvely mechanical ontologies. The new ideas thus offered a new opportunity to try to explain these phenomena that evidenced the most obvious overlap between heat theories and affinity theories. New components were formulated to affinity theories, assimilating often quite different understandings of specific and (less

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[184] Ibid.

often) latent heat. My exploration of these new components testifies to their lack of correlation with ontology. Components that were similar in kind were aligned with different ontological commitments, while quite different components apparently coexisted with the same or similar ontologies.

Neither Black nor Irvine ever published their theories, and indeed it seems that both were reluctant to speculate beyond their empirical measurements of heat capacities and latent heat. There is a historiographic parallel here between the dispersion or dissemination of their theories and the dispersion of affinity theories. For most people, access to the new theories was mediated through a network of student notes and recollections, hints and misinformation. Many chemists struggled to differentiate clearly between Irvine's and Black's theories, particularly as, from a phenomenological point of view, the differences were unintelligible. As with the dispersion of affinity theories, differences arose between the theories presented at the apex of the pedagogical pyramid, and the theories that were adopted in the lower ranks.

The first two sections examined components which sought to account theoretically for observed phenomena. In contrast, the third section explored those components that wrestled with some of the logical implications of the new theoretical accommodations. One of the beneficial effects of these more speculative efforts was that they led chemists to refine their understanding of affinity itself. Lines of demarcation between physical and chemical phenomena were clarified, and new lines were drawn between phenomena that might look like the actions of affinities but which were instead the result of some other cause. Attempts to answer the question of whether the affinities of heat were chemical affinities, and whether heat combined chemically with matter served not only to clarify thinking on the behaviour of heat, but also to shed light on what was meant by chemical combination and chemical affinity. As a result of this deeper consideration of these questions, the differences between heat capacity and affinity seem to have become more apparent.

My examination of these 'supplemental' components of affinity theories has emphasised the uncertainties that dogged the doctrine of affinity. It has become clear throughout this chapter, whether chemists endeavoured to extend their affinity theories in a spirit of theory preservation, assimilation or refinement, just how precarious their theoretical structures actually were. As I have shown, both Kirwan and Crawford were obliged to amend their components fairly quickly, (and very publicly) in consequence of new empirical and theoretical information. On the other hand, the very fact that they attempted to build these theoretical structures, indicates their belief that their affinity theories provided a solid foundation.

Thus we begin perhaps to see a new line of demarcation being traced between the pedagogical context and the research context. Kirwan and Crawford in general inhabited the latter, and perhaps their theories were more freely speculative in consequence. In contrast, Fordyce and, to a lesser extent, Elliot straddled both. Both Fordyce and Elliot were notably more cautious in their speculations in the pedagogical arena, with Elliot adopting Newton's tactic of inserting his more venturesome speculations in a set of queries in an appendix to his pedagogical work.

In Elliot's work we have also witnessed the translation of Crawford's complex, highly speculative explanation of the generation of heat into an appropriate form for the pedagogical context. The process is only rarely visible, and even here it is far from transparent, as we cannot know what works other than Crawford's Elliot was familiar with. It does, however, give some indication of the extent to which details of exceptions and anomalies were flattened, while the generalisation increased the scope beyond that justified by Crawford's empirical evidence. This process seems to be an interesting inversion of that carried out by Cullen in his translation of Geoffroy's research paper to his own pedagogical context. In that case, Cullen added considerably to Geoffroy's original theory in order to prepare it for its role in his pedagogy. Similarly, the very theory that Elliot was translating for pedagogical consumption was drawn originally from Irvine's theory, itself disseminated solely within the pedagogical context. It would thus be incorrect to assume that any such rudimentary line of demarcation between pedagogy and research was rigid. We must bear in mind first and foremost that relations between the two contexts were complex and traffic across the line of demarcation was rarely one way. Nevertheless, although we must be cautious in reading too much into this, there is some evidence that a distinction was being drawn in the minds of my actors between research and pedagogy.

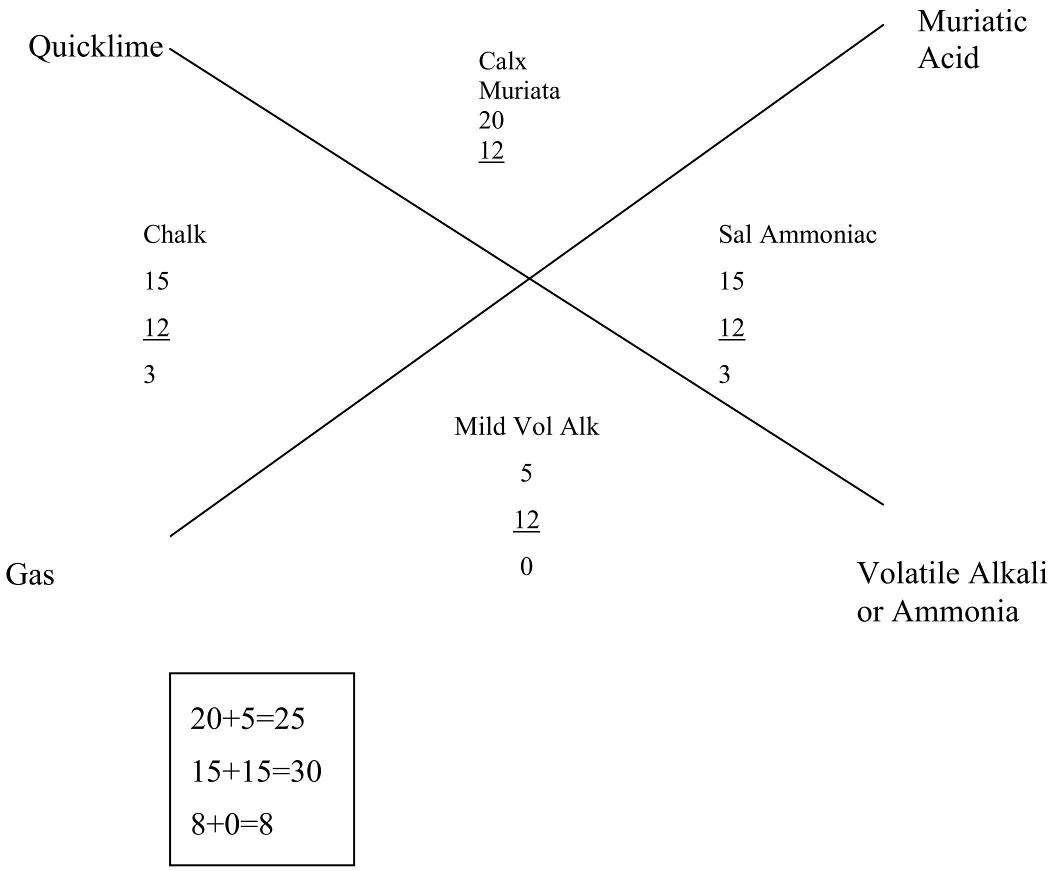

Figure 5: Diagram of the effects of Heat on Affinities, Fordyce 1788.

5. The Common Ground

While previous chapters have revealed the variety and diversity prevailing amongst the components of affinity theories, this one examines the underlying consensus. The phrase heading this chapter, ‘common ground’, is used in two senses. Firstly, it describes the components of affinity theories that were present in each individual theory without variation. Secondly, it refers to the role taken by the doctrine of affinity as a whole in providing a ‘disciplinary common ground’ for chemists.

My decomposition of an array of affinity theories into their constituent parts has revealed both variety and and underlying consensus. In addition to the structural similarities already highlighted, there were other, predominantly tacit, components of affinity theories to which all theorists subscribed. This bundle of components I call the ‘logical common ground’, and in the first section of this chapter I endeavour to parse this notion, revealing the components that formed the necessary (although not sufficient) elements of an affinity theory.

The common assumptions that constitute this logical common ground are distinct from the theoretical components set out above. Those in chapter 3 were functional component-types, providing rules or instructions to enable affinity theories to be practically utilised. Without a conceptual understanding of substance, combination and order the actual application of an affinity theory was simply not possible. In contrast, the components that I exhibited in chapter 4 as examples of ‘supplementary components’, were added to theories either to preserve or extend their explanatory and predictive power. For both functional and supplementary component-types, as I have shown, there was an element of choice within each component-type, which are perhaps best conceived as clusters of possible components. In contrast, the components of the common ground were ‘universal’; included in all affinity theories alike and forming the basis of each theory. To revert to the metaphor of chapter 3 above, if my decomposition of affinity theories has distilled off a variety of components, the common ground might be seen as the *caput mortuum*, the residue that remained after each distillation. As such, it perhaps offers the best way we have of characterising the ‘doctrine of affinity’, as the common basis of all the variety of affinity theories adopted by individuals.

The second section of this chapter details the various common assumptions that prevailed amongst chemists in consequence of the the role taken by the doctrine of affinity as a ‘disciplinary common ground’. This role was most clearly in evidence in chapter 2 above, as we saw how affinity became foundational to the discipline of chemistry. Although individual affinity theories undoubtedly varied, the logical common ground ensured that the doctrine as a whole appeared homogeneous, sufficiently so for the undoubted variety to be ignored. Cullen’s utilization of his affinity theory as a pedagogical tool transformed its status into a chemical tool. Affinity thus became foundational to the discipline, providing the disciplinary common ground that in turn, entailed certain common assumptions about the practice and aims of chemistry.

5.1 The Logical Common Ground

I begin with an exploration of the specific components of the logical common ground. Geoffroy’s affinity table was imprecise, limited in range and scope, and his articulation of his single law of affinity left many questions unanswered. Yet this very law (or an abstraction of it), together with the conceptualisation of the affinity table combined to form the logical common ground of the doctrine of affinity. The first section below examines the articulated component, the law of affinity. This component is not particularly difficult to elucidate; the same, unfortunately, cannot be said of the other component, the concept of the affinity table.

I unpack this predominantly tacit conceptualisation in section 2. The concept of tabulation in general necessarily implies that the relations depicted are both orderly and sufficiently consistent to be ascertained and represented. The very particular conceptualisation of the affinity table implied that such order was transitive. The concept of the affinity table also presumed a taxonomic system that discriminated the substances that were the subject of this ordering function, both from each other and from those that could not be so ordered.

The third sub-section explores the correlation between the components of the logical common ground and the functional component-types set out in chapter 3. As the assumptions of the former were common to all affinity theories, I argue that they provided the criteria for the formulation of the functional components, as well as restricting the scope of their variety.

5.1.1 **Articulated Affinity: The Law of Affinities**

The doctrine of affinity cannot be said to have originated anywhere but with Geoffroy's 1718 *Mémoire*. Although many have endeavoured to settle the origin firmly in England at Newton's feet (chapter 2 above), as I have shown this is somewhat specious. Geoffroy's law of affinity might, with hindsight, be perceived as implied by Newton's hypothesis, but Newton had not intended to formulate any such law. Indeed, there is no indication that he envisaged any further generalisation of the phenomena beyond the case that he cited. Geoffroy, on the other hand, drew on the regularities of similar phenomena to formulate an empirically justified law that was generalised across a range of different types of matter. As Klein has pointed out, the substances implicitly included in his table as the results of the various combinations included alloys, amalgams, metallic and neutral or middle salts.[1] The inclusion in the affinity table of generic columns (such as that for 'esprits acides') confirmed, if such confirmation were necessary, that this law was posited as a regularity of nature. A phenomenological belief in the existence of this regularity, rather than any of its specific manifestations or any particular causal factor, formed the basis of affinity theories.

The law was first enunciated in Geoffroy's *Mémoire*, and it was from this paper that the components of the logical common ground proceeded. The single articulated component of the common ground is plainly discernable, corresponding loosely to the text of *Mémoire* generalised in the form of the 'law' of affinity. To repeat the law:

> "Toutes les fois que deux substances qui ont quelque disposition à se joindre l'une avec l'autre, se trouvent unies ensemble ; s'il en survient une troisiéme qui ait plus de rapport avec l'une des deux, elle s'y unit en faisant lâcher prise à l'autre."[2]

This statement can be found reiterated in almost all presentations of affinity

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[1] Klein 1995, 80.

[2] Geoffroy 1719, 203.

theory in Britain with little amendment; for example Lewis's 1763 assertion:

> "a third body may have a stronger affinity to either of the component matters than they have to one another, in which case, on presenting to the compound this third body, the former union is broken, and one of the first bodies coalesces with the third, while the other is detached and separated."[3]

This is the familiar account of the action of affinity, setting out the epitome of what came to be known as single elective attraction or single affinity, the primary model of the action of affinity. This model was used firstly to ascertain, and then to demonstrate, the different affinities of substances. Nicholson offered essentially the same statement in 1790, although the details of his affinity theory are more complex than either Lewis's or Geoffroy's:

> "When a compound of two principles is so affected by the addition of a third, that a new compound is formed, of this last principle and one of the other two; at the same time that the principle which was part of the original compound, but does not enter into the second combination, is disengaged; the decomposition and new combination are said to be produced by simple elective attraction or affinity."[4]

Geoffroy's law was a practical law, a generalisation of observed phenomena. It did not postulate a force or attraction between substances, but set out what happened in a conjunction of three different substances with varying 'tendencies to join together'. The cause or causes of these phenomena, represented as inter-substance relations ('rapports'), were deliberately left unexplored. Nicholson's iteration is perhaps closer to the spirit of Geoffroy's original statement of his law than Lewis's, being quite clear in its primary commitment to the phenomena as experienced by the chemist. Lewis's version, in contrast, hypothesised a causal agent, affinity, which might be 'stronger' between some substances than others. In spite of these variations, emanating perhaps from divergent ontological or methodological commitments, the essence of the law remained, referring to the relative positions of substances in a 'triplet' of substances.

Certain of Cullen's lectures, though, set forth a subtly different form of the law

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[3] Lewis 1763, v.

[4] Nicholson 1790b, 77-78.

that made the link to the relative positions of substances in affinity tables overt:

> "This Table is easily understood being made in the same manner as Geoffry's [sic], the upper Substance will unite with any of the Lower, but if any of them be united with the Substance at the top of the column, any of the Intermediate ones will separate them."[5]

This version of the law, with its references to the relative positions of substances in each column clearly implied that Geoffroy's law was not to be considered to be the whole story of affinity. As we saw in 3.3.1 above, Geoffroy's law only compared the affinities between two different substances for a third. These relations can be set out in what I have called 'triplets'. The original formulation of the law referred to the initial comparison of affinities, to the experimental discovery of the relations between substances. Geoffroy translated his experimental observation according to his generalised law and then brought these observed relations between groups of three substances together in the form of a table. In contrast, Cullen's version of the law referred explicitly to the positions of substances in each column of his affinity table. It told his students how to translate the contents of the affinity table into practice. Geoffroy presented a generalised law that enabled the constitution of a useful synoptic table. Geoffroy's law could be understood and even utilised without an accompanying table; while the latter relied on the former, this was not a mutual relation. For Cullen's students, the law was more intimately bound to its accompanying affinity table to the extent that either without the other was meaningless. Cullen's pedagogy thus emphasised and enforced a new conceptual link between the law and the affinity table. This difference, subtle though it is, epitomises the conceptual change that took place as affinity theories assumed their status as pedagogical tools. Thus the law and affinity tables were necessarily coupled, as invariable components of every affinity theory. In this new conceptualisation, the law of affinity was only comprehensible (and useful) when set forth alongside an affinity table; any affinity theory necessitated a table of affinity.

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[5] Cullen n.d. [1760?], f 143r. The explanation given in Cullen 1757, f 97 matches this almost verbatim; it is sufficiently close a match to suggest that the two MSS are from the same course, which would date the British Library MS at 1757.

5.1.2 Tacit Affinity: The Concept of the Affinity Table

Under the influence of Cullen's pedagogy the law of affinity was explicitly linked to an accompanying affinity table. The criteria for such tables were not, however, particularised; the law did not necessarily refer to any particular affinity table, or even any particular form of table. Cullen's version of the law was not going to be particularly useful without an affinity table to refer to. On the other hand, it would at least be comprehensible so long as the chemist was familiar with the concept of an affinity table, with what such tables did, and what information was contained therein. I would suggest that the law, as Cullen presented it above, did not require an actual table to be meaningful (although it certainly would, to be useful), but it did require an appreciation or understanding of the concept of an affinity table. (Geoffroy's original law was both meaningful and useful without even the concept of an affinity table.) Cullen's teaching clearly tightened the bond between the law and the table; sufficiently so, that affinity theories became meaningless without some understanding of the concept of the affinity table to which they referred.

The concept of the affinity table which this section endeavours to unfold is not an easy conceptualisation for the historian to articulate. Perhaps the most important point that should be borne in mind is the fact that it refers to a conceptualisation of the *ideal* affinity table. Chemists constantly bemoaned the imperfections of their own affinity tables, and those of other chemists'. From Fontenelle who, even as Geoffroy's table was initially set loose on the world, looked forward to a more perfect table[6] to Cullen, who objected to so much of Geoffroy's table that he produced his own, to Fordyce, who, in the 1780s, was still telling his students that "although the Tables of Elective Attraction are not perfect yet as they are they are very usefull."[7] These chemists clearly maintained an ideal conceptualisation of the affinity table, to which the tables that they encountered were compared. This would comprise the essential criteria that distinguished such an ideal affinity table, referring to the type of information it was intended to convey, to its intended function. This, the

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[6] Fontenelle 1719, 37.

[7] Fordyce 1788, Lecture 14th Oct 1788.

concept of the affinity table, thus formed the tacit part of the common ground.

This section explores the two primary assumptions that can be discerned in the concept of the affinity table. The first assumption derives from the fact that affinity tables set out *ordered relations* between different substances. It presupposes that the tendencies set out in the table could be disposed to order, and that this order was transitive and consistent. The second derives from the fact that affinity tables set out ordered relations between *different substances*. The conceptualisation of the affinity table thus entailed the assumption of a unique taxonomy of the substances that would appear therein. This delineation of the facets of the concept of the affinity table is necessarily somewhat indistinct as a result of its tacit nature. Nevertheless, however shadowy, their outlines are discernible and I hope that my identification will be a first step in a ongoing process of historiographical familiarisation.

Geoffroy's original table was, of course, amended by chemists throughout the century according to individual empirical observations; many published tables modified Geoffroy's original, sometimes quite considerably. As we have seen in earlier chapters, extensive amendments took place both to the content and the form of the table. Poole's presentation of the first table published in Britain took the form of a series of sixteen individual 'tables' or series.[8] Lewis's first table took the form of a grid, but read from left to right rather than in columns,[9] while his second took the form of separate textual lists.[10] Lewis's researches on platina were apparently intended to supply further new affinity columns for the new metal, although these do not appear in his tables.[11] Practising chemists produced tables according to their own observations and preferences. It seems likely that most chemists kept their own affinity tables up to date, incorporating their own discoveries, and analyses and those of others. Cullen amended the contents of his affinity table throughout his career, including judicious corrections and additions until it was almost twice its original size.[12] Tables

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[8] Poole 1748, 383-386.

[9] Lewis 1753, xi. See Sivin 1962 for a detailed comparison of Lewis's and Geoffroy's tables.

[10] Lewis 1765, 28-29.

[11] They did, however, appear in those of Saunders n.d. [1766?], 52-55, and Warltire 1769b, 24-25.

[12] See e.g. the tables in Cullen n.d. [1760?], Cullen 1765.

were produced that incorporated other factors for convenience, as Elliot's table showed the resulting substance of each combination. Fordyce's of 1765 also showed new substances released when the action of affinity produced a decomposition of one substance.[13] Cullen, Black and, more conspicuously, Bergman divided their tables according to specific chemical practice as we have seen.[14] We have seen that affinity tables were easily able to accommodate the degree of translation necessitated by the Lavoisierian revolution.[15]

In spite of this variety amongst the form and content of affinity tables, all affinity tables, regardless of their particular form or content, performed the same function: they all ordered the relations that were believed to exist between different substances. The empirical bases of these relations were set out in the law, which, as we have seen, generalised the apparently preferential dispositions of different substances to combine. The law implied that the behaviour of groups of three substances was dictated by dispositional relations, or affinities, between pairs of substances within each group. These relations could be set out as 'triplets', as I showed in 3.3.1 above. Affinity tables brought together a variety of triplets to form columns or series that ordered the affinities of inumerable substances. This tabulation of these dispositional relations necessarily assumed that a transitive relation held between the relations set forth in the triplets. Thus the conceptualisation of an affinity table included the assumption that the relations depicted were necessarily both orderly and consistent.

The very concept of the tabulation of affinities necessarily implied a presumption of regularity and consistency. There are two aspects to this assumption; the first that the relations between pairs of substances were conformable to order and and the second that they were contextually consistent. The ordering of affinities into series in the pattern inaugurated by Geoffroy's table, extended beyond the triplets implied by his law. The version of the law as

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[13] Elliot 1782, facing page 105, Fordyce 1765, f 3-23.

[14] Black 1966, Cullen 1757, f 98.

[15] See George Pearson's enlarged version of Bergman's table of affinity which converted the phlogistic to the anti-phlogistic, with an apparent ease which rather belies the philosopher's insistence upon the incommensurability of the two theories. Anon [George Pearson] 1799.

set out by Cullen above makes it clear that a transitive relation was believed to hold between the affinities of substances within a column. The assumption of such a relation ensured that affinities (whatever they might be) could be ordered into relational series.

Geoffroy's law claimed that if substances B and Z were combined as BZ, and a third substance, A was introduced, if A had more *rapport* with B or Z than existed between them, it would replace it in combination. From such an operation, either the relative affinities of A and B for Z or of A and Z for B could be ascertained. But the ordering of these relations or affinities into tables consisting of more than three substances required a further assumption that the affinities held a transitive relation even across different 'triplets'. For example, experiment (i) might look like this:

$BZ + A = AZ + B$

This would produce triplets:

Z	A
A	Z
B	B

Experiment (ii):

$CZ + B = BZ + C$

would similarly produce triplets:

Z	B
B	Z
C	C

The tabulation of these affinities would then require the addition of the two triplets showing the affinities for Z. The two triplets setting out the affinities of A and B could not be combined. Two separate experiments had showed that the affinity A for Z was greater than that of B for Z and that the affinity of B for Z was greater than that of C for Z. Assuming, therefore, a transitive relation between affinities, such that if $AZ>BZ$ and $BZ>CZ$, then $AZ>CZ$, a column could then be produced showing the affinities of A, B and C for Z as below:

Z̲

A

B

C

The very concept of the affinity table thus implicitly assumed that affinity was a transitive relation. This was not implicit in Geoffroy's law; it was, however, implied by the concept of the affinity table.

The only way that the triplets that Geoffroy's law implied could be combined was by assuming that this transitive relation existed between the affinities for one particular substance. This was why the two triplets produced above showing the affinities of A and B could not be combined to produce a single affinity column. Affinities were only comparable as long as one of the substances in each pairing remained the same. This assumption of transitivity thus essentially determined the very particular configuration of an affinity column, and, by extension, of affinity tables.

It was this assumption of transitivity inherent in the concept of the affinity table, I would suggest, that naturally inspired many chemists to assume some sort of causal uniformity. Geoffroy, of course, did his utmost to avoid such a proposition, but his own affinity table, which took the form of a true table, with the columns lined up alongside each other, the whole encompassed by a thick black line, must have supported their assumption. It was perhaps this implication that led some chemists, beginning with Cullen, to translate the 'relations' of Geoffroy's table into an assumption of a single causal factor.

The cause of affinity was rarely overtly speculated upon, although it is clear that there was a variety of opinions on the matter. Although most chemists disavowed any particular causal allegiance, preferring, like Newton, to contemplate the effect rather than the cause, there seems little doubt that they only envisaged a single cause (whatever it might be) to lie behind the relations set out in the tables.[16] This assumption of a single causal factor forms part of the common ground as part of the concept of the affinity table. Although affinity tables only compared affinities within each column, a cross-columnar correspondence is in fact implied in the translation of the triplets implied by the law to the tabular form. To return to the experiments set out above, my two experiments (i) and (ii) had shown:

(i)(a)	(i)(b)	(ii)(a)	(ii)(b)
Z	A	Z	B
A	Z	B	Z
B	B	C	C

If we imagine two further experiments:

(iii) AB + C = AC + B and (iv) BC + D = BC + D, this would similarly produce triplets:

(iii)(a)	(iii)(b)	(iv)(a)	(iv)(b)
A	C	B	C
C	A	C	B
B	B	D	D

Experiment (iii) gives us another triplet for A and our first for C, while experiment (iv) gives us sufficient information to produce columns for B and C:

B	C
Z	A
C	B
D	D

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[16] There is perhaps an interesting correlation between the forms that affinity tables took and the causal explanation assigned. As an example of negative evidence, Lewis, who had eloquently and specifically rejected any causal implication of his affinity theory, divided his second affinity table into a set of 19 separate textual series. Lewis 1765, 27-29.

Note here though that the information gleaned from experiment (iv), which compared the affinities between B, C and D, is used (along with the triplets from the earlier experiments) to formulate both the columns showing the affinities of B and C. Thus, although the relations delineated in the affinity table were only intended to be compared within each column, avoiding any implication of cross-columnar relations, such cross-columnar relations were inherent in the very building of a table. The fact that triplets deriving from different experiments had to be pulled together to create the column for Z implied this, but it was confirmed in particular by the fact that the triplets from experiment (iv) enabled the formulation of two different columns showing the affinities for B and C. Although, as relational series, affinity columns could not be compared directly, the implicit cross-columnar consistency was to underpin Cullen's innovative analysis of double elective attractions, as well as Fordyce and Kirwan's attempts at comparison and quantification of complex affinities.

The use of the four experiments set out above to produce our three affinity columns also serves to illustrate a further aspect of the common ground that inhered in the concept of the table. The relations between substances as set out in affinity tables were both drawn from and applied to different experiments, and different combinations of substances in different contexts. Our four experiments were carried out at different times, perhaps in different places, under different conditions, using different substances and probably different equipment, possibly even by different operators. And yet the results of these experiments were brought together into a single table where the discrepancies between such circumstances became invisible. The concept of the table thus necessarily included an assumption that the affinities represented therein were contextually consistent. That is, in different places and at different times, and under differing circumstances, the affinities between substances did not change.

Of course it quickly became clear that the observed affinities of substances did, in fact, change in certain circumstances. Hence Bergman's introduction of a table that differentiated between affinities observed in 'the wet way' and 'the dry way'. But this did not necessarily refute the assumption that affinities were consistent. Bear in mind that we are trying to elucidate the concept of the *ideal* affinity table. Affinities as observed might be obstructed, destroyed, tempered or augmented by particular circumstances, but this was regarded as a secondary factor. The underlying affinities remained consistent, even though they were subject to perturbations as a result of external influences. Thus Bergman could talk of the 'free attractions' that he believed were observed in operations carried out in the wet way. While affinities were admitted to fluctuate in certain situations, as with the addition of heat, or in the presence of other affinities, or even (for some chemists) when one substance was present in excess, we have seen that such fluctations were assumed to be obstructing or perhaps perturbing the otherwise consistent affinities.

Other substances present in a mixture, particularly those that had been easily overlooked by Geoffroy and his contemporaries, substances like water and air, were regarded as fruitful sources of interference with affinities. Nevertheless, affinities were assumed to act consistently unless and until other forces or influences interfered. This was perhaps set out with greater clarity by Mill as the opposition between a natural *tendency* and a *disturbing force*.[17] Affinities were perhaps the archetypal tendency (they were, after all, often described as the 'tendency to combine') and as such acted in an orderly fashion according to natural law. As we have seen (particularly in Chapter 4), chemists recognised that apparent exceptions to affinities were in fact the consequence of external factors interfering with their action. That the underlying tendencies that were affinities remained consistent was a universal assumption. Similarly, as chemists sought to accommodate these interferences into their affinity theories, although their methods of accommodation were dissimilar, there seems to have been little doubt that the variations themselves would be found to be in accordance with some system, and thus themselves operate on a consistent, and possibly measurable, basis. Affinity was presumed to be orderly, even in its disorder.

As the above makes clear, the concept of the affinity table also incorporates an assumption that the information contained therein was derived directly from experimental observation. The law of affinity emphasises this connection. Evidence of the affinities between substances had to be gleaned from

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[17] Mill 1925, 293-294. For a modern take on this, see Cartwright 1989.

experimental examination of the way in which such substances behaved when brought into contact with each other. This was commonly perceived to be an unproblematic relation. However, this perception was not always altogether justified. For example, the column for B produced from the four experiments above shows the relative affinities of B for Z, C and D. This column predicts that if Z be added to a compound BD then the D would be expelled from the combination, leaving Z and B combined. But we did not have to actually carry out this experiment, in order to predict it, or for the relation to be included in our fledgling table. The column we have produced, derived from a series of experiments, with the assumption of a transitive relation between affinities, enabled this purely theoretical prediction. The prediction could, of course, be checked and confirmed experimentally, but it seems likely that the sheer number of such experimental checks that would be required would dissuade most chemists from such an action. This is probably why Bergman admitted that his table was not perfect, saying "when I reflected on the shortness of life and the instability of health, I resolved to publish my observations, however defective."[18]

The assumption of transitivity thus ensured that it was quite possible to depict relations in an affinity table that had not actually been proven by experiment. In reality, not every relation depicted in an affinity table could be assumed to derive directly from experiment, although it was undoubtedly true that many did. Bear in mind here that affinity tables were never presented alongside detailed explanations of the experiments from which the relations set out therein were derived. Even Bergman's *Dissertation*, which incorporated a great deal of information concerning how his immense tables had been put together, did not do this. It would undoubtedly have negated the point of affinity tables if this had been normal practice. Accordingly, the embedded discontinuity between the observations and the contents of the tables was not usually evident. Because a large proportion of the contents *were* derived from experiments, and because the compilers of the tables did not enter into lengthy digressions explaining precisely *which* relations were empirically proven and which were theoretically

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[18] Bergman 1970, 70.

derived, the assumption of empirical justification was universal. In any event, the concept of the affinity table has to be taken as referring to what might be termed an *ideal* affinity table. Such an ideal table was undoubtedly conceptualised as containing information derived straight from observation.

The second main point that can be extracted from the concept of the table derives from the fact that affinity tables showed the relations between *different substances*. Although admittedly some chemists argued that the same power was responsible for cohesion or aggregation acting within a single substance,[19] an affinity table was unable to show such a relation. The concept of the table therefore did not incorporate such a notion; the relations shown therein were between heterogeneous substances, 'particular species' of matter. This assumption was exemplified by the tabular concept, which both reflected and reinforced the distinctions between the various substances.

The concept of the table prescribed limits both on the class of matter with which chemists were primarily concerned, and on the degree of difference that marked the distinct species. My algebraic examples above of experiments, the information gleaned from them and the resulting columns of my affinity table relied upon the identification of letters with particular, different substances. There was no doubt in this example that A was not B (or indeed C, D or Z) and there was no indication that it was transmuted into B at any point. A was different from B, and remained so, but it was assumed that it could be recovered. The grids of affinity tables were intended to be filled by substances that behaved like this; identifiable as distinct from each other, they were not presumed to be absolutely simple, or indeed to belong to the same level on a scale of absolute complexity. They were merely required by the very conceptualisation of the table to be distinct from each other, stable in the context of the operations that constituted the tables, and recoverable from combination. Bergman's characterisation of some of the newly distinguished substances that appeared in his tables puts this assumption in a nutshell:

> "Should they be derived from others, they ought not, on this

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[19] Nicholson 1795, 155. Nicholson seems to have subscribed (on occasion) to some such idea. In general, it seems to have been a component that appeared more commonly in the affinity theories of French chemists, most notably Lavoisier. See Kirwan 1968, 46.

> account, to be excluded, for they are now different, have constant properties, exercise their attractive powers without decomposition, and can at pleasure be obtained perfectly alike"[20]

Klein has set out the criterion for the inclusions of substances in affinity tables, referring to the chemists' conceptualisation of substances that were homogeneous, relatively stable and retrievable from combination.[21] Her analysis essentially matches Bergman's description, and is also familiar from elsewhere. The function of an affinity table in listing the relations between different substances presupposed the heterogeneity of matter; it encompassed an implicit taxonomy based on such analysis that could be achieved by the exercise of a distinctively chemical methodology. This assumed taxonomy was inherent in the very conceptualisation of the affinity table. In Chapter 3 above we caught a brief glimpse of the basis of this classification of the bodies that were routinely included in affinity tables and that formed the basis of a useful, practical chemistry. Fordyce's notion of operationally contingent elements, concisely explained in Bergman's terms as substances which "exercise their attractive powers without decomposition"[22] was specified in his lectures as a component of his affinity theory, but this was one of the rare occasions on which a component that was intrinsic to the concept of the affinity table was glimpsed. The same notion is obliquely referred to by Nicholson in his explanation of Bergman's tables:

> "the substances enumerated are considered to be simple, *as far as relates to the facts exhibited* in these sketches."[23]

In practice this meant that the affinities between sulphur (for example) and metals could be exhibited in one column of an affinity table alongside the affinities between vitriolic acid (believed to be itself a constituent of sulphur) and metals. Sulphur was capable of combining with metals (to form hepars) without decomposition, and so too was vitriolic acid. The classification of the substances that appeared in affinity tables was thus based on a behavioural

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[20] Bergman 1970, 71-72.

[21] Klein 1996, Klein 1994, Klein 1995.

[22] Bergman 1970, 72.

[23] Nicholson 1795, 165 (my emphasis).

hierarchy, avoiding questions of absolute ontological complexity. Perhaps this tacit adherence to the distinctively chemical taxonomy implied by the concept of the affinity table might explain the apparent reluctance of most chemists to explicitly clarify or define the substances appearing in affinity tables on ontological grounds. On this view, such an explanation was unnecessary, as the affinity tables themselves provided a tacit definition.

5.1.3 **Correlation: The Logical Common Ground and the Functional Components**

In the introduction to this chapter, I mentioned that the logical common ground was a necessary but not sufficient part of an affinity theory. The logical common ground also entailed an assumption that the information depicted in affinity tables was empirically justified, and that it could be reapplied to chemical practice. Affinity theories were intended to be useful, to aid chemists in their practices. There was, however, a gap between the logical common ground and such a useful affinity theory. This gap was filled by the functional components set out in chapter 3.

All the component-types set out in chapter 3 were grouped together on the basis of their functional similarities. These component-types were also distinguished from those set out in chapter 4 as being required for the operational utility of affinity theories. To take an example from Nicholson's description of the construction of an affinity table:

> "If it were possible to procure simple substances, and combine two together, and to this combination of two to add one more of the other simple substances, the result of the experiment would in many cases determine, by the exclusion of one of the three, that its affinity to either of the remaining two was less than that between those two respectively."[24]

If we imagine trying to follow this description in practice, we can see that a diverse range of additional theoretical information would be required. For example, we might draw on our own ideas of what Nicholson meant by "simple substances" (how would one know?), and we would also want to know a little more about combination (combine in what proportions? Does it matter? How to

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[24] Nicholson 1795, 160.

know when they were combined?). The components of the logical common ground do not offer answers to these questions. Although, for example, the law of affinity implied a comparison between combined substances and expelled or free substances, it did not actually give any information how to distinguish the two. Or indeed how to identify the particular substance 'excluded'. The array of components set out in chapter 3 were formulated to supplement the logical common ground, by specifying methodologies and epistemic strategies that answered such practical questions. However, these strategies were at the same time founded on the logical common ground, presupposing both the law of affinity (in some form) and a conceptualisation of an ideal affinity table.

The components of the logical common ground incorporated an assumed dependence on chemical practice. The law of affinity was a generalisation of the observed behaviour of conjunctions of particular substances and affinity tables were conceptualised as matrices for the collation and representation of experimentally acquired knowledge. They purported to represent the observed behaviour of particular substances, and were understood as synopses of this behaviour. Importantly though, the information contained within such tables was believed to correspond to the behaviour of substances in the 'real' world. As tables were built by collating information gleaned in the laboratory, this information could be reapplied in the laboratory context when desired. There was a further principle inherent in the concept of the affinity table that, at least with regard to the model of single affinity (the model that derived from the law), they were predictive. Cullen's version of the law emphasises this point. He specifically described how the affinity table could be used in this predictive sense to guide the chemist in his endeavours to combine or to separate substances. This predictive function was assumed on the basis of the perceived dependency of affinity tables on observation and experiment.

Thus the components of the logical common ground point to the existence of a two-way link to the practice of chemistry. This link entailed, for example, the assumption that the contents of a table could be influenced by new empirical observations. The heuristic or predictive aspect of this link, however, also implied that part of the intended function of affinity tables was to guide chemical practice. Nevertheless, in spite of this fundamental connection between the logical common ground and the messy, manual practice of chemistry, the abstraction of the former from the latter was similarly ingrained. Thus, although the connection was perceived, the supplementary assumptions of the functional components were also required to enble the application of affinity theories to chemical practice.

As Nicholson's example shows, the building of an affinity table was not based solely on the logical common ground, but also on the functional components formulated to supplement the logical common ground. Mediating between the cognitive conceptualisation of the logical common ground and the observations, experiments and experiences that made up the actual physical activity of doing chemistry, the functional components bridged the concept-practice gap. Similarly, the application of the information contained in the table to actual chemical activity was informed by the practical instructions contained in the functional components. The functional components thus bridged the gap that existed between the theoretical concepts of the logical common ground and the practice of chemistry.

It will be noted that there seems to be a correlation between the two aspects of the concept of the affinity table set out above and two of the functional component-types that I picked out in chapter 3. The component-types dealing with the variety of concepts of substance identities are clearly linked to the assumed taxonomy of substances inherent in the concept of the affinity table. Similarly, the variety of components dealing with concepts of order would seem to correlate in some way with the transitivity assumption implicit in the concept of the affinity table. There is also a further correlation that is perhaps a little less obvious, between the 'combination' component-type and the law of affinity. Bear in mind that the latter type grouped together various components dealing with the effects and mechanisms of combination, while the law of affinity offers a model for the combination (and separation) of substances.

On the basis that the logical common ground by definition consists of the 'universal' components of affinity theories, this is perhaps not particularly surprising. The same conceptualisation of the affinity table was held by all affinity theorists, and formed a tacit part of their individual theories. The law of affinity (in whatever form it was articulated) was similarly a necessary component of all affinity theories. The fact that all the many and various functional components were founded on the same logical common ground thus perhaps accounts in part for the correlation with the component-types that appeared in chapter 3. All aspects of the logical common ground might be assumed to be influential on the formulation of the functional components Nevertheless, it is a correlation that deserves to be scrutinized a little closer.

Although the logical common ground formed the nucleus of every affinity theory, it was insufficient to provide a useful, applicable theory on its own. Any such practical application would necessitate the clarification of certain ill-defined notions, such as those of substance, combination and order. These notions were entailed or implied by the logical common ground, but were not determined by it. Hence the formulation of the functional components, which were thus both inspired by and, to a large extent, determined by the logical common ground.

The logical common ground provided the criteria that governed the variety of components set out in each functional component-type. As the affinity table was conceptualised in terms of its functionality, so it was its functional application that prompted the formulation of the functional components. My component taxonomy, grouping the individual components of theories according to their function, saw through the variety of articulated affinity theories to the logical common ground that underpinned them. In spite of their diversity, the scope of the components exhibited within each functional component-type was not boundless. No one would, for example, include a component in their affinity theories that suggested that affinities might be ordered by a method of throwing substances at a wall to see which slid down more rapidly. The scope of the variety that was exhibited in each component-type was clearly influenced by the logical common ground that underpinned each theory. No component could be legitimately formulated to be included in an affinity theory that contravened the components of the logical common ground. The creative powers of affinity theorists were restricted by the law of affinity and the concept of the affinity table, both of which tacitly constrained the degree of permitted divergence of components within each type.

5.2 The Disciplinary Common Ground

Having endeavoured, in the first section of this chapter, to shed some light on the logical common ground that formed the nucleus of each and every affinity theory, this section takes an entirely different focus.

Throughout this study (particularly in chapter 2) we have seen evidence of a tacit consensus amongst chemists concerning the status and role of affinity theories, and their relation to the discipline. Cullen's role in instituting this consensus was crucial. His deployment of his affinity theory as a pedagogical tool implicitly designated it as a unifying principle to the discipline. For his students, as affinity was one of the two agents of the chemist, affinity theories were seen as chemical tools. This new role taken by the doctrine as a foundation to the discipline in turn occasioned a series of disciplinary assumptions amongst chemists. These assumptions, although they did not form part of their affinity theories, were nevertheless common to all chemists who subscribed to the doctrine of affinity (in whatever particular theoretical form it might take). As such they formed what I have called the 'disciplinary common ground' amongst chemists.

The first of these disciplinary assumptions to be discussed below is the common assumption of the applicability of affinity theory to a chemical understanding of matter. Chapter 2 above indicated the role of pedagogy in installing the the doctrine of affinity (by which, of course, I mean a sort of aggregate of all the actual and potential affinity theories) as the basis of the discipline of chemistry. Implicit in this common subscription by chemists to the doctrine was an assumption that affinity was usefully applicable to their discipline and the expectation that it would continue to be so. This aspect of the disciplinary common ground might be seen as the assumption of the heuristic value of doctrine of affinity. It is evident both in the prevalence of affinity in chemical thinking, and in the apparent expectation of chemists that affinity would be of continuing and even increasing utility.

The routine coupling of the doctrine to the discipline, a union that was first instituted in Cullen's pedagogy, also resulted in the gradual identification of the theory with the discipline itself. Cullen's adoption of his affinity theory as a pedagogical tool involved the close identification of affinity with the discipline, to the extent that the methodological and epistemic boundaries implied by affinity were similarly applied to the discipline itself. This identification gave rise to a consensus amongst practitioners that the aims and practices of the discipline reflected the implicit boundaries of the doctrine of affinity. These implicit boundaries were another aspect of the disciplinary common ground examined in the second section below.

5.2.1 **Applicability: Utility and Expectation**

I have already indicated that the logical common ground incorporated the presumption of a reciprocal relation between affinity theory and chemical practice. As the tools of the chemist, affinity theories were intended to assist in the accomplishment of a performance, in the practical work of the chemist. Polanyi states that the creation of a tool necessarily involves the envisaging of the "operational field"[25] in which the tool will be applied. Cullen initially adopted his affinity theory as a pedagogical tool, assisting him to impose a coherent and unifying structure that underpinned his didactic endeavours. In the process, however, as he defined affinity as one of the two agents of chemical change, he invested his theory with the status of a chemical tool that allowed chemists to manipulate matter, to exploit its natural tendencies. The primary function of affinity theories began to be perceived in terms of the successful performance of the chemist's art. Note here the change in operational field. Cullen's affinity theory was invoked in his pedagogical performance, but as a result of this pedagogical strategy, the doctrine of affinity was coupled to the practice of the discipline. Affinity thus became a chemical tool. As Polanyi explains, "the identification of a thing as a tool … implies that a useful purpose can be achieved by handling the thing as an instrument for that purpose."[26] Where Geoffroy's affinity theory was a passive portrait of chemical practice and operations, for Cullen's students the theory became the paintbrush, the instrument that assisted the chemist in his endeavour to redesign matter. The discipline of chemistry and the doctrine were bound together by the implicit assumption that it was in this operational field that it was applicable.

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[25] Polanyi 1962, 60.

[26] Ibid, 56.

The use of any tool requires the user to have some understanding of its applicability, of where and when it should be used, and in order to achieve what result. A theoretical tool is no exception to this rule. In spite of the diversity amongst affinity theories that I noted in chapters 3 and 4, there seems to have been little doubt about where and when to utilise those theories. Chemists were clear on this aspect but nevertheless this may be the most tacit (in the Polanyian sense of being unarticulable rather than merely unarticulated) of the common ground components – and hence, for the historian, irretrievable. Nevertheless, I believe that this component can be glimpsed in operation in the case of the assimilation of novel, unexpected phenomena into the doctrine of affinity.

Bas van Frassen points out (as something of an aside) that the first response of scientists to new phenomena "whether actually encountered or imagined" is to widen an existing theoretical framework. [27] For my actors this widening of the framework to accommodate new phenomena could be accomplished, if necessary, by the addition of new components to their affinity theories. But when the chemist encountered the new phenomena, how was he to know that his affinity theory was the appropriate theoretical framework for the new phenomena he was dealing with. Was an affinity theory a useful tool for tackling this new phenomena, or not; was it applicable? Such circumstances put pressure on chemists to publicly justify their theoretical decisions. An example of some of the particular new phenomena in which affinity theories were judged to provide the appropriate framework will perhaps shed light on the criteria of applicability tacitly employed as part of the disciplinary common ground.

I have shown in chapter 4 above that from the 1760s onwards affinity theories were expanded by the inclusion of components linked in various ways to heat. Amongst these we noted that new components were formulated that postulated that heat itself was possessed of its own set of affinities. These components (explored in detail in 4.4 above) were formulated in response to Black's work on latent and specific heats, which described the newly discovered phenomena

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[27] Van Frassen 2000, 182. Van Frassen specifies that "by 'new' I mean here that there is no room for these phenomena in the models provided by the accepted theory." For Van Frassen, this is only the first phase of the response, which he couples with a second phase in which the framework is again narrowed in order to retain predictive power.

that heat was apparently absorbed by substances at different rates, and that during a change of state vast amounts of heat were absorbed or expelled from matter with no concomitant change of temperature. As we have seen, some chemists endeavoured to explain these phenomena in terms of their affinity theories, suggesting that the apparently absorbed heat was chemically combined with ordinary matter. This is the type of framework-widening exercise that van Frassen refers to; the amendment or extension of an existing theory in order to explain new phenomena. I have already indicated in 4.3 above that there was a fairly widespread perception that affinity theory was (or at least could be) usefully applicable to these new heat phenomena. Some particular aspect of the conjunction of heat with ordinary matter, apparently conformed (at least in part) to a model or pattern which chemists identified as being characteristic of affinity. The perception of such a pattern was the outcome of a non-verbal process of recognition and classification. Chemists were adept at using analogy to draw comparisons and it seems likely that this was a similar process.

For the historian, the details of this pattern are likely to be predominantly inaccessible. Nevertheless, we can make some relatively safe generalisations of the factors that suggested that affinity theory was applicable. It is clear from chapter 4 that those chemists who believed that affinity theory could be applied to the phenomena of specific and latent heat probably did so because they believed firstly, that heat was a material substance and secondly, that it was capable of combining chemically with other matter. The apparent absorption of heat by ordinary substances without any apparent change in temperature could certainly be viewed as suggesting combination, while the accompanying change of state accorded with the understanding of many that chemical combination resulted in an apparently new substance with new properties. What is interesting, though, is how far the phenomena could appear to depart from the pattern of the action of affinity, while still being judged to exemplify such action.

Examples of this kind of pattern-almost-matching abound in the literature of affinity theories. For example, platina, which could hardly be doubted to be a ‘material substance’, appeared to dissolve only in aqua regia and, with some difficulty, mercury. Platina barely had any affinities to speak of; but nevertheless, these were still classed as affinities when recorded by Lewis, who apparently never doubted that, few though they were, these were the same kind of affinities exhibited by other substances. Phlogiston, which had "never been got by itself",[28] was intangible, invisible and imponderable. And yet, it had been included in affinity tables from Geoffroy's onwards, as being possessed of clear and (relatively) distinct affinities that could be empirically justified. Heat too was not visible, and was not believed to possess weight, but it was apparently possessed of clear and precisely differentiated relations to all ordinary substances, particular to each and every different combination. For some, specific heat was an indicator of these affinities. The pattern here was not entirely matched, but it seems that such correspondences as did exist were sufficient for chemists to hurdle the gap and assume the materiality of heat. Viewed from this context, the widespread belief in a material heat assumes a more rational form than historians have so far appreciated.

As we saw in chapter 3, not all chemists believed that substances lost all their properties in combination (although admittedly most British chemists, following Cullen's lead, did). For those who did not, who believed that the properties were carried into combination, the apparent absorption of heat on change of state might not be so easily characterised as combination. The lack of any increase in temperature of the new substance would tend to refute the idea that the heat was chemically combined. These chemists would presumably be reluctant to incorporate a new component into their affinity theory that assigned heat its own affinities. Others objected to the assignment of affinities to heat on the grounds of the immateriality of heat, and here the default lay in the 'materiality' criterion. Such theorists (Fordyce, for example) would not attempt to explain these new phenomena by reference to their affinity theory. What is important here is that the pattern or grounds for applicability were accepted even by those who refused to allow that heat was subject to its own affinities. The assumption, drawn by analogy from familiar examples of the actions of affinity, that a material substance that could combine chemically was possessed of ascertainable affinities remained untarnished by exception.

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[28] Cullen 1765, MS 1920, f 72v.

The 'applicability' component of the common ground, the heuristic of the doctrine of affinity might thus be cautiously enunciated in the form of the pattern or model above. But how enlightening is this? After all, all that it does, is link chemical combination (however that might be defined) with the action of affinity. This component was implicit in the law of affinity tacitly assimilated by the tyro as he became familiar with the doctrine. It conferred on the affinity theorist the ability to extend his theory to cover novel phenomena or substances, or a new type of use, through the conviction of applicability. In the case of heat, those who did believe that affinity theory could be used to explain the phenomena of latent heat brought heat as a substance into the chemical fold, admitting it to the canon of objects of chemical (rather than philosophical or mechanical) investigation, in addition to its more traditional instrumental role.

Margaret Masterman's discussion of Kuhnian 'paradigms' offers a useful mode of analysis that sheds light on both this notion of 'applicability' and on the status of the logical common ground.[29] Masterman discusses at length the 21 different senses of the word 'paradigm' used by Kuhn in his *Structure of Scientific Revolutions*.[30] She orders these into three classes: Metaphysical paradigms; Sociological Paradigms; and Artefact or Construct Paradigms. The fundamental type of paradigm is what she calls the *construct paradigm*, which is a barely articulated

> "practical trick-which-works-sufficiently-for-the-choice-of-it-to-embody-a-potential-insight".[31]

Masterman's detailed exploration of the pre-science/science barrier leads her to argue that this notion of a trick, artefact or technique which seems to produce worthwhile results, but is no further developed theoretically is nevertheless paradigmatic. Masterman specifically argues that in this early stage of paradigmatic science the 'formal theory' is not yet formulated:

> "In a new science, … a very great deal of high-powered scientific activity is aimed at the right choice of the moment when it will be worth the labour to construct it. The alternative is 'just going

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[29] Masterman 1972.

[30] Kuhn 1996.

[31] Masterman 1972, 70.

> on as we are now'; that is, with some trick, or embryonic technique, or picture, *and an insight that this is applicable in this field*. And it is this trick, plus this insight, which together constitute the [construct] paradigm"[32]

I believe that the logical common ground, together with this insight of applicability exemplifies Masterman's construct paradigm. Cullen reconceptualised Geoffroy's original law of affinity to set out an 'embryonic technique' which incorporated the exemplar of the affinity table, and his invokation of this technique throughout his pedagogy implicitly claimed that it was useful to the practice of the discipline. Later affinity theorists adopted this construct paradigm, adding components according to necessity and practice. Masterman argues that the construct paradigm must be able to be used analogically in order to provide the 'metaphysical paradigm or metaparadigm' which is the next step before the 'sociological paradigm' or acceptance by the community of scientists. The attempts that we noted above to utilise the doctrine of affinity to decode the apparent combinations of matter and heat might be seen as an initial (somewhat faltering) step towards such a metaparadigm. The process of formation of the full affinity paradigm was clearly lengthy and throughout the 18th century scientists were working from the fundamental construct paradigm, without having settled on a metaparadigm. Masterman of course is expanding on the Thomas Kuhn's philosophy of paradigms and periodic revolutions; and her analysis is undoubtedly fruitful with regard to affinity. It is vital for my purposes, however, not to lose sight of that part of her explanation that even she finds difficult to articulate as part of the construct paradigm. Her notion that a new science requires the '*insight that this is applicable in this field'* cannot be underestimated in its importance as part of the disciplinary common ground. Without this insight, the logical common ground (the artefactual element of the construct paradigm), is ineffectual. This confidence that the 'trick' of the table will work, and will assist the chemist in the practice of his discipline is part of the disciplinary common ground, a universal, though unarticulated, assumption that in part accounts for the prevalence of affinity throughout the period under consideration.

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[32] Ibid, 69.

For the historian this opens up a new way of looking at scientific hypotheses, placing a greater emphasis on the role of pedagogy and training in scientific discovery. Galison and Assmus have emphasised the crucial importance of pedagogy and training in scientific explanation of novel phenomena in their study of CTR Wilson's researches into meteorological phenomena. Wilson's training at the Cavendish Laboratory in Cambridge, during which he "imbibed … the tradition of ion physics" meant that "for each new phenomenon, he would search for an ion-theoretical account".[33] Similarly, the foundational role allotted to the doctrine of affinity in Cullen's pedagogy naturally led he, and his students to turn to their own affinity theories to explain new or unfamiliar phenomena. Thus chemists used their theories to firstly identify new practices and new observations that might potentially impinge on the discipline, and where necessary to respond to them by formulating new theoretical components to their theories, bringing the new phenomena firmly within the bounds of their affinity theory and their discipline. I have shown elsewhere that in the 1760s Cullen developed a theory of heat and combustion that clearly indicated the dominant role that his affinity theory was taking in his philosophical chemistry.[34] This theory rested on a causal chain that was topped by chemical affinity, on which many heat producing phenomena (including fermentation and respiration as well as combustion) depended. Cullen taught his students that all chemistry involved the manipulation of the two agents of the chemist, heat and elective attraction (affinity). With the agency of heat brought within the ambit of affinity theory, the domination of affinity theory over chemistry would be complete. The role of affinity theory in such assimilations argues for the importance of affinity theories as part of the identity of the new science of chemistry.

5.2.2 **Boundaries: The Autonomy of Chemistry**

The previous section referred to Cullen's exploitation of his affinity theory as a pedagogical tool, and its concomitant coupling with the discipline of chemistry. Cullen also used his affinity theory, as we saw in chapter 2, to demarcate the

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[33] Galison and Assmus 1989, 266.

[34] Taylor 2006.

methods and aims of chemistry from other branches of natural philosophy. As he pursued this strategy, and as the doctrine of affinity became routinely identified with his discipline, the methodological and epistemological boundaries that were inherent in the doctrine of affinity were projected onto the discipline itself.

Chapter 2 gave a précis of Cullen's chemistry courses. To recap briefly, he taught that chemistry was the investigation of particularised matter, differentiated substances with distinct qualities. The role of the chemist was to engender new qualities on matter by combining and separating substances.[35] Combination and separation were thus the principal operations in chemistry. Affinity, the power in substances to combine together with a concomitant (according to Cullen's theory) change in properties, was responsible for all such combinations. It was also responsible for many separations. Early in each course of lectures, Cullen carefully demarcated physical from chemical methods of separation:

> "If I have a mixture of common sand & finely powdered chalks & want to separate these each from the other, one way of doing it is by affusing water, which will keep the chalk suspended after the sand had subsided; this is mechanical: the other way by Chemistry is by pouring on Vinegar, which will unite with the Chalk but leave the sand untouch'd."[36]

The general laws in operation in these two methods of separation belonged to different disciplines and indeed it was the distinction between these general laws that distinguished the methods of each. Lewis described the distinction thus:

> "The act of combination, whether in bodies brought into fusion by fire, or in such as are naturally fluid, is truly chemical, and the laws of the mechanical philosophy have no place in it."[37]

The mechanical method was based on the differing specific gravities of the substances concerned, subject as it was to measurement and mathematical comparison. The chemical separation of chalk and sand, using vinegar, was an

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[35] Cullen 1766, Lecture 19.

[36] Ibid, Lecture 9.

[37] Lewis 1763, ix.

instance of the operation of the law of affinity. The distinction of the methodology of affinity theory thus served also to demarcate the discipline of chemistry from natural philosophy. The latter at this time was concerned with "the general properties of matter such as impenetrability, figure, size, etc."[38] Chemistry, in contrast, dealt with "particular properties", and those changes that could be brought about in matter using chemical methods or agents.

Only the chemical agencies of fire and affinity had the ability of separating bodies once chemically combined, while affinity alone was responsible for such combinations. We have seen in Chapter 2 how Cullen's teaching made the alignment between between affinity theory and chemical methodology explicit, categorizing all the chemical processes into solution, fusion and exhalation on the basis of his affinity theory. All these operations, though, relied on the chemical agencies of affinity and fire. This became a core tenet of the discipline, as can be seen from the structure of Book I of Nicholson's *First Principles of Chemistry*, which similarly set these two agencies as the foundation of the discipline.[39] This sheds further light on the movement noted in chapter 4 to bring the understanding of heat within the compass of the doctrine of affinity.

Affinity theories thus determined the methodological boundaries of the discipline. Chemical processes and operations, the things that chemists actually did, were all classed on the basis of their theories. Anything else was just not chemistry. It might, of course, be pointed out here that distillation, an undoubtedly chemical process, could be carried out without additions, and that this process did not involve the action of affinities. However, as we saw from the components set out in chapter 4, this type of process, separating chemically combined substances, was conceptualised in terms of affinities. The affinities subsisting in the compound substance being distilled were somehow being overcome by the application of heat. Chemical union or combination, as Lewis made clear, was not subject to mechanical methods of decomposition:

> "As the chemical union, and the properties thence resulting, are

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[38] Cullen 1766, Lecture 9.

[39] Nicholson 1790b, 26-106.

> exempt from all known mechanism, so neither can the bodies be separated again by mechanic force."[40]

Cullen's discipline was characterised above all by its methodology and this was founded on his affinity theory. For all those chemists who followed his lead and set affinity theory at the heart of their discipline, their affinity theories set the bounds of chemical methodology.

Cullen's positioning of affinity theory at the base of his discipline similarly served to set ontological boundaries to its practice. For Cullen, his students and successors, combination and separation could only be accomplished by the agencies of fire and affinity, and only those substances whose affinities were set down in the affinity table were susceptible to the informed manipulation of the latter. The connection between chemistry and the doctrine of affinity was thus so intimate that the discipline, as taught by Cullen, could only be practised by reference to affinity, making use of substances with affinities that either had been or could be ascertained. We have already noted above the behavioural taxonomy that was implied by the concept of the affinity table. The universal adoption of this classificatory aspect of the concept of the affinity table led to a a social consensus that identified knowledge of substances with knowledge of their affinities. Knowledge of the affinities and behaviour of individual substances was necessary for them to become objects of chemical practice and this knowledge was codified in tables of affinity. Harriet Ritvo has noted the development of systems classifying the natural world that similarly reflected the "particular needs and experience" of a variety of interest groups "although they seldom bothered to articulate them theoretically."[41] It might be stretching a point to suggest that a substance that had no ascertained affinities was not yet recognised as a substance, but perhaps it would not be going too far to say that it was not yet recognised as a *chemical* substance.

This notion of recognition and identification by affinity was, of course, a circular relation. I have shown in Chapter 3 above that substances were recognised as individuals (or indeed classed into genera) in many cases by

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[40] Lewis 1763, v.

[41] Ritvo 1997, xi-xii.

identification of their affinities. When Cullen reached the point in his lectures of where he taught "the chemical history of bodies",[42] he marched his students through the classes of bodies, salts, earths, metals, inflammables, waters and in latter years, airs. The structure of this part of his courses seems to have remained pretty much the same right the way through his career, discussing firstly the class as a whole and then each individual member. He ran through:

> "an account of the properties to be found in every body, whether as produced by nature, or by artificial composition, & of the methods by which these properties may be changed."[43]

Accordingly, each property was particularised by its origin, the methods for its extraction/isolation, and by its affinities, by the action of which its properties could be changed. Affinity tables particularised and demarcated these distinct species and set out their chemical identities even as they relied on the identification of individuals for the articulation of their affinities. The classification system inherent to affinity theory thus became invisible and "the system's description of reality becomes true", a phenomenon that has been labelled the "principle of convergence".[44]

As the assumed correspondence between affinity and chemistry imposed and enforced methodological and ontological limits on chemistry, so too it entitled the discipline to its explanatory autonomy. As affinities were signalled by the activities of macro-scale property bearing substances, so explanations of observations in terms of affinities were deemed to be sufficient for the chemist. This is not to say that explanations that went a stage further were not attempted; we know that Cullen himself made at least one optimistic, but ultimately doomed, attempt to explain affinity in terms of the action of a Newtonian aether.[45] Although some progress was made towards explaining the mechanical movement of two heterogeneous particles towards each other by the action of the aether, he was unable to account for the elective nature of this movement. Indeed, the mechanical account of affinity may have thrown up more problems

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[42] Cullen 1766, Lecture 44.

[43] Ibid.

[44] Star and Bowker 1999, 49.

[45] Christie 1983, 91-95.

than explanations: if the changing density of the aether forced the particles together, how could this account for the preferential tendencies of matter? As I explained above, Cullen eventually seems to have settled upon an explanation of heat and combustion which set affinity at the top of the causal hierarchy; in this scheme the explanatory buck stopped with affinity.[46]

For the most part, Cullen's pedagogy explicitly discouraged causal speculation:

> "the Great Newton again introduced only an Effect or Phenomenon often taking place & defines Attraction to be that power by wch Bodies are dispos'd to approach each other, without saying how it was caus'd. With this Caution we might have expected it wou'd have been Universally admitted, but Foreigners have rejected it, … all these Abuses we shou'd avoid, & only call it the Determination of Bodies to each other, without pretending to say whether they are really drawn & forced towards one another."[47]

To cite the affinities of bodies as the cause of their combinations and separations was thus seen as being just as legitimate as to cite gravity as the cause of bodies falling to earth. Explanations which reduced dynamics to ontology were always likely to cause conflict, and even to be misunderstood on the grounds that there were such widely differing ontologies in circulation (compare, for example, Priestley's Boscovichian point atoms, Cullen's aetherial ontology and Nicholson's shaped particles).[48] Any explanation on ontological grounds was more likely to cause dissent and divert attention away from the grounds for consensus and agreement. The adoption of affinity as the foundation of chemistry implied a tacit agreement amongst chemists that for chemical purposes, explanations of phenomena that drew on knowledge of affinities were sufficient. Hence a physician called Edward Bancroft, for example, 'explained' the reason why silk was more difficult to dye with indigo than was wool by claiming that it had less affinity for the indigo than did the wool.[49] While Keir explained that

> "Metallic substances are in general more difficultly dissolved by

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[46] Taylor 2006.

[47] Cullen n.d. [1760s] A, 87-88.

[48] See Heimann P E and McGuire 1971; Taylor 2006; Nicholson 1790a, 154-5.

[49] Bancroft 1794.

> the marine than by the vitriolic and nitrous acids, because the first has less affinity than the other two with phlogiston, which is the medium of union betwixt metals and acids."[50]

As we saw in chapter 2, this same attitude was exhibited by Cullen throughout his chemistry courses; in the familiar separation of potash from aqua fortis by exploiting the former's stronger affinity for vitriolic acid. A chemical explanation was framed in terms of affinity. Nothing further was required.

Thus the doctrine of affinity, in providing a disciplinary common ground amongst practitioners of the discipline provided an explanatory language which could be understood and adopted by each and every chemist. This common language enabled communication between chemists, comparison of their results and understanding of each other's actions. As Elliot explained, the chemist with a knowledge of affinity theory would be able

> "to understand many particulars of the philosophy of chemistry, not … discoursed of. … he will now be capable of comprehending the reasonings of chemical writers, when treating of the theory of their art, or giving the rationale of any particular process; … he will also be enabled to comprehend the reason of the several general operations of chemistry."[51]

So, we can discern evidence of a tacit consensus amongst chemists that the methodological, ontological and explanatory boundaries implied by affinity theories, were projected onto the discipline of chemistry. An affinity theory was certainly not a *sufficient* condition for the practice of chemistry, but Cullen's pedagogy instituted an assumption that it was a *necessary* condition. As it became increasingly correlated with the discipline so too the conceptual boundaries implicit in the logical common ground reflected the boundaries of the discipline itself.

5.3 Conclusion

The components of the logical common ground formed the nucleus of each individual's affinity theory. The combination of the law of affinity with the conceptualisation of the affinity table entailed a number of universal

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[50] Keir 1789, 77.

[51] Elliot 1782, 131.

assumptions that underpinned each affinity theory. These assumptions are not easy to extract from the various theories examined above, being rarely if ever articulated, but I would suggest that they formed the 'essence' of the doctrine of affinity.

In spite of the variety inherent in the doctrine of affinity, chemical communication does not evoke a tower of Babel, nor a multitude of incommensurable theories. Quite the reverse, in fact. As Cullen transformed his affinity theory into a pedagogical tool that conferred both disciplinary identity and order on didactic chemistry, so he set affinity at the heart of chemistry, implicitly identifying the doctrine with the discipline itself. We have referred above to the pedagogical pyramid which disseminated affinity theories throughout British chemistry. Through this dissemination, the doctrine of affinity became foundational to most individuals' chemistry. For the majority of British chemists of the second half of the 18th century the discipline of chemistry was, to all intents and purposes, *defined* by the doctrine of affinity. The logical common ground, lying at the heart of all the affinity theories in circulation, conferred upon chemists a common basis for communication and on which to base their beliefs and understanding of their discipline. In this way, the doctrine of affinity, founded upon the logical common ground of Geoffroy's law and the concept of the affinity table, itself formed a disciplinary common ground for practitioners.

6. **Summary**

The previous three chapters have decomposed the doctrine of affinity into its constituent ingredients. In this final summary of my research, I reconstitute the doctrine from what I have learned, bringing it together with the chronological narrative of chapter 2. This will retell the story of the doctrine of affinity in Britain and assimilate what I have learned from my research.

Prior to Geoffroy's presentation of his *Mémoire*, chemists had few grounds for certainty in the material world. Traditional metaphysical ontologies were in doubt after the works of Boyle, Descartes and Newton. Causation was becoming an empirically questionable concept, while the properties and qualities of matter were believed by many to be mere appearances. About the only thing chemists seem to have been sure of was that what they saw was NOT what they had got. They were standing on shifting sand, with nothing against which to brace themselves. The majority, as I have shown, believed that the bodies that they mixed and separated were neither pure nor simple. Some, like water, were believed to be simple, but were thought to be impossible to get without impurity. Others, like the metallic substances (for those who held to some variation of the phlogiston theory), were believed to be compounded, but of what, was unclear. In his laboratory the 18th century chemist was doing well to keep the ambient temperature constant, the furnace functioning and the water out; the effects of other variables that might interfere with the action of affinity was impossible to foresee.[1] Where, in this chaotic world, were chemists to place their faith?

While perhaps factually accurate, the tone of my representation is in error. It reflects my present-day assumptions and conjectures: my knowledge of atoms and elements, of quantum mechanics and organic chemistry leads me to describe the 18th century vista as a panorama of ignorance, of things *not yet known*. I am guilty of allowing my knowledge of the extent of what my actors did not know to cast a shadow over their position. They could not have regarded their predicament so, and it is vital that the historian resists the

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[1] Eklund 1975, 4-7.

temptation to describe it thus. To correct the fault does not require revision of the basic picture, but rather a change of focus. Rather than contemplating in despair (as we tend do on their behalf) the extent of the *not yet known*, my actors were active in seizing on the regularities that did come to their attention, on what they *could* know. The regularities of affinity stood out against this background of chaotic unpredictability. In an arena with so few theoretical certainties or even observational regularities, those regularities that were apparent were made all the more manifest, and carried correspondingly greater conviction.

In 1718, Geoffroy presented his *Mémoire* to his colleagues at the Académie Royale des Sciences setting out the law that he had generalised from his observations, together with the synopsis of those observations, the table des rapports. The rapports set out in Geoffroy's table summarised familiar knowledge, both in the Academy and in the workshops of metallurgists and apothecaries.[2] The phenomena thus depicted were familiar to Geoffroy (and his contemporaries) long before he formulated his law and table. The table converted these *a posteriori* relations into spatial relations; knowledge summarised and made visible. Geoffroy's presentation of his law and table made it clear that the table served as a digest of observed rapports; he gave little indication that the relation between the table and the empirical observations that populated it might be reciprocal. The law and table were new, but perhaps it was not clear what practical use they might serve.

In Britain, there was apparently no interest in Geoffroy's *Mémoire*, either on publication or for some years afterwards. The gentlemen of the Royal Society made no comment at all on either the law or table. In the early stages of this research, when I was seeking evidence of the use of affinity theories in the pages of the *Philosophical Transactions*, I was daily disappointed. I struggled to reconcile this apparent lacuna with the ubiquity of affinity tables in books of chemistry published over the same period.

After some ten years or so, Geoffroy's *Mémoire* was assimiliated into the pedagogical arsenal. A few entrepreneurial private lecturers found that there

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[2] Klein 1996.

was some demand for the learning of chemistry. At this stage, chemistry was hardly taught at all in the university environment, being restricted to sporadic lecture courses at a few Universities. Shaw, a private lecturer, began to draw attention to Geoffroy's *Mémoire* in his lectures, suggesting to audiences that it offered a useful digest of the relations between substances. This view of the *Mémoire* persisted for some further fifteen years; we find no further mention of it until 1748 when we find a flurry of references appearing all at once. Lewis, physician and lecturer, pursuing a career along the same lines as that of Shaw, promised that a table showing the affinities between different substances would appear in his *Commercicum Philosophico-Technicum*.[3] Poole reprinted Geoffroy's table in his *Chymical Vade Mecum*, and Cullen began to teach chemistry in regular lecture courses at Glasgow University.

Between Geoffroy's *Mémoire* and this sudden activity, a change took place in the relationship between the law and the table. As we saw in chapter 5, Cullen presented the law of affinity in a new form that contrasts with Geoffroy's generalisation of empirical observation. The law now took the form of an instructional rule for the predictive use of the affinity table. This change is also evident in Poole's work[4] and Lewis's later *New Dispensatory*.[5]

The law and table were thus intertwined, dependent on each other for comprehensibility. This was the genesis of what became the logical common ground of the doctrine of affinity. It is unclear at what point, and under whose influence this change took place, but when Shaw referred his audience to Geoffroy's table he might well have explained it thus.[6] Shaw's lectures introduced the table in the context of an explanation of the resolution of substances by the addition of others, and the new conceptualisation would have been appropriate in this context. In any event, by the time Cullen began teaching chemistry, it seems that the reciprocal relationship between the table and the law was established, and the logical common ground was available to be built on.

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[3] Lewis 1748, 18.

[4] Poole 1748, 383.

[5] Lewis 1753, xi.

[6] Shaw n.d. [1733?].

My work has emphasised the foundational role of the doctrine of affinity in 18th century chemistry, as well as revealing the role of pedagogy in assigning it this role. A pathway can be traced following the changes in the way in which affinity was conceived, from Geoffroy's useful synopsis, to a pedagogical tool, to a chemical tool as part of the norm of the discipline. Cullen was responsible for initiating both these conceptual changes through his influential teaching at Glasgow and Edinburgh Universities. The first took place when he allotted his affinity theory the role of a pedagogical tool. The second followed directly on from this pedagogical strategem, as his students absorbed Cullen's teaching and with it, the assumption that an affinity theory was an essential tool in the practice of chemistry.

From the first years of his didactic career, Cullen enlisted his affinity theory in the service of his pedagogy. As we saw in chapter 2, he taught his students that affinity was the chemical agency responsible for all combinations, and many separations. As his students were taught chemistry they were taught his theory of affinity before they witnessed any of the phenomena that gave rise to it. It was presented early in the course, prior to the examination of individual substances and their affinities.[7] Cullen's transformation of his affinity theory into a pedagogical tool corresponded with its transformation into a general principle of his discipline. From this point forth, for novice chemists, the knowledge of the principle anticipated knowledge of the phenomena. Affinity was presented as one of the general principles of chemistry, and individual substances were characterised in terms of their affinities. Cullen also derived a new taxonomy for the processes of chemistry from the role of affinity as a general principle of the discipline. In consequence of the pedagogical need for structure, for principles upon which to hang his lecture course, his theory became a pedagogical tool.

The limited assumptions of the logical common ground were insufficient for Cullen's pedagogical purpose. For affinity as a general principle to be worth its salt it should be both practically useful and applicable beyond the contents of Geoffroy's original table. Cullen's lectures specifically advocated the use of

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[7] Cullen 1748, ii.

affinity tables as predictive tools, embracing the implications of the logical common ground. Geoffroy had not explained how affinities might operate in more complex scenarios, for example, nor had he specified any practical conditions for how substances should be mixed, how the chemist might know when substances were combined, or what other factors impinged on the order of their affinities. These rather routine details were omitted perhaps due to the context in which the original paper had been presented. Geoffroy's research had been presented to a community of experienced chemists and it would have been inappropriate for him to relate such mundanities in this context. Much of his audience would have been familiar with this tacit knowledge.

Cullen's lectures were presented in a different country almost a generation after Geoffroy's paper; they were removed both temporally and geographically from Geoffroy and his contemporaries. The information that Geoffroy had omitted to provide was unlikely to be available to Cullen. Even less was it likely to be available to his audience. Cullen's theory was to be presented to novice chemists. The details of how to apply knowledge of affinities in a laboratory context needed to be spelled out. Affinity theories and tables were formulated on a base of empirical observation, and as I have shown, the instructions set out in the functional component-types were essential to both the compilation of affinity tables and their application. Cullen expanded Geoffroy's table himself, and the practical information that Geoffroy had neglected to incorporate needed to be added both in order that he might use the theory himself, and that he might teach it.

Cullen accordingly formulated new, functional components to his affinity theory, to supply some of the details that Geoffroy had omitted. His practical specifications that one substance in any combination must be fluid, and that combination resulted in a change of properties (and could be distinguished from other sorts of mixture on this basis) were included in his lectures. He also developed entirely novel 'chemical equations' that enabled the easy depiction of the various separations and recombinations that occurred when two compound substances combined together.[8]

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[8] Crosland 1959, 75-6.

Not all of his new components were directly relayed to his students, however. Some, such as his apparent assumption that the intensity of heat required to separate combined substances was proportional to the strength of the affinity between those substances (noted in 3.3.1 above), can only be discerned obliquely from the notes of Cullen's lectures, and it would seem that these did not form part of his affinity theory in its guise as a pedagogical tool.

Cullen's pedagogy was cautious with regard to the cause of affinity and, indeed, to most speculations that lacked empirical justification. Although he translated Geoffroy's 'rapports' into 'attractions', Cullen was clear that this signified only the "determination of bodies to each other"[9] rather than the cause of such determination. As we saw in chapter 4, he would not be drawn on the paradoxical role of heat in increasing and reducing affinities. Only rarely did his private speculations spill over into his pedagogy, as in his 1765 exposition of his hypothesis of heat and combustion.[10] We might also suspect that the practical exigencies of pedagogy influenced the way in which he presented his affinity theory to students. Like Geoffroy, he did not have time to explain in detail how he arrived at the orders of affinity shown in his table, nor what might happen if heat (or indeed cold) was applied.

The second conceptual change that I noted above occurred even as Cullen presented his lectures, as his students watched and listened. Perhaps to best understand this change, we need to return to the demonstration described in the prologue to chapter 2. Cullen used the combination of potash and nitrous acid to synthesise nitre and the latter's subsequent analysis using vitriolic acid to demonstrate both the combining power of affinities, and their manipulation to produce analysis. This demonstration was also intended to convey to the students the "meaning of separating and combining",[11] responsible for all the changes in the qualities of bodies that were the particular concern of the discipline. Cullen picked this demonstration for maximum effect, to shows his students early in the lectures how chemical combination and separation could

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[9] Cullen n.d. [1760s], A, 87.

[10] Taylor 2006.

[11] Cullen 1749, 26.

change such qualities of bodies as fixity, hardness, elasticity and so on. Later of course, he specified that separation of bodies could also be accomplished by the action of fire, but this does not appear to have been specifically illustrated by a practical demonstration. From the students' point of view, then, they learned early in the course that combination and separation both involved the action of affinity, and that affinity was thus the primary agent of the chemist. Cullen's pedagogical decision perhaps implied a little more than he had intended.

Similarly with his comparison of mechanical and chemical separations (see 5.2.2 above). In this case, the particular form that his demonstration took specifically aligned chemical methodology with affinity by the exploitation of the different affinities of the sand and chalk that he was endeavouring to separate. These substances were not even chemically combined together, but they were still separated by the action of affinity. Again, from Cullen's point of view, this was probably the simplest and most effective demonstration of the difference between mechanical methods and chemical. From the students' point of view it was a further indication that to practice chemistry was to manipulate affinities.

From the viewpoint of Cullen's students, chemistry must have appeared to be predominantly about affinities. And Cullen's use of his affinity theory as a pedagogical tool emphasised this implied correspondence throughout. Thus affinity theories began to be perceived as chemical tools, as part of the chemical norm. This was the second conceptual change, and it was this change that set affinity at the heart of the discipline. Cullen's chemistry lectures, given over the course of nearly twenty years, initiated the construct paradigm composed of the logical common ground together with the assumption that it was applicable throughout the discipline. Cullen's students propagated this construct paradigm, basing their own lectures, textbooks and of course chemical practices on it. The pedagogical pyramid thus ensured that the construct paradigm continued to underpin the discipline throughout the Lavoisierian revolution and into the 19th century.[12]

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[12] It is worth noting that Jane Marcet's *Conversations on Chemistry* was still introducing affinity to its amateur 19th century audience as one of the 'general principles' of chemistry in 1817. Marcet 1817 Conversation 1, 1-25.

I would thus argue that it was Cullen's adoption of affinity as a pedagogical tool that caused the revival of interest in affinity that is clearly evident in chemical sources from the middle of the century. The process was of course continued by Cullen's own students, Black, Fordyce and Saunders amongst others. Cullen's students embraced his emphasis on affinity and included it in their own chemistry lectures, as indeed did their students in turn (particularly Black's).[13] This is what I have referred to as the pedagogical pyramid through which the doctrine of affinity was disseminated and dispersed. Subscription to a theory of affinity gradually became a mandatory qualification for the practice of chemistry. In this way, the doctrine of affinity came to provide a disciplinary common ground as part of the norm of chemistry.

From around 1760 then, the majority of British chemists regarded the doctrine of affinity as fundamental to the discipline. While the British pedagogical pyramid was clearly significant in prompting this viewpoint, it was supported by publications originating from elsewhere in Europe. Macquer's *Dictionary* and other French chemistry textbooks all ascribed great importance to affinity, but perhaps the most influential work was Bergman's *Dissertation*.[14] Although there is little explicit evidence (other than the sheer ubiquity of affinity in chemical publications from the 1760s onwards) that confirms this new status, many of the attempts to formulate new components set out above testify to this new perception. I explored in chapter 3 efforts by Fordyce and Kirwan to 'perfect' the doctrine by introducing a mathematical precision to the ordering of affinities. Such travails were unlikely to have been lavished on a theory that was not perceived to be of value. The English translator (Thomas Beddoes, according to Duncan)[15] of Bergman's *Dissertation* explained his decision to include textual versions of Bergman's tables as well as copies of the original tables thus:

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[13] Of course, not all chemical pedagogues from the 1760s to the 1790s were part of the Cullen headed pedagogical pyramid. Hadley, teaching chemistry at Cambridge from 1759 provides an example of a pedagogue who was apparently not connected with Cullen or his students. Hadley did incorporate an affinity theory as a large explanatory element of his teaching, although he did not use it in the same organisational way as Cullen.

[1414] Macquer 1771, Macquer 1758, Bergman 1970.

[15] Bergman 1970, Appendix 1.

> "as most Chemists will wish for a set to stand always open for inspection, the two sets will scarce be thought superfluous by any."[16]

The fundamental status of affinity is also emphasised by the consideration of theoretical components dealing with the relation between heat and affinity set out in chapter 4. The very precariousness of some of the attempts to include the phenomena of heat in the doctrine of affinity testifies to the perceived solidity of the foundation on which they were relying. A similar phenomenon has been noted in the appropriation and adaptation of zoological classification systems by stockbreeders, where the very "boldness of the changes" has been correlated by Ritvo with the perceived solidity of the foundation on which the change was based.[17] These supplementary components added to affinity theories testify to the increasingly common assumption that affinity was both crucial to chemistry and sufficiently reliable to build on. The trend, clearly apparent in chapter 4, to bring the phenomena of heat to a similar state of order as prevailed over the tendencies of matter testifies to the role of the doctrine as a model of a reliable, predictive chemical tool.

As my research has also amply demonstrated, however, individual theories differed both from each other and from Cullen's theory. I have shown that the doctrine of affinity in fact encapsulated a variety of theories differing in their functional components. I suggest that the logical and disciplinary common grounds underpinned this diversity. We saw in chapter 5 that the logical common ground both entailed and governed the functional components, requiring them by its very insufficiency, and yet only superficially limiting their scope. Similarly the disciplinary common ground, offering a set of disciplinary assumptions that further limited the scope for dissent, legitimised the diversity, providing a disciplinary context in which variety was obscured.

Any ascription of a cause of the variety that prevailed within the doctrine can unfortunately only be tentative, but I would like to offer two suggestions of likely influencing factors. The first relates to the fact that the difference between the pedagogical context in which an affinity theory was initially set

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[16] Ibid, Preface, v.

[17] Ritvo 1997, 83.

forth and the practical context in which it was later utilised, while the second tentatively postulates a further distinction between the theory as promulgated and the same theory as it was understood by the listening student.

I have already noted that Cullen's pedagogical presentation of affinity was chary of causal speculation. In addition, there is a clear distinction between the degree and species of detail appropriate in the pedagogical context, and that required for the practical application of what has been taught. Polanyi asserts that:

> "the conceptual framework of applicable knowledge is different from that of pure knowledge. It is determined primarily in terms of the successful performances to which such knowledge is relevant."[18]

There were two different types of 'performance' in which an affinity theory was utilised. The first was pedagogical, in which case it acted as a pedagogical tool; the second was in the normal practice of chemistry as a more general chemical tool. In the same way that the context in which Geoffroy's original paper was set forth influenced its content, so too the pedagogical context in which Cullen disseminated his affinity theory impinged on its content. Cullen's affinity theory as it was set out in his lectures, was not confined simply to the logical common ground, incorporating a number of functional components. Even so, many of the details of these components remained sketchy, to say the least. His lectures conveyed the various assumptions of the logical common ground quite clearly, but were often vague concerning more functional aspects of the application of the theory. Cullen's successors, Black, Fordyce and Saunders amongst others, were similarly cautious in their pedagogical presentation of their theories. We have similarly seen in chapter 4 evidence of a tacit demarcation between theoretical explanations that were deemed suitable for the pedagogical context and those more conjectural components that were not.

Moreover, pedagogy necessarily generalises, smoothing over the lumps and bumps of reality, and taking a broad focus to the detriment of the particular. The mismatches and anomalies of actual practice and experience are brushed

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[18] Polanyi 1962, 175.

under the carpet, as are the boring details about how the facts presented were ascertained. On this view, the parts of Cullen's affinity theory that were not referred to in his pedagogy were just as influential on the affinity theories of his students as those that were. To take an example, Cullen's explanations to his students of how his own affinity table had been produced, were brief and didactic. He avoided giving particulars of experiments, presumably believing such details to be confusing and unnecessary. The result was that his affinity table was presented as a whole, the product of known and understood affinities, rather than of painstaking experiment and observation, contingent on a variety of factors and potentially subject to future amendment.

The roles of individual affinity theories differed from the pedagogical to the practical context, in which they took on the role of more general chemical tools, and as a result of these different roles, gaps opened up between the practice of chemistry and its theory. The use of an affinity theory in chemical practice, as a generally applicable chemical tool, required certain adjustments to be made to allow for a different context of performance. Individuals amended and adapted the affinity theories they learned as they began to utilise them to guide their practices and procedures. Accordingly, new components began to be formulated, either to fill in the gaps left out by the pedagogical presentation, or to replace such components in the light of the chemist's own experience.

A further modifying factor can be tentatively postulated as resulting from the inevitable disjunction between the theory set forth in a lecture, and the theory as conceived by the listening student. The findings of modern researchers in chemical education have indicated that students tend to formulate their own individual 'mental models', 'manifold conceptualisations' of the metaphors and models that they are taught, that are not always clearly distinguished and often differ somewhat from the original.[19] The examples investigated by Keith Taber involve (perhaps serendipitously) models of chemical bonding, and his investigations emphasise the variety of mental models inspired by such common phrases in chemical education as "the sea of electrons".[20] As with the

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[19] See also Coll and Treagust 2003, Harrison and Treagust 2000.

[20] Taber 2003.

contextual discrepancy noted above, such misunderstandings tend to result in theoretical lacunae, in a conceptual gap opening up between the affinity theory of the lecturer and that of the student. The best answer to a theoretical gap, of course, is to fill it, and I have already suggested that a large proportion of the functional components were originally conceived as theoretical 'filling'. Taber argues that where this type of theoretical hiatus exists, students "'fill the explanatory vacuum' with the most likely suspect."[21] I would suggest that this might well account for many of the discrepancies noted in my study. Cullen's students, like those of today, when struggling to apply the theory that they had been taught, drew on the 'most likely suspect' for components to fill in the gaps.

Perhaps one of the most direct examples of the difficulties caused by the difference between the information a lecturer thought he had conveyed and the way in which such information was conceived by the student is evident in the exchange between Fordyce and Cullen discussed in 3.3.2 above. This correspondence concerned Fordyce's attempt to formulate a generalised law that would enable the chemist to predict *a priori* the result of any combination of four or more substances. As one of the most clearly articulated functional components of Cullen's theory, this might not be thought to have been problematic. But the correspondence shows that even when a component was carefully and explicitly explained both in a lecture and in writing, the lecturer's and the student's conceptions could nevertheless be widely at variance. Cullen and Fordyce appear never to have resolved their conceptual differences. It is clear from the correspondence that Cullen did not understand Fordyce (writing to a friend - "He has puzled me these eight days with his compounded - I had almost said confounded - attractions & you should have saved me, by telling him honestly how difficult his piece was"),[22] and Fordyce did not understand Cullen's objections to his theory. It is perhaps significant that from the 1760s the law that Cullen had tentatively proposed in 1757 governing the predictive power of his diagrams disappeared from his lectures. Perhaps his experience with Fordyce had suggested to him that this particular aspect of the diagrams

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[21] Ibid, 752.

[22] Fordyce 1759-1774.

was liable to misinterpretation by his students.

It is worth bearing in mind when considering this point that chemistry students up to the end of the 18th century did not have the benefit of a standardised range of approved textbooks offering a 'received view' of affinity theory. Cullen referred in his lectures to an array of works dating back to classical times, but he recommended only a few recent works to his students, only one of which was available in English; and he did not entirely approve of any of them.[23] Of the works that Cullen recommended, only Macquer's contained an affinity theory that went beyond the synoptic view of Lewis and Shaw. In some sense, the pedagogy of Cullen and his students was closer to the research of today in being at the margins of knowledge. Students who encountered the type of theoretical lacunae I have described would have been unable to simply look the answer up.

It is impossible to assign a single cause to the variety that undoubtedly obtained amongst affinity theories, but I would suggest that all these factors were influential. As Simões has argued, in the early stages of disciplinary development, there is little difference between the pedagogical and the research contexts.[24] We have seen that only towards the end of the century did a line begin to be drawn between the two. Even then, as we have seen, new ideas and concepts were translated between contexts with little mediation or delay. This in itself is sufficient to infuse uncertainty into the fledgling discipline.

Nevertheless, despite all the variety, this was not anarchy. The period I am concerned with saw an explosion in communication between chemists. The network of correspondence emanating from Cullen, Black and Kirwan has already been mentioned, but such associations as the Royal Society and the Lunar Society, Kirwan's unnamed coffee house society, the large teaching hospitals and the universities fostered further contact between chemists. Chemists were able to discuss and compare their activities, relying often on their affinity theories, and sometimes referring to them. They made use of a

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[23] In 1766 Cullen recommended (but with caveats) works by Stahl, Boerhaave, Macquer and Wallerius. Cullen 1766, Lecture 10.

[24] Simões 2004, 300.

common idiom or lexicon that derived from their affinity theories.[25] This was clearly a powerful unifying bond, as I have found little evidence of disagreement or controversy over the undoubted discrepancies between their affinity theories. Both the disciplinary and the logical common ground lay behind this apparent harmony.

Cullen taught that affinity was one of the two 'general principles' of philosophical chemistry, and at the end of the century it still featured as one of Nicholson's two 'chemical agents'.[26] From Cullen to Nicholson, from Glasgow to London, the teaching of chemistry necessarily involved the teaching of an affinity theory. In pedagogical sources affinity theories underpinned the innumerable particulars of chemistry. Affinity theories were taught to medical students and apothecaries, novice chemists, rather in the same way that student chemists are now taught about atoms, molecules and chemical bonds. Affinity theories were part of the norm of 18th century chemistry. And yet, I have shown that there were wide ranging discrepancies between many of the components of individual affinity theories. Nevertheless, the scope of divergence was limited; the very fact that the variety of theoretical components could be ordered into component-types confirms this. This underlying organisation resulted from the unifying hub of affinity theory, the logical common ground. This was the essence of the doctrine of affinity, encompassing the law of affinity and the conceptualisation of the table that brought together the relations described in the law. The doctrine of affinity thus provided a disciplinary common ground between chemists, providing a mediating level of understanding and communication for all those who subscribed to the doctrine of affinity, in spite of their detailed differences.

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[25] In a similar vein, Laszlo has recently pointed out some of the advantages accruing to chemists of the 1960s from the NMR revolution, amongst which he lists a new idiom which improved communication. Laszlo 2006, 106.

[26] Nicholson, 1790b.

Appendix 1: On Compound Elective Attractions

Glasgow University Library

Cullen Papers MS 89: Paper sent to William Cullen by George Fordyce in 1759 with letter contained in MS 180

Archived as: “Account of Mr Slake’s Paper to the Chemists at Paris on Compound Elective Attractions”

“1st

Of Compound Elective Attractions

Mr Stahl proposed to the Chemists at Paris to separate wt no greater heat than that of the Human Body the Vitriolic Acid from the Vegetable Fixt Alkali in vitriolated Tartar. As each of these substances attract the other stronger than any thing besides that could be combined with it, in that heat they could none of them solve this Problem till Mr Stahl the son showed them it might be done by means of solution of silver in the nitrous acid by the following Process:-

Take a perfect solution of Silver in the nitrous acid drop it into a solution of Vitriolated Tartar in water. The vitriolic acid will leave the vegetable fixt alkali and joining the Silver (as solution of silver in that acid is not but in small proportion soluble in water) part of

2nd

of it will be precipitated along with part of the Silver, the nitrous acid remaining joined to the alkali and forming with it common Nitre.

It was found afterwards that several other menstruums could be separated from their solvends by joining two compounds and this was called double Elective attractions.

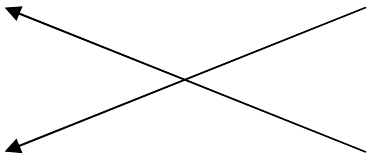
There were commonly said to be four cases in which this would happen and in all these cases setting the substances combined together on the same side, one substance on each side attracts another on the other side stronger than the substance it is combined with.

This may be marked wt a dart cross from the substance which attracts the other stronger than the one it is combined with to the substance so attracted.

Thus Instance First:-

1m 2m

Vitriolic Acid ⊕▷ ⦶▷ Nitrous Acid



1s 2s

v^ Vegetable fixt alkali Silver ☾

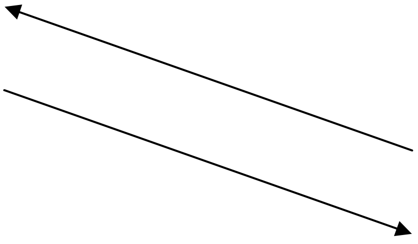
i.e. the nitrous acid attracts the vegetable fixt

3rd

fixt alkali stronger than it attracts the silver and the silver attracts the vitriolic acid stronger than it does the nitrous. Instance second which is the reverse of the first.

1m 2m

Vitriolic Acid ⊕▷ ⦶▷ Nitrous Acid



2s 1s

Silver ☾ v^ Vegetable fixt alkali

i.e. Vitriolic acid attracts the vegetable fixt alkali stronger than Silver and vegetable fixt alkali attracts the vitriolic acid stronger than the nitrous.

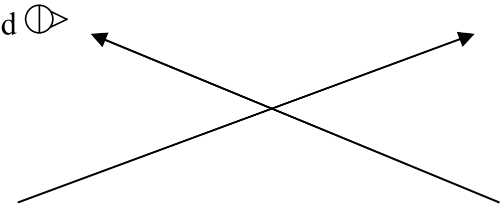
Instance Third

Im to 1s

1m to 2s

Nitrous Acid ⦶>

⊖> Muriatic Acid



2s

1s

Silver ☾

v^ Vegetable fixt alkali

Earth of Alum

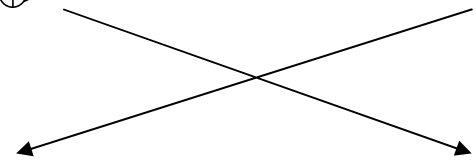
i.e. vegetable fixt alkali attracts the nitrous acid stronger than the muriatic acid and silver attracts the muriatic acid stronger than the nitrous. Instance Fourth

2m

1m

Nitrous Acid ⦶>

⊖> Muriatic Acid



1s to 1m

1s to 2m

Silver ☾

☿ Quicksilver

4th

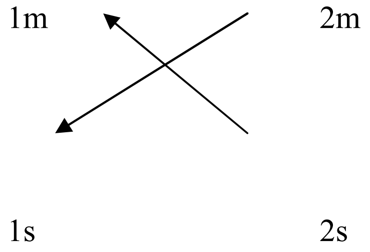
i.e. Nitrous Acid attracts Quicksilver stronger than Silver and Muriatic Acid attracts Silver stronger than Quicksilver. In all these instances a decomposition takes place the menstruums changing solvends. The two last evidently takes place always as will afterwards appear it remains for us to find out in what circumstances the two first do. We must first observe in general than in Instance first and Second the one Menstruum attracts the same solvend strongest [marginal note: and in the same manner the Solvend] that the other does and the same Solvend weakest that the other does and therefore are both a comparison of the same attractions. In the third instance the one solvend attracts the one menstruum strongest and the other the other. In the fourth instance the one menstruum attracts the one solvend strongest and the other menstruum the other and wherever either of these happen they follow the same rule as in the particular instances.

5th

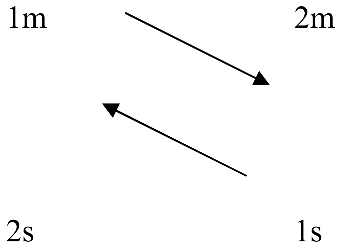
instances given. Thus

Instance

First

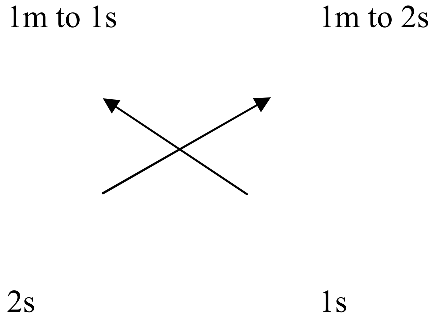


Second

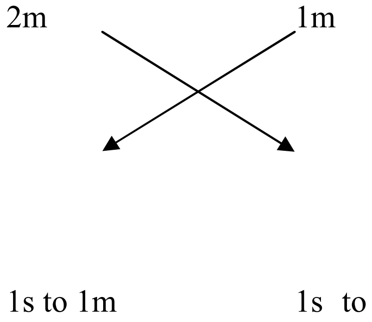


[marginal note: 1 strongest 2 weaker]

Third



Fourth



We shall consider now these attractions as so many given powers, the stronger attractions as the stronger powers acting to disjoin or join substances. Then in the first and second instances the powers 1ms attraction→ to 1s and 2m →to 2s act against 1m → 2s + 2m → 1s but as 1m → 1s is the strongest & 2m → 2s the weakest and they are both on one side and 1m → 2s and 2m → 1s the middle powers acting on the other side and as these powers can't be defined by numbers a priori

[marginal note: because if 1m joins 1s 3m must join 2s & contrary]

6th

priori we can never say whether the first or second instance will take place. In the third instance and likewise the fourth by supposition the strongest powers are on one side that is in instance third 1s → 1m to 1s is by supposition stronger than 1s → 1m to 2s and 2s → 1m to 2s by supposition stronger than 2s → 1m to 1s but 1s → 1m to 1s + 2s → 1m to 2s is the powers endeavouring to join 1s to 1m to 1s and 2s to 1m to 2s and 2s → 1m to 1s +1s → 1m to 2s the powers endeavouring to join 1m to 1s to 2s and 1m to 2s to 1s. therefore the stronger powers being on one side this attraction must always take place which is confirmed by all the experiments yet made.

In the same manner instance 4th the powers endeavouring to combine 2m & 1s to 1m and 1m to 1s to 2m are 2m → 1s to 1m + 1m

7th

1m → 1s to 2m and 2m → 1s to 2m + 1m → 1s to 2m all the powers endeavouring to join 2m to 1s to 2m and 1m to 1s to 1m but 2m → 1s to 2m is by supposition stronger than 2m → 1s to 1m and 1m → 1s to 2m therefore the two stronger powers acting on the same side that must of necessity be strongest this too is confirmed by every experiment made on this subject therefore we ma conclude a priori & posteriori that the 3rd & 4th instances always take place Q.E.D.

N.B. In this demonstration we have supposed the bodies being mixt together disjoined.

It only remains to determine what will be the combination of the four substances 1m 2m 1s 2s this as we have said before can only be determined by Experiment (1.2.) and every experiment I

8th

I have as yet tried proves that 1m → 2s + 2m → 1s is stronger than 1m → 1s +2m → 2s for in a moderate degree of heat 1m is joined to 2s and 2m to 1s and if the other combination has already took place the two compounds are decomposed but on the other hand in a very great degree of heat and by distillation the other combination may often if not always happen, but as a large degree of heat is necessary and as a certain degree of heat will decompose substances that are not both equally volatile by distillation or sublimation we have sufficient reason to conclude that 1m → 2s + 2m → 1s is stronger than 1m → 1s + 2m → 2s. (3)

We might repeat a great number of Experiments which we have made of this sort but as they are so common and so easy we shall only give a few instances by way of note.

Corollary

9th

Corollary. The difference between the strongest menstruum attraction to the strongest solvend and the same menstruum attraction to the weakest solvend is less than the difference betwixt the weakest menstruum attraction to the strongest solvend and the same menstruum's attraction to the weakest solvend. i.e.

1m → 1s – 1m → 2s is less than

2m → 1s – 2m → 2s for add to

1m → 1s + 2m → 2s a quantity |a| equal to the difference betwixt that powers and

1m → 2s + 2m →1s then

1m → 1s + 2m → 2s +a = 1m → 2s + 2m →1s subtract 2m → 2s from both sides then 1m → 1s +a = 1m → 2s + 2m → 1s – 2m → 2s again subtract 2m +2s then

10th

1m → 1s – 1m +a = 2m + 1s – 2m → 2s therefore 1m → 1s – 1m →2s is less by a than 2m → 1s – 2m →2s.

The same is true of the solvends.

These principles being laid down we will next attempt to show in what manner any number of substances mixt together will combine themselves and first supposing three menstruums and three solvends mixt which bear the relations 1m, 2m, 3m, 1s, 2s, 3s I say that 1m will join 3s, 2m 2s and 3m 1s for these can only be combined in six ways viz! –

1st

1m to 1s	2m to 2s	3m to 3s
1m to 2s	2m to 1s	3m to 3s
1m to 3s	2m to 2s	3m to 1s
1m to 1s	2m to 3s	3m to 2s
1m to 2s	2m to 3s	3m to 1s
1m to 3s	2m to 1s	3m to 2s

that is, there are six powers acting against one

11th

one another viz

1m → 1s + 2m → 2s + 3m →3s

1m → 2s +2m →1s + 3m → 3s

1m → 3s + 2m → 2s + 3m → 1s

1m → 1s + 2m → 3s + 3m → 2s

1m → 2s + 2m → 3s +3m → 1s

1m → 3s + 2m → 1s + 3m → 2s.

Of these powers 1m → 1s + 2m → 2s + 3m → 3s

Is less than 1m → 2s + 2m → 1s + 3m → 3s

For 1m → 1s + 2m → 2s is less than

1m → 2s + 2m → 1s and 3m → 3s is

common – therefore

1m →1s + 2m → 2s + 3m →3s

is less than 1m → 2s + 2m → 1s + 3m → 3s.

Q.E.D.

In like manner it may be proved that

1m → 2s +2m →1s + 3m → 3s is less than

1m → 3s + 2m → 1s + 3m → 2s and this less than

1m → 3s + 2m → 2s + 3m → 1s.

therefore

12th

Therefore

1m → 3s +2m →2s + 3m → 1s is greater than

1m → 3s + 2m → 1s + 3m → 2s or

1m → 2s +2m →1s + 3m → 3s or

1m → 1s + 2m → 2s + 3m → 3s again

1m → 1s + 2m → 3s + 3m → 2s is by the above method of reasoning less than

1m → 2s +2m →3s + 3m → 1s which is also less than

1m → 3s + 2m → 2s + 3m → 1s Therefore

1m → 3s + 2m → 2s + 3m → 1s is the strongest

of the six powers. Therefore 1m will join 3s, 2m 2s & 3m 1s. Q.E.D.

Example:

1m	Vitriolic acid
2m	Nitrous acid
3m	Muriatic acid
1s	Fixt alkali the fossil

2s Calcareous earth

3s Caustic volatile alkali

13th

will form

1. Vitriolic ammoniac 1m3s

2. Nitrous selenites 2m2s

3. Common Sea Salt 3m1s

By the same method of reasoning it may be proved that in any number of menstruums and solvends mixed bearing the relations

1m 2m 3m 4m &c &c &c

1s 2s 3s 4s &c &c &c

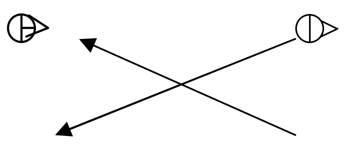
the strongest menstruum will always join the weakest solvend and the weakest the strongest and so on thro the remaining menstruums & solvends.

~~Q.E.D.~~

To conclude

In the first instance a Double Elective attraction will take place generally if not always in small degrees of heat except when the weakest menstruum bears no proportion

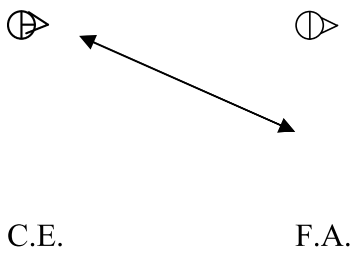
[in the margin:



F.A. C.E.]

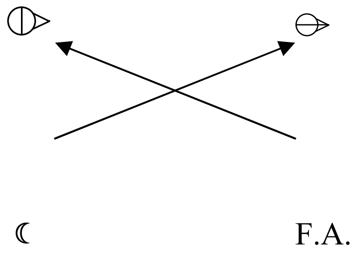
to the strongest.

In the second instance a double decomposition will take place in great degrees of heat and where the

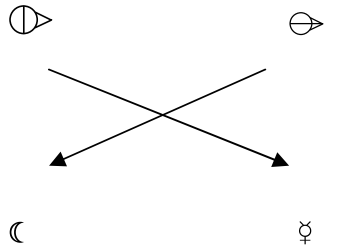


weakest menstruum bears no proportion to the strongest.

In the third instance a double decomposition always takes place.



In instance fourth a double decomposition likewise always takes place



Where more than two compounds substances are mixt bearing the same relation to one another as those in the first and second instances the strongest menstruum will (in the circumstances in which Instance First takes place) always join the weakest solvend and the weakest menstruum the strongest. Where more than two compounds are mixt from which arise a complication of instance first and second with either of the third and fourth instances or both or where the third and fourth are complicated together the combinations they will form may be found out by considering first all the possible combinations then the powers arising from them lastly comparing these powers as in demonstration page (10,11,12) as it would be endless here to consider all the possible complications.

Notes

(1)

No. s This is only meant of acids and their solvends for there are some cases in which acids are not the menstruums where 1m → 1s is greater alone than 1m → 2s + 2m → 1s.

Example	1m	Vitriolic Acid
	2m	Oil
	1s	fixt alkali
	2s	Magnesia

Here tho' the oil does not disolve the magenesia yet the attraction of the Vitriolic acid to the fixt Alkali is greater than its attraction to the magnesia and the oils attraction to the fixt Alkali taken together therefore the soap is decomposed. And this may serve to explain why a contrary combination takes place in

---

(2)

heat; for the connection of bodies of different degrees of volatility is by heat diminish'd and destroy'd, as may be proved by the distillation of acids from vitriol of Iron, sea salt, and Nitr and several other experiments of the same nature.

It likewise appears from the corollary (page 9) that the attraction of the weakest menstruum will be diminished in greater proportion than the strongest. For considering the strongest menstruums attraction to both solvends first in its strongest state of attraction and again as diminished by heat you will have a stronger and weaker menstruum.

i.e.1m, 2m, but 1m → 1s – 1m →2s

is less than 2m →1s – 2m → 2s.

---

(3) Notes

therefore if 1m → 1s be diminished to 2m → 1s as we suppose, 1m → 2s will be likewise diminished to 2m → 2s and consequently in greater proportion than 1m → 1s.

In like manner it may be proved that 1s → 1m will be diminished in less proportion than 1s → 2m but 1m → 1s acts against 1m → 2s and 2m → 1s and if diminished in less proportion than either will at last become greater than both and hence in very great heat instance 2d almost always if not always takes place as in distillation of Aqua Fortis by means of alumn or vitriol.

No. 2 Altho in all the experiments I have made no exception to this rule has appeared yet it is possible there may be some but that will only affect the following reasoning

(4) with regard to them

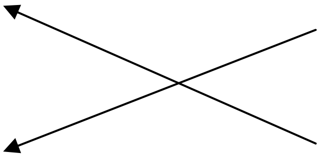
(5) No. 3 Notes

Experiments

The darts show what substances combine themselves together

Expt 1st 1m 2m

Vitriolic Acid Nitrous Acid

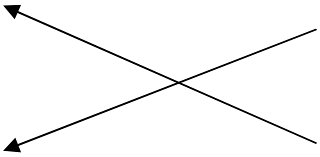


1s 2s

Vegetable fixt alkali Silver

Expt 2nd 1m 2m

Vitriolic Acid Muriatic Acid

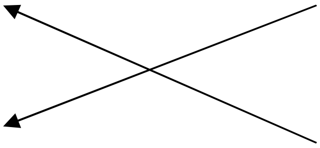


1s 2s

Fossil fixt alkali Magnesia

Expt 3rd 1m 2m

Vitriolic Acid Muriatic Acid

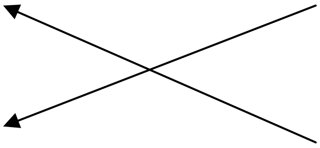


1s 2s

V fixt alkali Calcareous Earth

Expt 4th 1m 2m

Muriatc Acid Nitrous Acid



1s 2s

Zinc Copper

Expt 5

$$\begin{tikzcd}
\begin{array}{l}\text{1m}\\ \text{Muriatic Acid}\end{array} & \begin{array}{l}\text{2m}\\ \text{Nitrous Acid}\end{array} \arrow[dl] \\
\begin{array}{l}\text{1s}\\ \text{Zinc}\end{array} & \begin{array}{l}\text{2s}\\ \text{Lead}\end{array} \arrow[ul]
\end{tikzcd}$$

(6)

Expt 6th

$$\begin{tikzcd}
\begin{array}{l}\text{1m}\\ \text{Muriatic Acid}\end{array} & \begin{array}{l}\text{2m}\\ \text{Nitrous Acid}\end{array} \arrow[dl] \\
\begin{array}{l}\text{1s}\\ \text{Zinc}\end{array} & \begin{array}{l}\text{2s}\\ \text{Iron}\end{array} \arrow[ul]
\end{tikzcd}$$

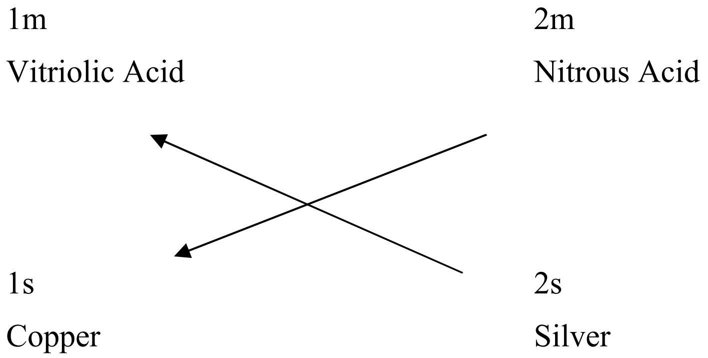
Expt 7th

$$\begin{tikzcd}
\begin{array}{l}\text{1m}\\ \text{Muriatic Acid}\end{array} & \begin{array}{l}\text{2m}\\ \text{Nitrous Acid}\end{array} \arrow[dl] \\
\begin{array}{l}\text{1s}\\ \text{Lead}\end{array} & \begin{array}{l}\text{2s}\\ \text{Copper}\end{array} \arrow[ul]
\end{tikzcd}$$

Expt 8th

$$\begin{tikzcd}
\begin{array}{l}\text{1m}\\ \text{Muriatic Acid}\end{array} & \begin{array}{l}\text{2m}\\ \text{Nitrous Acid}\end{array} \arrow[dl] \\
\begin{array}{l}\text{1s}\\ \text{Copper}\end{array} & \begin{array}{l}\text{2s}\\ \text{Silver}\end{array} \arrow[ul]
\end{tikzcd}$$

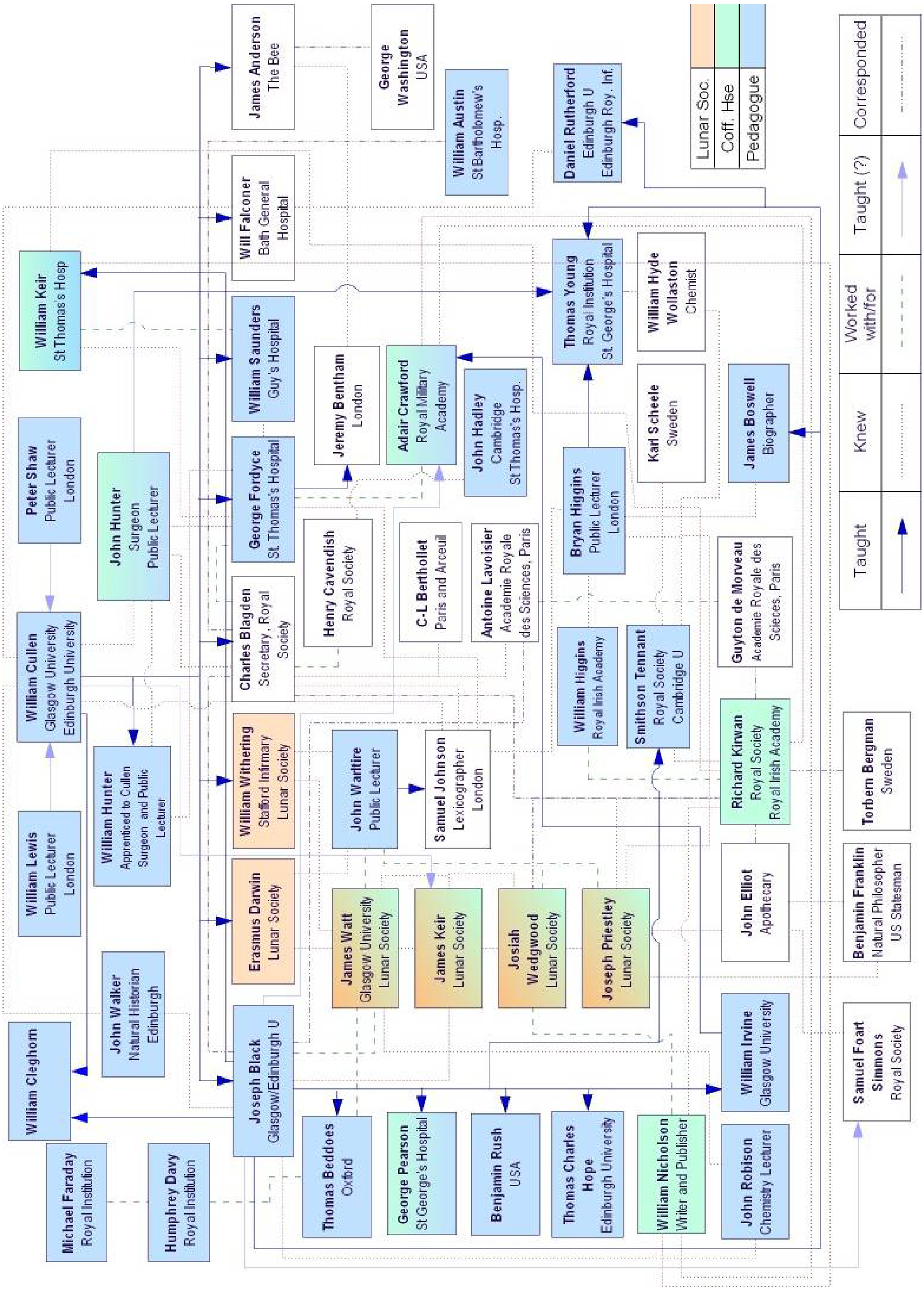
Expt 9th



As part of this MS there is also a single column of an affinity table:

Nitrous Acid
Fixt Alkali
Calcareous Earth
Volatile Alkali
Magnesia
Zinc
Tin
Lead
Iron
Regulus of Antimony
Bismuth
Copper
Regulus of Arsenic
Quicksilver
Silver
Earth of Alumn
Water
Camphor Ether

Appendix 2: The Pedagogical Pyramid



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