The Chemistry of Relations
The periodic table examined through the lens of C.S. Peirce's philosophy

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Declaration

I, Christopher John Campbell, 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.

Abstract

This thesis explores Charles Peirce’s reception of Dmitri Mendeleev’s periodic arrangement of the chemical elements, the further impact of chemistry on Peirce’s philosophy, such as his phenomenology and diagrammatic reasoning, and the relations between Peirce's theory of iconicity and Mendeleev's periodic table. It is prompted by the almost complete absence in the literature of any discussion of Peirce’s unpublished chemistry manuscripts and the lack of attention given to the connections between Peirce’s early study of chemistry and his later philosophy. This project seeks to make a contribution to this otherwise neglected area of Peirce scholarship.

Acknowledgements

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Above all else, this thesis would not have been completed without the continuing love and support (and editing skills!) of my wife, Jan.

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ABBREVIATIONS

References to Peirce's work are abbreviated as follows:

W

Writings of Charles S. Peirce, 8 vols. to date, ed. Max H. Fisch, Edward Moore, Nathan Houser, et al. Bloomington: Indiana University Press, 1982–99. Referenced by W followed by volume number and page number, separated by a colon. Example: W 6:287.

CP

Collected Papers of Charles S. Peirce, 8 vols., ed. Charles Hartshorne, Paul Weiss, and Arthur Burks. Cambridge, MA: Harvard University Press, 1931–58. Referenced by CP followed by volume and paragraph number, separated by a full stop.
Example: CP 4.123.

EP

The Essential Peirce, 2 vols., ed. Peirce Edition Project. Bloomington: Indiana University Press, 1991, 1998. Referenced by EP followed by the volume and page number. separated by a colon. Example: EP 1:39.

NEM

The New Elements of Mathematics. 4 vols. Edited by Carolyn Eisele. The Hague: Mouton, 1976. Referenced by NEM followed by the volume and page number separated by a colon. Example: NEM 4:39.

PPM

Turrisi, P. 1997. 'Pragmatism as a Principle and Method of Right Thinking' in Turrisi, P (Ed.) *The 1903 Harvard Lectures on Pragmatism Charles Sanders Peirce*. State University of New York Press . Referenced by PPM followed page number separated by a colon.
Example: PPM:19.

MS

Manuscript numbers correspond to *Annotated Catalogue of the Papers of Charles S. Peirce*. Richard S. Robin. Amherst: University of Massachusetts Press, 1967.

Introduction

> It has been generally acknowledged for the last half century, at least, that no man's philosophy can be well understood until one knows how he came by it.
> [Charles Peirce. MS 619: 1, 1909]

A cursory glance at the biographical details of Charles Sanders Peirce and Dmitri Ivanovich Mendeleev reveals that both lived at approximately the same time during the nineteenth and early twentieth centuries. Peirce was born in 1839 some five years after Mendeleev who, dying in 1907, predeceased Peirce by seven years. Both trained in science but whilst Mendeleev's contribution to chemistry is well documented and widely celebrated it takes more than a cursory glance at Peirce's details to discover that he too both trained and published in chemistry. Scholars readily refer to Peirce's achievements in areas such as mathematics, logic and metaphysics. Less well known is that in 1869, the year of Mendeleev's first published arrangement of the chemical elements in order of their atomic weight, Peirce too published a similar attempt. These are no doubt serendipitous discoveries. So too is that Peirce formulated a theory of iconicity as part of his wider semiotics and that Mendeleev's periodic table is often proclaimed as an *icon* of science, such as this from the historian and philosopher of science Eric Scerri (2006:xii),

> The periodic table of the elements is one of the most powerful *icons* in science: a single document that captures the essence of chemistry in an elegant pattern. Indeed, nothing quite like it exists in biology or physics, or any other branch of science, for that matter. One sees periodic tables everywhere: in industrial labs, workshops, academic labs, and of course, lecture halls. (emphasis added)

This integrated project in the history and philosophy of science began with such seemingly coincidental connections between the works and research interests of Peirce and of Mendeleev. Whilst Peirce knew of Mendeleev's achievement of the periodic table in detail, Mendeleev as far as I can tell had no knowledge of Peirce - they neither met nor corresponded. This inquiry seeks to explore the fruitful *relations* between the works of these two philosopher-chemists bonded, among other things, by their common work on the periodic table. To borrow an analogy from photography, this thesis is not an attempt at a 'double exposure' where aspects of Peirce and Mendeleev's writings are brought together as a single image. Quite the contrary; I believe the individual images of their respective work and practice are both illuminated and brought into sharper focus by the (unintended) insights of the other. Take for example these two approaches from the literature that will feature later in this thesis.

Andrea Woody (2014:143) argues that the periodic table 'is valuable because of its ability to reveal, or make perspicuous, certain relations [between the chemical elements]'. I will argue that by viewing the periodic table from the perspective of Mendeleev's representational practice and as a dynamic constituent of his inquiry, Peirce's formulation of iconicity offers a coherent account of how the 'relations' between the chemical elements were 'revealed' and made 'perspicuous'.

Secondly, many scholars, when considering Peirce's construction of diagrammatic reasoning, focus on the foundational importance of mathematics and of logic to his approach. For example Frederik Stjernfelt (2007:xiii) argues that for Peirce logical understanding is not devoid of observation but is 'the meticulous observation of general diagrams. As Peirce puts it: all mathematical reasoning is diagrammatic, and that all necessary reasoning is mathematical reasoning, no matter how simple it may be…'(NEM 4:47, 1902). Whilst not seeking to contradict Stjernfelt (or Peirce!) I will show how Peirce's study of chemistry also made an important contribution to his formulation of diagrammatic reasoning. This connection to chemistry, like much of Peirce's work in this subject, is rarely commented on in the literature. Part of this project is to demonstrate the importance of Peirce's early study of chemistry to his later philosophy.

Whilst Mendeleev's connection to the periodic table is well characterised, the periodic table also featured prominently in Peirce's writings – often by way of analogy to illustrate his philosophy but also, and in common with Mendeleev, as a chemist inquiring into the relations between the chemical elements. I will show that Charles Peirce's own early and published attempt at ordering the chemical elements by atomic weight was independent of Mendeleev's original work. I will draw on Peirce's unpublished chemistry manuscripts and contextualise Peirce's writings in the broader history and historiography of chemistry. In particular I will argue that Peirce's continued writings on in the periodic table were in direct response to Mendeleev's original attempt and motivated by a belief that, in common with the laws of physics, it was underpinned by an exact mathematical foundation.

Peirce and Mendeleev built and reworked the periodic table in a way that would make the relations between its chemical objects visible. More broadly the works of these two philosopher-chemists were concerned with making clear the *relations* between the world's material elements and between its cognitive elements. I will also show that Peirce adopted this chemical model – with its very emphasis on *visualising relations* – in developing his form of diagrammatic reasoning. I will argue for the foundations of Peirce's diagrammatic reasoning as stemming from his time as a graduate chemistry student at Harvard's Lawrence Scientific School under Josiah Cooke. I will show that the concept of *relations* was important to both Peirce and to Mendeleev in setting out their respective positions. It is the language of *relations* that connects Peirce to his study of chemistry at Harvard and to his methods of diagrammatic reasoning. *Relations* and diagrammatic reasoning later proved to be two of the essential pillars on which Peirce built his philosophical system. For example the Peirce scholar Mats Bergman (2009:72) states that 'Peirce's analysis of *relations* and phenomenological categories…is a highly complex issue full of false leads and outright contradictions' (emphasis added). I will show that it was to his background in chemistry and the periodic table that Peirce returned many times in order to exemplify his analysis of *relations* and his metaphysical categories.

Having considered the impact of chemistry on Peirce's thought I will consider how Peirce's philosophy illuminates Mendeleev's inquiry into the chemical elements and his representation of their physiochemical relations - the periodic table. I will demonstrate the epistemic merit of viewing Mendeleev's periodic table – his practice of representation - from the perspective of Peirce's theory of iconicity. At its early inception Mendeleev's representational practice can be identified in the two-fold way he engaged with the construction of the periodic table both as means of directing and also of projecting his thought processes. That is firstly directing the process whereby the sixty or so known elements might be accommodated in atomic weight order into a scheme whereby natural families of elements with similar chemical properties are grouped together. And secondly in enabling Mendeleev to project his thought processes towards previously unknown elements such as the three now famous eka-elements: eka-boron, eka-aluminium and eka-silicon. I will argue that a coherent account of Mendeleev's representational practice, as encapsulated by his construction and use of the periodic table as just described, is captured in Peirce's formulation of iconicity. I will argue that a major factor in choosing iconicity as an interpretative framework is Peirce's emphasis on the potential for making of new discoveries by an inquirer experimenting on the (iconic) sign itself – thought experiments on the periodic table. I will show how the periodic table played just such a role in Mendeleev's inquiry – the periodic table as an iconic sign.

During Mendeleev’s lifetime the veracity of the periodic table came under some pressure. For example Mendeleev’s initial arrangement was unable to accommodate a number of newly discovered elements such as the noble gases. Furthermore, whilst Mendeleev used his periodic arrangement of the elements successfully to project towards a number of new discoveries, there were also a number of erroneous predictions such as ether and coronium. I will show that during these times Mendeleev’s table retained its capacity to promote creative thoughts in the minds of chemists and will introduce the term *iconic robustness* to account for its continued epistemic value and productivity. In addition I will argue that such an approach to Mendeleev’s representational practice, illuminated by Peirce’s account of iconicity, offers an alternative perspective to the current and long-running ‘accommodation-prediction’ debate around the periodic table and to be found in the literature.

Positioning Peirce’s chemistry manuscripts within the wider framework of his history and historiography of chemistry I will show how he changed his view on Mendeleev’s achievements and how this is linked to Peirce’s own and unsuccessful search for an exact mathematical foundation to the periodicity of the chemical elements. In an article for *The Nation* on *The Periodic Law* Peirce (1892) pays fulsome tribute to Mendeleev’s ‘wonderfully vivid conception’ and his ‘clear perception of its evidence’ demonstrated ‘by the formal and audacious descriptions he gave of the properties of several elements then undiscovered, but required to fill blank spaces’. He concludes that ‘very few inductions in the whole history of science are worthy of being compared with this as efforts of reason’ (W8:285). I will show how a number of Peirce’s unpublished manuscripts are punctuated by failed attempts to discover an exact mathematical key to unlock the periodic table’s foundational structure. This lack of success is reflected in a later and more nuanced view of Mendeleev’s scheme where Peirce laments its lack of mathematical exactitude, commenting ‘that the time has yet come when it is worthwhile to take up that question for its own sake’ (EP2:110, 1901). The successful discovery of Mendeleev’s eka-elements, which Peirce earlier praised, he later describes as useful support only by having ‘proved that there is some truth in one part of Mendeleéfs theory’ although it is ‘founded on pretty superficial characters’ (EP2:111, 1901). Three years later and after a further search for the periodic table’s ever elusive mathematical key, Peirce comments, ‘I need not point out the tantalising appearance of *relations* among the atomic weights which are wanting in exactitude, for this speaks for itself; and the more it is studied the more perplexed it shows itself to be’ (MS694, 1904).

In developing this thesis I will also show that Peirce's research interests and methods as a chemist were common to others of his time and stand in stark contrast to the sometimes heroic rhetoric that accompanies commentaries on his philosophy. Towards the end of their lives Mendeleev and Peirce each responded differently to the 'new chemistry' of early twentieth century; Peirce accepted the impact on chemistry of the discovery of the electron whilst Mendeleev did not.

An overview of the coming chapters

As has been suggested already in this introduction, chemistry and the periodic table connect Charles Peirce both with Dmitri Mendeleev and more broadly, as I will argue later, with aspects of his philosophy. In **chapter one** I set out the context of Peirce's educational experience as a postgraduate student at Harvard's Lawrence Scientific School between 1861 and 1863. I will establish that Peirce was taught by the highly regarded teacher and chemist Josiah Parsons Cooke who rejuvenated the chemistry curriculum by introducing a programme much influenced by the French chemists Jean Baptiste André Dumas and Henri Victor Regnault as well as the German chemist Justus Liebig. I will set out how Cooke increased the mathematical demands made of his students and, in common with Mendeleev, framed chemistry in terms of the *relations* between substances and their empirically determined properties. In one of his early papers, Cooke (1854), Peirce's tutor, developed his own system for the chemical elements and one based on the *relations* between the elements and their atomic weights. What is important to appreciate at the beginning of the project is that by studying chemistry under Cooke's direction, Peirce was immersed in the language of *relations* that was later to feature so prominently in his later philosophy. But there was more to be gained by Peirce in studying under Cooke's direction.

As part of his reforms to the chemistry curriculum at Harvard, Cooke introduced several of his own texts, one in particular being *Chemical Physics* (1860). In **chapter one** we see how by using this particular text Cooke encouraged his students to develop a form of diagrammatic reasoning where, by engaging with the printed diagrams of crystallographic structures, Cooke's students came to an understanding of the structural relations underpinning the whole range of different crystallographic types. Furthermore I show that Cooke, in constructing his own system of the chemical elements as set out in his paper 'The Numerical Relation between the Atomic Weights' (1854), used a number of diagrammatic representations in order to generate new knowledge. Importantly this chapter seeks to establish that, whilst studying chemistry at Harvard, Peirce engaged with a teaching approach which promoted an understanding of the subject in terms of *relations* and diagrammatic reasoning. In this chapter I establish how Peirce’s training at Harvard in chemistry contributed to his thinking on the epistemic and logical value of diagrams. Also, this training led by Josiah Cooke made a substantial contribution to Peirce’s way of thinking diagrammatically and in terms of *relations.*

In **chapter two** we will see how after graduating from the Harvard’s Lawrence Scientific School, Peirce maintained his interest in chemistry, being the subject of two of his earliest papers. The first (1863) is a contribution to atomic theory of a distinctly Kantian flavour where we see Peirce, unlike many nineteenth century chemists, prepared to ground his arguments in metaphysics. The second paper, significantly, is an attempt to devise a system for the chemical elements based on atomic weights and published in 1869, coincidently the same year as Mendeleev’s own first attempt at a systematisation of the chemical elements. This paper is an early indication of Peirce’s particular and lasting interest in the periodic table. I will show that Peirce continued to engage with Mendeleev’s table throughout his life, both in an oft repeated search for its exact mathematical foundation and by way of analogy for his later philosophy. This chapter is important to this thesis as it demonstrates that Peirce’s study of chemistry endured beyond his studies at Harvard. The impact of Mendeleev’s periodic table, and of chemistry, on Peirce is deeper seated than a chemist’s interest in classifying the chemical elements for it threaded through his later philosophy. There is very little in the secondary literature that connects Peirce’s early study of chemistry with his later work in philosophy. This project seeks to establish the value of this connection to a wider study of Peirce.

Peirce and Mendeleev – both being philosophical chemists - are connected by the emphasis each places on the foundational nature of *relation*s in their respective inquiries. In **chapter three** I will establish how the concept of *relations* connects these two philosopher-chemists. I will show how Mendeleev with a focus on the world’s material elements, and Peirce in focussing on its cognitive elements, were both committed to surfacing the otherwise latent *relations* that are the foundations of their respective inquiries. Chemical valency is founded on the bonding relations between atoms; the periodic table on their physiochemical relations. I will argue that in his formulation of phenomenology, Peirce draws on his knowledge of the periodic table and his understanding of chemical valency as a framework to explore phenomenological relations diagrammatically. This is not an approach that features much in the literature.

In **chapter four** I will present Peirce's three orders of signs – icon, index and symbol – and further introduce iconicity by considering nineteenth century chemical graphs as iconic diagrams. Iconicity as a means of representation is a controversial topic in the philosophy of science. This chapter will also attempt to counter some of the major objections to iconicity around the notion of *resemblance*. Ursula Klein (2001) rejected Peirce's formulation of iconicity in her study of Berzelian chemical formula as *paper tools* in the creation of new knowledge. Klein's rejection was based on her – in my view faulty - analysis of the relations between an icon and that which it represents. I will argue that Peirce's formulation of iconicity would have provided Klein with an effective interpretative framework for her study, removing the need for the neologism *iconic symbol.* Before making this argument I will examine more closely – via Mauricio Suárez's (2010) account - the different types of relations that are possible between a representation and its object of study. I will also suggest Peirce's formulation of iconicity as a means of avoiding Suárez's dyadic approach – *the analytical inquiry* and *the practical inquiry* - by taking the process of scientific representation as integrated within the creative process of scientific inquiry.

In **chapter four** I will also show how the periodic table was integrated into Mendeleev's inquiry into the relations between the chemical elements. In this context it is more useful to speak of the periodic table in terms of Mendeleev's *representational practice*. Working from two of Mendeleev's early sketch diagrams I will argue that the periodic table acted as an iconic representation: through the practical pen and paper exercise of its construction and a capacity for promoting thought experiments involving its further re-construction, it informed Mendeleev's thinking as he accommodated the existing elements and projected novel knowledge. Furthermore, Mendeleev's first publication of his scheme makes claims for the periodic table's future epistemic fruitfulness which, I would argue, are consistent with its functioning as an icon.

Originally published in 1869, Mendeleev's periodic table later came under pressure from what Hasok Chang (2012:215), in his account of *active realism,* describes as 'nature's *resistance'* (emphasis in the original). Nature's *resistance* here takes the form of the rare earth elements and the appearance of the noble gases, all of which failed initially to comply with Mendeleev's scheme. In **chapter five** I examine these occasions where Mendeleev's periodic table experienced such clashes with nature. Combining these case studies with Peirce's account of fallibilism, I will argue that the periodic table demonstrates *iconic robustness* in retaining its capacity to promote thought experiments and to generate new knowledge, whilst undergoing structural changes in response to nature's resistance in the form of known elements such as the rare earths and in the appearance of novel elements such as the noble gases. At the beginning of **chapter five** I will define *iconic robustness*.

One of the current debates around the periodic table concerns those factors that seemingly weighed most heavily in favour of its eventual acceptance by the chemistry community. Does the prediction of new elements such as scandium, germanium and gallium carry greater epistemic weight over the successful accommodation of those elements existing at the time of its inception or is the reverse more likely (Brush 1996, Scerri and Worrall 2001)? In **chapter six** I will argue that focussing on Mendeleev's practice of representation, as revealed by his iconic periodic table, provides a new and fruitful understanding of its epistemology. The claims and counter claims of what is sometimes known as the 'accommodation/prediction debate' (Douglas and Magnus 2013) fail to offer a coherent account of Mendeleev's representational practice. I will argue that treating the periodic table as an iconic representation achieves what Andrea Woody (2004:782) describes as an '*articulated awareness* of the nature of the objects and relations' (emphasis in the original) constituting Mendeleev's periodic table. Scientific representations such as the periodic table Woody (2004:780) claims can be viewed 'as pragmatic tools for acquiring the sort of articulated knowledge that is the hallmark of nontrivial knowledge'. Drawing on Woody I will argue that the polarised 'accommodation/prediction' accounts fail to demonstrate the means whereby Mendeleev's table functioned as a 'pragmatic tool' for extending his appreciation – or 'non-trivial knowledge' - of the relations between the chemical elements. An *articulated awareness* whereby the predictive power of Mendeleev's table in discovering new relations between its chemical objects, as well as its construction, is revealed from the vantage point of Peirce's iconicity, as integrated functions of his practice of representing.

Chapter One

The Chemistry of *Relations*: Peirce and Experiments with Diagrams

1.1 Introduction

The philosopher Charles Sanders Peirce graduated (A.B.) from Harvard in 1859. In 1861 and after a year with the U. S. Coast and Geodetic Survey, he entered Harvard's Lawrence Scientific School to study chemistry. The *Catalogue of the Officers and Students of Harvard University fort the Academic Year 1861-62* lists[1] Peirce's father, a founding force behind the Lawrence Scientific School, as 'Benjamin Peirce, LL.D., Parkman Professor of Astronomy and Mathematics'. His son's chemistry tutor, Josiah Parsons Cooke, is listed as Erving Professor of Chemistry and Mineralogy. There are fifty seven[2] 'scientific students' listed, including 'Peirce, Charles S., A.B', studying chemistry. Peirce graduated (Sc.B.) *summa cum laude* in 1863 and that same year published his first paper in the *American Journal of Science and Arts*, 'Chemical Theory of Interpenetration'.

Peirce's time at the Lawrence Scientific School is generally referred to by Peirce scholars as simply a biographical detail. For example Max Fisch records Peirce's chemical training as a period leading on to his later achievements in logic and science,

> Chemistry at that time offered the best entry into experimental science in general, and was therefore the best field in which to do one's postgraduate work, even if one intended to move on to other sciences and, by way of the sciences, to the logic of science as a whole. (W1:xxi)

I will argue that a different perspective on the role of chemistry for Peirce's later work emerges by examining the nature of the chemistry curriculum at Harvard during Peirce's time. This is not an approach that appears to feature in the literature. To begin with it is worth focussing on the innovations led by Peirce's chemistry tutor, the Erving Professor of Chemistry and Minerology, Josiah Parsons Cooke. This will provide the context for Peirce's study of chemistry.

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[1] Page 6

[2] Pages 71-73

Eisele’s Law, after the scholar Carolyn Eisele, states that ‘Peirce's philosophy and logic can be understood only in the context of his mathematics’ (Tursman 1987:68). Tursman is referring to Eisele’s *Charles Sanders Peirce, The New Elements of Mathematics* (in four volumes), a work of great scholarship which according to Arthur Burks (1978:913), is the result of ‘edit[ing] about 2500 pages of the unpublished manuscripts, encompassing pure mathematics, numerous applications, and some rather ingenious textbook materials’. Other scholars have agreed with the spirit of Eisele’s Law. For example, Kenneth Ketner (1982:329) describes Peirce’s account of diagrammatic thought as, ‘simply… mathematical thought [as] the thought that works by diagrams’. Christopher Hookway (2003:2) asks the rhetorical question, ‘[w]hy did he [Peirce] take mathematics to be a discipline which needs no foundations but can provide foundations for philosophy?’ More recently, Matthew Moore (2010:xv) claims that Peirce’s ‘philosophy of mathematics plays a vital role in his mature philosophical system’. These scholars privilege mathematics whilst crediting chemistry with no part in the development of Peirce’s philosophy.

In *Prolegomena to an Apology of Pragmatism* (c1906), Peirce describes the process of experimenting with diagrams by using a description drawn from chemistry,

> One can make exact experiments upon uniform diagrams; and when one does so, one must keep a bright lookout for unintended and unexpected changes thereby brought about in the relations of different significant parts of the diagram to one another. Such operations upon diagrams, whether external or imaginary, take the place of the experiments upon real things that one performs in Chemical and Physical research. Chemists have, ere now, I need not say, described experimentation as the putting of questions to Nature. Just so, experiments upon diagrams are questions put to the Nature of the Relations concerned. (CP 4.530, c1906)

Whilst not refuting Eisele’s emphasis on mathematics I take Peirce’s experimental chemist putting ‘questions to Nature’ as more than a literary device – an analogy – for the logician experimenting on diagrams and putting questions ‘to the Nature of the Relations concerned’. In this chapter I argue that chemistry was an important material source that informed and directed Peirce’s thinking about the epistemic and logical value of diagrams and diagrammatic reasoning; that along with mathematics, chemistry contributed substantially to his way of thinking diagrammatically and in terms of *relations*. The mathematical and chemical thinking that formed part of Peirce’s study of chemistry at

Harvard provided a conceptual basis for his later account of diagrams; an account that has so far been neglected in the literature. Before making any direct connection between Peirce's training as a chemist and his later philosophy it is worth first examining the chemistry curriculum at Harvard during his time there and the reforms introduced by his teacher Josiah Cooke.

1.2 Josiah Cooke: the rejuvenation of the chemistry curriculum at Harvard

The American chemist Frank Wigglesworth Clarke (1878:190) and a graduate (1867) of the Lawrence Scientific School, describes the introduction of science courses into many American colleges as being, 'controlled almost exclusively by men of classical training and bias – men wholly outside of scientific life'. Science was studied by rote learning and recitation, supplemented by lectures and occasional practical demonstrations where, as Clarke (1878:190) describes,

> Students come to the professor of chemistry much as they would go to see a conjurer; expecting to be stunned, dazzled, and delighted but dreaming of no real study except an occasional recitation and the cram for examinations at the end of a term.

It is not surprising that, as William Jensen (1988:8) claims, '[m]ost 19th-century American chemists seeking advanced chemical training during this period went instead to Germany, where it has been estimated that roughly 600 received graduate degrees of some sort'. The German universities were attractive for reasons, summarised by Edward Beardsley (1964:14-15) as being, 'fashionable… and because German training was an index of culture'. Principally, American universities were not research minded and German universities 'offered a level of chemical education that no American institution could match'. For, as Beardsley (1964:15) continues, study in Germany 'offered the in-comparable opportunity to work under such masters of chemistry as Friedrich Wohler at Göttingen, Heinrich Rose at Berlin, August Kekulé at Bonn, Justus von Liebig at Giessen and later Munich, and Robert Bunsen at Heidelberg'. The American Chemical Society was founded in 1876 and yet for the first thirty years, claims Robert Budd (1985:191),'six out of ten ACS presidents had been trained in German universities, while another three out of ten came to chemistry via medical training'.

One American chemist who trained in Germany was Ira Remsen[3] who, states I Bernard Cohen (1959:671), 'went to Göttingen to work under Fittig and Wöhler, receiving his PhD in 1870'. Remsen's original intention was to study with Liebig at Munich but Liebig was accepting no additional students at this this time. Returning from Germany to America in 1872 Remsen was appointed professor of chemistry at Williams College. Once in post Remsen discovered that his students had no access to a laboratory. On applying for funds to establish a teaching laboratory, Cohen (1959:671) records the college president replying 'you will please keep in mind that this is a college and not a technical school. The students who come here are not to be trained as chemists or geologists or physicists. They are to be taught the great fundamental truths of all sciences. The object aimed at is culture, not practical knowledge.' This attitude by the university authorities underlines a division that existed during the first half of the nineteenth century over the relation between theory and practice in respect to chemistry teaching; practical chemistry often being dismissed as being a craft when set against the more exact sciences of physics and mathematics: the higher calling being to 'teach the great fundamental truths of all sciences…culture not practical knowledge'.

This was not an attitude located solely in America. When the German chemist Liebig approached the University Senate at Giessen to recognize his institute within the university he was, states Holmes (1989:127) 'voted down on the grounds that the proper role of the university was to educate future civil servants, not to train apothecaries, soap makers, brewers, and other craftsmen, important though such training might be'. This rejection reflects the conflict in German universities at the time, Holmes argues (1989:127), 'between the ideal of a general education to cultivate the mind (Bildung) and the goal of training specific skills (Ausbildung). Chemistry, argues Alan Rocke (2003:108), was viewed by the university authorities as being 'too applied, and consisted mostly of compounding of pharmaceuticals, boiling of soap, and preparation of heavy chemicals such as potash, soda, salt, and mineral acids'. It was, Rocke (2003:108) explains, the aim of Liebig and others to overcome this position and who, 'powerfully influenced by the Romantic and neo-humanist movements were at great pains to stress that chemistry was a true *Wissenschaft*, independent but complementary to other sciences such as physics, mathematics and even philology and history'.

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[3] In 1876 Remsen was appointed as inaugural professor of chemistry at Johns Hopkins University which Rocke (2003:113) states was 'the first truly successful transplant of German-style graduate education to the United States'

The connections between Eben Horsford (Rumford Professor of the Application of Science to the Useful Arts), the Lawrence school and the method for training chemists developed by Liebig in Giessen are important in understanding Peirce's own training as a chemist. It is worth saying something in brief about Liebig's pedagogy. Studies by historians of science (e.g Holmes 1989; Fruton 1988) have emphasized how at Giessen, Liebig established a laboratory where students and assistants worked on projects alongside one another. These projects usually stemmed from Liebig's own interests. For example Holmes (1989:160) records how in 1839 Liebig's research interests turned to the fatty acids deciding that, 'there were still some questions worth reexamining'. Fatty acids are organic molecules with relative high molecular weights and containing large numbers of carbon and hydrogen atoms in addition to smaller numbers of oxygen atoms. On analysis, small differences in their percentage composition would give correspondingly large differences in their molecular formula. To inquire into this problem Holmes (1869:160) describes how 'Liebig organized for the first time in the winter of 1839/40 the research efforts of a sizable group of his students into a coordinated attack on a single large problem, the investigation of the fatty acids'. By this time, explains Rocke (2003:101), it was Liebig's practice to 'take his most experienced *Praktikanten* and give them research assignments'. In stark contrast to the methods of rote learning and recitation Clarke had observed in American colleges, Rocke (2003:106) states that Liebig's method was not a training but an education for '[t]hose who learned about both empirical phenomena and theory by active learning in the laboratory had learned how to think, not simply how to mix drugs. Such chemists would also be far better able to apply their learning, by comparison to those who had trained in a craft, apprentice-style, merely by rote'. Catherine Jackson (2011:65) captures a sense of Liebig's teaching methods when she states, '[s]tudents and assistants worked together in a communal laboratory, learning by doing and by watching more experienced chemists perform operations in which they were not yet expert'.

It was against this background that the Lawrence Scientific School was founded which, Beardsley (1964:2) claims, was one of the colleges which 'led the way in giving chemistry a respected place in American higher education'. In 1843 Benjamin Peirce – Charles' father and Harvard professor of mathematics and astronomy - proposed a radical revision of how the sciences were to be taught at Harvard. The plan, explains Mary Ann James (1992:68), was that the Rumford Professorship for the Application of Science to the Useful Arts 'should be the focal point at the new school of practical science'. The school was founded in 1847 and named the Lawrence Scientific School after its benefactor, the local industrialist Abbot Lawrence. The new School added an extra dimension to Harvard's curriculum by providing courses that focussed on both the theory and practice of science. In 1847 Eben Horsford was appointed Rumford professor, having previously graduated in civil engineering from the Rensselaer Institute at Troy, New York - one of American's earliest colleges of science and civil engineering. After graduating, Horsford studied chemistry at Liebig's laboratory in Giessen for the two years between 1844 and 1846 before returning to America. In an early account of the beginnings of laboratory teaching in America, Frank Whitman (1898:203) explains that it was Eben Horsford and 'a favourite pupil of Liebig [who] brought to Cambridge the methods and ideas of the Giessen laboratory' – a point of agreement with Rocke (2003:113) who states that, 'Horsford modelled his institute closely and explicitly on Liebig's'.

It was Horsford's connections with Liebig, whose practical approach was highly regarded in America, argues Keith Sheppard (2006:567), which contributed to persuading Abbot Lawrence 'to donate fifty-thousand dollars' for the school's foundation – a record amount at that time. In addition Horsford was also connected to manufacturing, having patented the first formulation for a baking powder based on calcium phosphate – this too would have likely impressed Lawrence who was also a manufacturer. In addition Lawrence's experience as a manufacturer had, states Beardsley (1964:7), convinced him that, 'bleacheries and print works sorely needed skilled chemists'. It is Sheppard's (2006:567) view that 'Eben Horsford was most influential in transplanting Liebig's methodology to the United States' with the new School being 'modelled along Liebig's lines'. A point corroborated by H Benninga (1990:81) in stating that Horsford organised his chemistry department 'in accordance with the principles he had learned from Liebig'; also by Aaron Ihde (1984:270) who described the teaching being 'patterned on the Giessen model'. The historian of science Margaret Rossiter[4] captures Horsford's plan succinctly: to create 'a Giessen on the Charles' in Cambridge, Massachusetts.

In 1847 Horsford's first laboratory course in chemistry had a total of twelve students. Nine years after his appointment Horsford founded the Rumford Chemical Works (1856) and divided his time between his commercial interests and his academic post – a situation likely motivated in part by the relatively low level of academics' salaries. This had an adverse impact on Horsford's teaching and it is for this reason, argues van Klooster (1949:13), that 'the laboratory work in the beginning was meagre'. Eventually a combination of ill health and his ever growing commercial interests resulted in Horsford devoting less time to his

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[4] cited in Salzman (1986:1649)

academic post with student numbers declining as a result; Horsford resigned from Harvard in 1863. A second reason for the failure of Horsford's project, Rocke (2003:113) gives is that only half of Lawrence's donation of $50, 000 went to support Horsford's laboratory; 'the essential difficulty was always lack of sufficient funds…there can be little doubt that the endeavour *would* [otherwise] have succeeded' (emphasis in the original).

Whilst it was Horsford who brought the Liebig's laboratory method of teaching to Harvard, I will show in the next section that it was Cooke who, motivated by his contact with the French chemists Jean Baptiste André Dumas (1800 – 1884) and Henri Victor Regnault (1810 – 1878), resurrected the laboratory programme after its subsequent decline. The chemist and historian Stephen Weininger (2013:97) captures the twin effects of Horsford and Cooke on chemistry at Harvard by stating that whilst Horsford was 'a prominent conduit to the US for the Liebig program' nevertheless Harvard undergraduates 'had to wait half a decade longer before a select few had the opportunity to undertake laboratory work in a cramped room without gas and running water under the new Erving Professor, Josiah Parsons Cooke Jr.'.

In 1850 Josiah Cooke, having been appointed originally as a tutor in mathematics, was appointed Instructor in Chemistry and Mineralogy. In that same year and only two years after graduating, Cooke was advanced to the Erving Professor of Chemistry and Mineralogy and, argues Sidney Rosen (1982:525), 'the reason for this promotion was that chemistry teaching at Harvard had become virtually non-existent'. The mathematician turned chemist Cooke then set about to reawaken an interest in the study of chemistry and the laboratory teaching method first developed by Liebig and introduced at Harvard some years earlier by Eben Horsford. This was no easy task for as Beardsley states (1964:9) 'there was no laboratory for teacher or pupil, nor did the college own a single piece of chemical apparatus'. The year before Cooke's appointment John Webster, an earlier professor of chemistry, was found guilty of the murder of a Boston physician and hanged.

1.3 Josiah Cooke's laboratory

Once appointed Erving Professor of Chemistry and Mineralogy, Cooke travelled to Europe in search of apparatus for his new department. At the same time he took the opportunity to attend lectures in Paris given by the French chemists Dumas and Regnault. So impressed was Cooke, states Ralf Hamerla (206:173), that he 'befriended and idolized' the two French chemists, realising that 'the mixture of lecture, demonstration and hands-on experimenting so popular in Europe during this period was a component missing from academic instruction in chemistry in the United States'. Writing on Dumas over thirty years after his appointment, Cooke recalls attending his lectures in Paris in 1848 and 1851. In his article Cooke (1884:752) recollects 'that exuberance of fancy' which 'made Dumas one of the most successful of teachers, and one of the most fascinating of lecturers'. In addition to praising Dumas's lecturing style as a great theatrical performance, Cooke (1884:750) also applauds the point that 'Dumas early recognized the importance of laboratory instruction in chemistry, for which there were no facilities at Paris when he first came there, and in 1832 founded a laboratory for research at his own expense'.

On his return to Harvard, Cooke set about re-establishing a laboratory based method of teaching chemistry. As Sheppard (2006:567) explains, Cooke 'returned to set up a private laboratory at Harvard emulating Horsford's laboratory at the Lawrence Scientific School' – and to rekindle Liebig's laboratory method of teaching first introduced by Eben Horsford. The impact of the French chemists that so influenced Cooke was wide ranging, for example Mary-Jo Nye (1993:53) notes that 'influenced by his experiences in Regnault's Parisian laboratory of chemistry, William Thomson (later Lord Kelvin) organized a physical laboratory near his lecture room at Glasgow in 1850'. It took a further ten years for a second similar laboratory to teach the theory and practice of electricity to be established at University College, London. Nevertheless Cooke's new Boylston Hall laboratory at Harvard, record Stephen Contakes and Christopher Kyle (2011:3), 'enabled Cooke to introduce instruction in chemistry by Liebig's laboratory method in 1858, albeit as an elective course'. This elective quickly established its worth whereby, states Hamerla (2006:175), 'Cooke was able to expand his lab to attract the attention of the most gifted students'. Peirce was one such 'gifted student'. In his memoir of Cooke, a former student and later colleague of Cooke and America's first eminent organic chemist Charles Loring Jackson (1902:178) describes his teacher's lack of formal training and how he often referred to himself as a 'self-taught chemist, but 'the fact that he had taught himself chemistry by his own experiments showed him the value of this method for other students'. Nonetheless, records Jackson (1902:177/8), with such seemingly limited experience Cooke reformed a situation where 'chemical teaching in Harvard College had become extinct and must be re-established' against a situation where 'the college was wedded to methods of teaching excellent for classics and mathematics, but entirely unfit for a subject like chemistry', and also recalling 'the zeal with which he [Cooke] threw himself into these tasks led to substantial results much more quickly than could have been expected'. As Liebig had achieved earlier in Germany, Cooke in Jackson's opinion (1902:178) 'was called upon to take a prominent share in the great battle to introduce science into the college course on an equality with the humanities'. It was through the commitment and enthusiasm of scientists such as Horsford and Cooke that Liebig's laboratory methods founded at Giessen in 1826 travelled to America. In addition to promoting Liebig's methods, Cooke – as we shall see - modified the chemistry curriculum by adding a greater degree of mathematical rigour.

The *Catalogue of the Officers and Students of Harvard University fort the Academic Year 1861-62* outlines the curriculum for each subject. The entry[5] under chemistry states that the course of instruction will include 'recitations in Experimental Chemistry, Qualitative Analysis, Chemical Physics, and the Applications of Chemistry to the Arts'. The academic lectures available included chemistry, physics, botany and anatomy as well as laboratory sessions to do with chemical analysis, manufacturing chemistry, metallurgy and pharmacy. Of particular interest are the text books that were used as these give some insight into the content of the chemistry curriculum. Students were expected to have 'an acquaintance with Stöckhardt's *Elements of Chemistry* (1858) in addition to Cooke's *Chemical Physics* (1860) and Regnault's *Elements of Chemistry* (1853).

In addition to being highly regarded as a chemist, Cooke was also an excellent teacher and popular with his students. Jackson, his former student, recalls[6], 'I had had an excellent course of lectures on inorganic chemistry from Professor Cooke'. Another of Cooke's students, Francis Storer and a later co-founder of the Massachusetts Institute of Technology, described Cooke[7] as 'first and foremost among the great chemical teachers'. With similar enthusiasm Sidney Rosen's (1982:525) profile states that Cooke's 'greatest success was as an inspiring teacher of chemistry' who 'eschewed technical details and talked about the inspiring aims, needs and methods of chemistry' – and with such an approach is not surprising that 'Cooke literally packed them in the aisles'.

As well as admiring Dumas as a teacher, Cooke also holds his skills as an experimental chemist in high regard. Both Dumas and Cooke shared a research interest in establishing accurate atomic weights. Whilst a number of other nineteenth century chemists worked in this area, it is Cooke's (1884:752) view that 'in none of his work did he [Dumas] show greater experimental skill…[where Dumas's]…determination of the atomic weight of oxygen by the synthesis of water, and of that of carbon by the synthesis of carbonic dioxide, are models of quantitative experimental work'. In 1887 Cooke in association with Theodore W.

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[5] Page 75

[6] Cited in Forbes (1964:98)

[7] Cited in Contakes and Kyle (2011:4)

Richards published a paper titled *The Relative Values of the Atomic Weights of Hydrogen and Oxygen.* America's first Nobel prize for chemistry (1919) was subsequently awarded to Theodore Richards for his work on the accurate determination of atomic weights first begun under the direction of Josiah Cooke.

1.4 Josiah Cooke's reforms to the mathematical demands of chemistry

Mathematics was Cooke's first degree. He graduated from Harvard in 1848 and subsequently was appointed as a tutor in mathematics. One of Cooke's reforms to the chemistry curriculum was to introduce a greater degree of mathematical rigour. This is of relevance to this project for it coincides well with the mathematical mind-set scholars often attribute to Peirce. Later in his life Peirce was to write '[m]y special business is to bring mathematical exactitude, I mean modern mathematical exactitude into philosophy, and to apply the ideas of mathematics in philosophy' (NEM:x c1894). By increasing the mathematical content of chemistry Cooke was perhaps acting on the rhetoric of the time that such a move would establish chemistry more on an equal footing with physics. There is also a second reason: Cooke believed mathematics to be an essential tool to logical thought. In a tribute to Cooke, the American agricultural chemist and his former student Francis Storer (1894:528) wrote, 'it was by his mathematical studies more particularly that Cooke acquired that habit of thinking clearly and reasoning closely which distinguished him through life'. In his book *The Credentials of Science: the Warrant of Faith*, Cooke (1888:94) explains that, for the application of the deductive method in science, 'mathematics is the most important tool'.

But for Cooke (1888:101) mathematics was important to the study of science not only as a mechanism for deductive reasoning but also for the reason that 'mathematics is the science of quantitative relations wholly independent of their material expression'. As I will show later on, this is remarkably similar to Peirce's treatment of mathematical equations as 'icons'. The nineteenth century saw the rise of physical chemistry with mathematics being central to its study and understanding. Later in the same volume, when dealing with the solubility in water of a wide range of compounds at varying temperatures – a problem in physical chemistry – Cooke (1888:192) comments that the processes occurring 'cannot be understood without some understanding of mathematics'. Such an approach is likely to have appealed to Peirce's mathematical inclinations. It is worth therefore exploring how Cooke approached the role of mathematics to the laboratory method of chemistry teaching, inspired by the French chemists Regnault and Dumas who were introducing Liebig's pedagogical methods in France.

As we will see Cooke went on to bring a degree of mathematical rigour to the study of chemistry – to present chemistry as an exact as well as a descriptive study. The impact this had on chemistry can be followed by looking at the text books Cooke chose and also authored for his courses. Shortly after his appointment as tutor in mathematics and chemistry in 1850 Cooke sought and gained Harvard's governing council's (the Corporation) permission to introduce Julius Stockhardt's text *Principles of Chemistry*. Why Cooke thought such high-level permission was needed is not clear, but Charles Eliot (1894:532), President of Harvard during this time, recalls 'I know of no other instance within the last fifty years in which the President and Fellows have passed a vote concerning the adoption of a text-book'. Perhaps Cooke anticipated the changes he was about to make, with less emphasis on rote learning and a greater focus on mathematical rigour and problem solving through laboratory based investigations, might be unpopular with some of his students. His 'permission' was perhaps a form of insurance against the possibility of later complaints by students unhappy with this increase in mathematical rigour and difficulty. Even twenty-five years after his first intake of students, Cooke (1875:528) comments that 'mathematical studies are peculiarly well adapted to train the logical faculties'. Nonetheless because of the widespread practice of rote learning found in many American schools Cooke (1875:530) follows up with the observation that students arriving on his course 'will solve an involved equation of algebra readily enough so long as they can do it by turning their mental crank, when they will break down on the simplest practical problem of arithmetic which requires of them only thought enough to decide whether they shall multiply or divide'. The changes Cooke had made were in part an attempt to compensate for this perceived weakness in the school system.

America was not as far advanced in physical chemistry compared to some other parts of Europe. In his essay 'Between Physics and Chemistry: Helmholtz's Route to a Theory of Chemical Thermodynamics', Helge Kragh (1993:426) argues that Hermann von Helmholtz's work 'exerted a considerable influence on French and German chemists, it does not appear to have had a similar impact on British or American Chemistry'. During the early 1880s Helmholtz had developed a mathematical theory of thermodynamics for chemical processes. Other European chemists such as Svante Arrhenius, Jacobus van't Hoff, Friedrich Ostwald and Walther Nernst were also contributors to what was becoming a powerful research programme in physical chemistry. The growing branch of physical chemistry demanded a sophisticated understanding of mathematics. Why were American chemists seemingly reluctant to engage with physical chemistry? During the nineteenth century

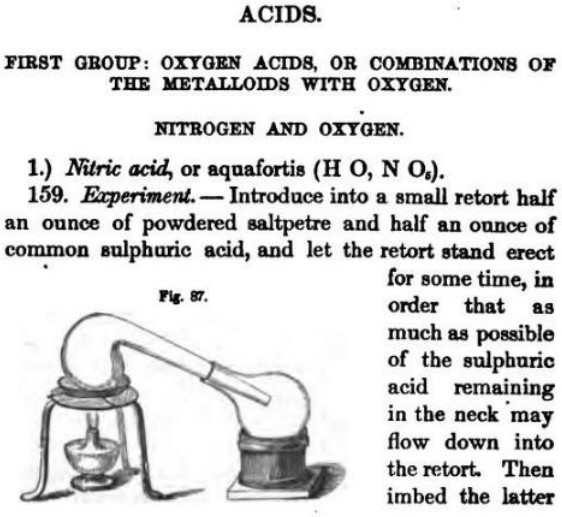
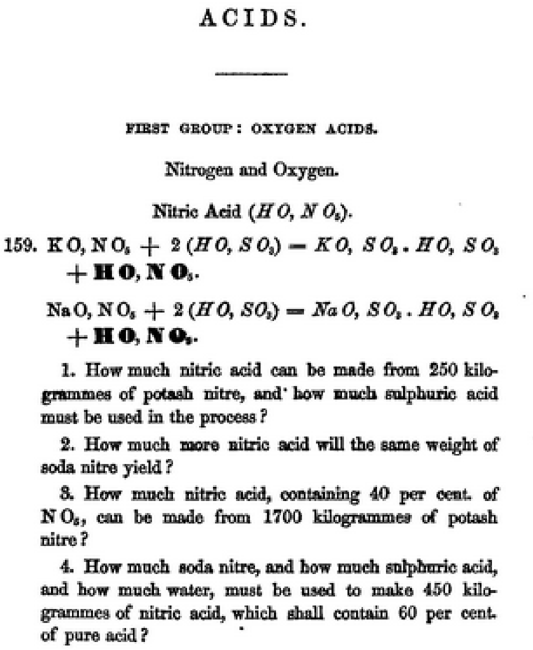
European chemists and other physical scientists received a greater education in higher mathematics than was the case in America. The American historian of science John Servos (1990:179) argues that whereas European students of the physical sciences ‘typically received a mathematical preparation at early stages in their careers that was both intensive and extensive’ in America ‘secondary schools, colleges, and even graduate programmes in physics gave mathematics short shrift’. In her comparison of nineteenth century physics teaching in German and American universities Kathryn Olesko (1988:111) states that where, ‘German physics students might be expected to work out elliptical integrals and transcendental equations’, American students in general ‘did not go beyond elementary differential and integral calculus, and most often they deployed simple algebraic calculations’.

One of the reasons for this lack of mathematical training, argues Servos (1990:180), lies in the Protestant values of nineteenth century America which, ‘encourages scientists to dedicate themselves to laboratory work’ believing that there was something ‘sinful’ in deploying ‘mathematical cunning to determine how nature worked’. However, as Servos (1986:612) explains in an earlier paper, during the nineteenth century America specialised in ‘typically field or laboratory sciences, heavily dependent on observational or experimental evidence and techniques’; American scientists were in general experimentalists not theoreticians. The reason for this, argues Servos (1986:614-5), is not simply because American scientists ‘exulted in collecting facts and feared demon mathematics, an idol that could pervert an unprejudiced understanding of nature’, but also a result of ‘the quality of mathematical training given [to] American scientists’ at the time. German and French secondary education provided a far superior training in mathematics than American high schools. Of greater significance Servos (1986:616) argues were the changes occurring in American colleges and universities where ‘with the expansion of the curriculum and the growth of elective studies after the Civil War, mathematics was the subject that suffered the greatest losses, save perhaps Greek’. At Yale for example mathematics suffered at the expense of creating more time for the laboratory sciences. I would argue that Cooke sought to build in his students a great level of skill and confidence in mathematics so they were better able to manage the quantitative aspects of chemistry, something he aimed to redress through his text books. As a mathematician this was something Cooke was well placed to do.

1.5 Josiah Cooke's text books

1.5.1 *Chemical Problems and Reactions to Accompany Stöckhardt's Elements of Chemistry* (1857)

The first text book Cooke published was in 1857 and titled *Chemical Problems and Reactions to Accompany Stöckhardt's Elements of Chemistry*. This was a companion to Stöckhardt's own text which Cooke had sought Harvard's permission to introduce. Before looking to see how Cooke's text contributed to the mathematisation of chemistry, it is first worth considering the original by the German chemist Julius Stöckhardt. The introduction to the 1852 edition of Stöckhardt*'s Principles of Chemistry* states that the work was recommended for translation by Harvard's Eben Horsford. The translation was, states Max Fisch, carried out by Charles's uncle Charles Henry Peirce and his aunt, Charlotte, 'whose German was excellent' and who did most of the translating' (W1:xviii). In his introduction to *Stöckhardt* (1852:x), Horsford explains that the book is aimed to offer a laboratory based practical course where 'the apparatus necessary for many of the most instructive and interesting chemical experiments would cost but a few dimes, and as many dollars would furnish the requisites for all, or nearly all, the most important experiments…'. The purpose of Cooke's text as an accompaniment to Stöckhardt's original text can be illustrated by comparing the two pages below. The format of Cooke's book mirrors Stöckhardt's by setting problems to accompany the practical exercises – note that both entries refer to experiment 159.

 ACIDS. FIRST GROUP: OXYGEN ACIDS, OR COMBINATIONS OF THE METALLOIDS WITH OXYGEN. NITROGEN AND OXYGEN. 1.) *Nitric acid*, or aquafortis ($H O, N O_5$). 159. *Experiment.* — Introduce into a small retort half an ounce of powdered saltpetre and half an ounce of common sulphuric acid, and let the retort stand erect for some time, in order that as much as possible of the sulphuric acid remaining in the neck may flow down into the retort. Then imbed the latter Fig. 87.	 ACIDS. FIRST GROUP: OXYGEN ACIDS. Nitrogen and Oxygen. Nitric Acid (HO, NO_5). 159. $KO, NO_5 + 2(HO, SO_3) = KO, SO_3 . HO, SO_3 + \mathbf{HO, NO_5}$. $NaO, NO_5 + 2(HO, SO_3) = NaO, SO_3 . HO, SO_3 + \mathbf{HO, NO_5}$. 1. How much nitric acid can be made from 250 kilogrammes of potash nitre, and how much sulphuric acid must be used in the process? 2. How much more nitric acid will the same weight of soda nitre yield? 3. How much nitric acid, containing 40 per cent. of NO_5, can be made from 1700 kilogrammes of potash nitre? 4. How much soda nitre, and how much sulphuric acid, and how much water, must be used to make 450 kilogrammes of nitric acid, which shall contain 60 per cent. of pure acid?
Figure 1: Preparation of nitric acid Source: Stöckhardt*'s* (1852) *Principles of Chemistry,* page 152	**Figure 2**: Calculating the yield of nitric acid from the reaction between potash nitre and sulphuric acid Source: from Cooke's (1857) *Chemical Problems and Reactions* to *Accompany Stöckhardt's Elements[Principles] of Chemistry*, page 63

Here Stöckhardt describes an experiment to produce nitric acid whilst Cooke sets his students a number of quantitative problems based on this practical situation – for example to determine the mass of nitric acid that can be made from a known mass of potash nitre (sodium nitrate) and sulphuric acid. Notice too in passing that Cooke represents chemical change as an equation with an 'equals' sign (=) separating the reactants from the products. The introduction of arrows to show the direction of change was not made until 1884 by the Dutch chemist Jacobus van't Hoff in his book on chemical equlibrium *Étude de Dynamique Chemique* (Studies in Chemical Dynamics) where double reversed arrows where used to indicate reversible reactions and the dynamic nature of chemical equilibrium.

The content of Cooke's *Chemical Problems* included what today would be described as stoichiometric calculations as well as problems using the gas laws, solubilities, specific gravities and converting quantities from one system of units to another. The mathematical demand is limited to an understanding of the four rules of arithmetic and an appreciation of proportionality. Whilst Stöckhardt's text was a course of practical chemistry, Charles Jackson (1894:5126) recalls Cooke's view was that 'it did this at the sacrifice of all that is distinctive and peculiarly valuable in the study of an experimental science' - a laboratory based problem solving approach involving quantitative methods. By establishing his laboratory method Cooke also emphasised a number of skills essential to experimental chemistry. These included the need for accurate working when making and recording observations, the ability to process numerical data and to draw deductions from experimental results. In this way Cooke led his students to appreciate that chemistry was both a descriptive and quantitative science. In the opinion of a former president of the Kansas Academy of Science, F P Dains (1911:30), Cooke's *Chemical Problems* was 'the first book of the kind with which I am acquainted, and it shows his desire to promote the rigid accuracy which forms the basis of any adequate science teaching'. In more recent times William Jensen (2011:14), in a survey of physical chemistry texts books before the German chemist Friedrich Ostwald (1853–1932),finds that although there were several German text books in physical chemistry published in the 1820s, Cooke's *Chemical Problems* was 'the first specialized English-language book to deal specifically with the subject of chemical calculations'. In Cooke's opinion the lack of quantitative work in Stöckhardt's original text made it 'insufficiently developed for the purposes of college teaching'[8].

1.5.2 *Elements of Chemical Physics* (1860)

Some three years later in 1860 Cooke published his second book, *Elements of Chemical Physics*, believing that his students should have a good grounding in physics and its quantitative methods. Early in chapter one Cooke (1860:5) distinguishes the study of chemistry as 'the study of chemical change' from physics which 'deals with physical properties and the physical changes of matter'. There are only three occasions when Cooke uses the term 'chemical change'. Firstly when describing the process of adhesion, secondly in an account of dissolving, and thirdly in an explanation of melting which Cooke (1860:47) describes as the process where solids can 'bear the change of temperature without undergoing chemical change'. For notwithstanding Cooke's choice of title this is primarily a physics text covering such topics as dynamics, crystallography and heat. There are numerous references to Regnault, whose interests as a professor of both chemistry and physics coincided with a number of the topics dealt with by Cooke's book. In his tribute to Cooke, Charles Jackson (1902:515) states, 'Regnault especially inspired him [Cooke] with the warmest affection, as is pleasantly shown by the enthusiastic reverence with which he is invariably mentioned in his book on Chemical Physics'. The relative lack of sophisticated mathematics in this text is frankly acknowledged by Cooke (1860:iii), who states that 'only

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[8] Cited in Jensen (2003:1248)

an elementary knowledge of mathematics' is required in order to complete the exercises. On several occasions, for example when dealing with centre of gravity, Cooke (1860:61) indicates that a detailed treatment is not possible, 'since these methods depend on the principles of higher mathematics'. Whilst Cooke has increased the mathematical demand on his students the methods required were relatively straightforward.

The impact of this new quantitative and problem solving approach is recalled by Jackson (1902:518), and one of Cooke's students as follows: 'neither of these books was popular with the students…as they obliged their readers to think, and there is no occupation more distasteful to the undergraduate'. Nonetheless Jackson (1902:518) acknowledges the educational value of Cooke's two books described here and his desire to develop the mathematical competence, accuracy and problem solving ability of his students,

> I can well remember the utter despair which settled upon me when I attacked my first problem in the Chemical Physics. I had never been called upon to think unassisted before, and at first I doubted the possibility of the process. But in this very demand on the thinking powers of the student lay the chief usefulness of these books, and their educational value on this account can hardly be overestimated. Nor would the fact that this work was distasteful have troubled him much, as he often expressed his disapprobation of the sugar-coating now so generally considered essential on educational pills.

Accepting Jackson's recollection, the success of Cooke's texts lay in presenting chemistry as an experimental inquiry and not as a sequence of facts and 'recipes' of methods, the ability of a chemist to problem solve and to process numerical data being treated as essential to their experimental practice.

What was the impact of Cooke in his attempt to introduce a greater degree of mathematical formalism to the teaching of chemistry? A reviewer[9] for the *American Journal of Science* (1869:435) of Cooke's third text book *First Principles of Chemical Philosophy* (1868), judges the text to be an 'important manual of instruction' by Cooke to whom 'more than to any American, is due the credit of having made chemistry an exact discipline in our colleges'. But to what extent was Cooke's project an attempt to introducing a degree of mathematical formalism to chemistry? As we have seen earlier, Cooke himself regards the

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[9] Also cited in Jensen(2011:17)

mathematics that his approach demands as relatively straightforward and points his readers to ‘higher mathematics’ for a more sophisticated treatment of chemical physics. I would argue that Cooke was preparing his students so that they would have the necessary mathematical skills and confidence to operate and to problem solve within the quantitative branches of chemistry. The American historian Servos (1990:179) regards Cooke’s *Chemical Physics* as ‘being a quantitative physics, but not a mathematical physics’. It is quantitative in that Cooke expects his readers to process problems requiring relatively unsophisticated arithmetical methods but not mathematical in the absence of more exacting and sophisticated mathematical techniques. For example, Cooke in his treatment of an oscillating pendulum makes no mention of simple harmonic motion which would lead on to an analysis involving calculus and differential equations – one of the higher mathematical techniques Cooke points towards but leaves out. Overall and in terms of Cooke’s practice as a chemist, I would argue that he was using mathematics in a non-reductive sense.

1.6 Josiah Cooke’s treatment of *relations*

In common with other nineteenth century chemists Cooke framed aspects of his approach in terms of the nature of the *relations* operating between concepts, quantities and entities. This section examines Cooke’s approach to *relations*, one that his student Charles Peirce would have been exposed to. This is of relevance as the nature of *relations* was to figure prominently in Peirce’s later scientific and philosophical writings.

The term *relation* was frequently used by nineteenth century chemists when discussing the degree of correspondence between two or more chemical objects. For example John Dalton (1808:339) in his *New System of Chemical Philosophy,* in observing that 100 volumes of what he describes as nitrous gas will form 48.5 volumes of nitrous oxide and 28.3 volumes of oxygen, comments that ‘it is very remarkable that these *relations* should have so long escaped observation’ (emphasis added). Here Dalton is discussing the correspondence between numerical quantities but he also deploys the term *relations* when describing how substances react. For example, when discussing the reactions of silex (a form of silica found in flint) Dalton (1808:539) reports that he has ‘succeeded pretty well by investigating its [silex] *relations* with potash, lime and barytes’ (emphasis added).

The use of the term *relations* occurs many times in Humphry Davy’s *Elements of Chemical Philosophy* (1812). In common with Dalton, Davy too uses the concept of relations when dealing with numerical quantities. For example, in a section dealing with what today we would describe as empirical formulae – the simple whole number ratio in which elements combine to form compounds – Davy (1812:62) writes, ‘the element which unites in the smallest quantity being expressed as unity, all the other elements may be represented by the *relations* of their quantities to unity’ (emphasis added). So for example in more modern terminology, the formula of sodium oxide is Na_2O, with the quantity of sodium being represented by its relations to oxygen being set as unity or with the value one.

In February 1863 *Chemical News* carried a paper by the English chemist John Newlands (1837-1898) titled *On Relations among the Equivalents* which Eric Scerri (2007:xix) describes as one of the ‘early periodic systems’. In introducing his proposed scheme of correlations between equivalent weights[10] and the physiochemical properties of the chemical elements Newlands (1863:70) states that what follows ‘are among the most striking *relations* observed on comparing the equivalents of analogous elements’ (emphasis added). In this version of his arrangement, Newlands produces a scheme of eleven groups of elements setting out the numerical correlation between each element’s equivalent weight. An example of Newland’s (1863:71) approach can be seen from this extract,

> Group XI.-- Mercury, 100; lead, 103.7; silver, 108.
> Lead is here the mean of the other two

Having demonstrated many such correlations for each of his eleven groups Newlands (1863:72) offers this final caveat as a closing sentence: ‘I also freely admit that some of the *relations* above pointed out are more apparent than real; others, I trust, will prove of a more durable and satisfactory description’ (emphasis added). It is not perhaps surprising that when Cooke proposed his own scheme this too was framed in terms of the numerical *relations* between the atomic weights of the elements.

In 1896 Francis Preston Venable (1856 – 1934), an American research chemist, university teacher and president of the University of North Carolina and the American Chemical Society, published *The Development of the Periodic Law.* This work covers in detail the development of the periodic law from 1817, when the German chemist Johann Döbereiner (1780 – 1849) put forward his *law of triads***,** through the numerous developments of the nineteenth century and including the contributions of Cooke, Peirce and Mendeleev. The

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[10] Scerri (2007:19) states: ‘The equivalent weight of any particular metal, for example, was originally obtained from the amount of metal that reacts with a certain amount of a chosen standard acid. The term “equivalent weight” was subsequently generalized to denote the amount of an element that reacts with a standard amount of oxygen’.

term *relation* occurs many times over to describe patterns existing between the properties of the chemical elements and their atomic weights. In the opening sentence, where he introduces the scope of the book, Venable (1896:1) writes, 'this work is intended as a study of the development of the natural law underlying the *relations* of the elements and their properties to one another' (emphasis added). The book was very well reviewed in the *American Journal of Science* (1897:280) with the reviewer (W.A.N.) capturing the ubiquitous term relations in this context in stating,

> The scope of the book includes an account of the numerous attempts which have been made to discover numerical and other *relations* between the atomic weights and also an account of speculations as to the origin of the elements and their *relation* to some fundamental form of matter. (emphasis added)

The reviewing author deploys the term relation to connect a correspondence between the atomic weights of the elements. Also mentioned is the relation between individual elements and some primary form of matter as suggested by the English chemist William Prout (1758 – 1850). The term relation was commonplace in the literature of nineteenth century chemistry - a term that Peirce would have understood clearly in its application.

1.6.1 Josiah Cooke – 'The Numerical Relation between the Atomic Weights, with Some Thoughts on the Classification of the Chemical Elements' (1854)

This paper was published seven years before Peirce joined the Lawrence Scientific School in 1861 and is relevant to this chapter as it shows Cooke writing in terms of the *relations* between the atomic weights of the chemical elements. Thus Peirce experienced at first hand his tutor Cooke's research interest in systemising the chemical elements based on an approach that emphasised *relations*. As we shall see later, Peirce also published an arrangement of the chemical elements in terms of their atomic weights[11].

In 1854, and whilst striving to establish the status of chemistry as an academic subject within Harvard's curriculum, Cooke published, 'The Numerical Relation between the Atomic Weights, with Some Thoughts on the Classification of the Chemical Elements'. In the very first sentence Cooke (1854:33) states the focus of his paper to be, the 'numerical *relations* between the atomic weights of the chemical elements' (emphasis added). Whilst noting that a number of elements can be grouped into triads, where the atomic weight of the

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[11] Peirce's own scheme was published in 1869 and will be considered in chapter two.

middle element is the approximate arithmetical mean of the other two – such as lithium (6.5), sodium (23.0) and potassium (39.2[12]) – Cooke (1854:33) further claimed that such triads 'are only parts of series similar in all respects to the series of homologues of Organic Chemistry, in which the differences between the atomic weights of the members is a multiple of some whole number'. Taking his lead from organic chemistry Cooke (1854:33) placed chemical elements with similar properties into one of the 'six series' each with a general formula,

	Series 9	**Series 8**	**Series 6**	**Series 5**	**Series 4**	**Series 3**
General Formula	8 + n9	8 + n8 or 4 + n8	8 + n6	6 + n5	4 + n4 or 2 + n4	1 + n3

Each series is characterised by a general formula which is related to the atomic weight of each element within the series. For example for Series 9 with the general formula 8 + n9, the differences in atomic weights between each element in the series are always a multiple of nine. The elements of each series had similar chemical properties and were often isomorphous[13]. In devising his scheme Cooke emphasised the resemblance of his system with the various homologous series to be found in organic chemistry. There were some problems with this arrangement which Cooke fully acknowledged – for example oxygen appeared in three of the six series – series 6, 8 and 9. Notwithstanding such anomalies, Cooke (1854:239) saw his major achievement was in 'the discovery of the numerical *relation* between the atomic weights' of the chemical elements (emphasis added).

When describing his system, Cooke (1854:236) explains it as 'bringing together such elements as were allied in their chemical *relations* considered collectively' (emphasis added). The initial motive behind both Cooke's attempt to systemise the elements was pedagogic – to rationalise the chemical elements for easier comprehension and assimilation by his students. For, as Cooke (1854:238) explains, although his system may be found to have 'defects', it was devised as a teaching aide. This is consistent with Cooke's project which was to establish a laboratory based and problem solving approach to learning with less reliance on rote and recitation.

By attempting to systemise the chemical elements, Cooke was seeking a way of presenting their chemical properties as a table of chemical relations, making their connections less a

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[12] Atomic weight values as in Cooke (1854:269)

[13] identical crystalline forms

subject of memory and more one of logical reasoning. As we will see in chapter three this was an aim shared also by Mendeleev in his systemisation of the chemical elements. In his paper Cooke laments the lack of classification schemes in chemistry such as exist in natural history. In many chemistry texts elements of similar properties are scattered throughout the body of the work. Even where the system metal and metalloid (non-metals) is used, great anomalies arise: for example selenium with a shiny metallic like surface is classified as a metal, where sulphur is grouped with the metalloids, even though they share a number of similar chemical properties. As Cooke comments (1854:237), 'for a zoologist to separate the ostrich from the class of birds because it cannot fly, would not be more absurd, than it is for a chemist to separate two essentially allied elements, because one has a metallic lustre and the other has not'. The original purpose of Cooke's (1854:388) classification was to avoid such unhelpful groupings and to bring together elements of similar physiochemical properties, 'to facilitate the acquisition of chemistry [by his students]'. Nonetheless as Cooke (1854:239) explains, he would not have sought publication of his scheme, 'had it not led to the discovery of the numerical *relation* between the atomic weights' (emphasis added).

In his essay 'American Forerunners of the Periodic Law', George Kauffman (1969:129) describes how Cooke's paper was hailed as 'the most complete classification depending upon the atomic weights of the elements, which had up to that time appeared'. Although it was widely praised, Kauffman (1969:129) still considers Cooke's contribution to the periodic law to be an 'unjustly neglected contribution'. Nevertheless the influence of Cooke's paper reached beyond America. For example, Kaufmann (1969:129) mentions the Dutch chemist Guillaume Elsen's view that 'Cooke's table shows a strong similarity to that of Mendeleev, so that we can state that in 1854 the first foundations of the periodic system were nearly laid'. In his memorial to Cooke, Charles Jackson (1894:517) recalls that 'Benjamin Peirce in particular hailed it [Cooke's paper] as a wonderful discovery'. It is not perhaps too great a speculation to suggest that Charles Peirce's father Benjamin carried this view home, given his teenage son's known interest in chemistry.

1.7 Charles Peirce – *relations* between the chemical elements and their atomic weights

Peirce's first degree studies at Harvard had not culminated in great success where he was a 'poor student, typically in the bottom third of his class'[14]. It is perhaps easy to appreciate

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[14] Cited in Burch, Robert, "Charles Sanders Peirce", *The Stanford Encyclopedia of Philosophy* (Winter 2014 Edition), Edward N. Zalta (ed.), URL = <http://plato.stanford.edu/archives/win2014/entries/peirce/>.last visited 23/09/2016

how he flourished at the Lawrence Scientific School under the inspirational teaching of Josiah Cooke who placed such a high value on mathematical reasoning. I believe it was this exposure to Cooke's teaching and to his thinking on the numerical relations between the atomic weights that first sparked Peirce's own interests in this area – one founded on *relations* – a concept that later underpinned so much of his own work. As will be described in chapter two, Peirce's paper 'The Pairing of the Elements' published in an 1869 edition of *Chemical News,* followed the interests of his tutor Cooke by outlining an arrangement of the chemical elements based on their atomic weights. This indicates Peirce's interest as a chemist in this prominent nineteenth century research programme.

As part of his introduction to the history of the periodic table Scerri (2006:xix) suggests William Prout, Johann Döbereiner and Leopold Gmelin as three historical actors 'who began to explore numerical relationships among the elements', with 'early periodic systems' being developed by William Odling, Julius Lothar Meyer and others, 'culminating with Mendeleev's tables'. Once Mendeleev published his periodic system in 1869, Scerri (2006:80) records that the English chemist '[John] Newlands began to publish a series of letters setting out his priority in arriving at the first successful periodic system'. There were a number of other priority counterclaims, for example the German chemist Lothar Meyer became engaged with Mendeleev in what Scerri (2008:93) describes as, 'a rather bitter priority dispute'. In America during March 1892, the debate to which Scerri refers was played out in *The Nation* to which Peirce also contributed. In an article titled *The Periodic Law* (1892) we see Peirce commenting on a research programme that he too shared an interest in as a young graduate chemist with his tutor Josiah Cooke. At the start of his article Peirce makes the following powerful claim for his old tutor as the foremost herald of Mendeleev in stating,

> The principal precursor of Mendeléef was, as it seems to us, that penetrating intellect, Josiah P. Cooke, who first proved that all the elements were arranged in natural series. (W8:284, 1892)

In his inquiry into American precursors of the periodic law, Carl A Zapfee (1969) identifies the Harvard chemist Oliver Wolcott Gibbs (1822 – 1908) and Josiah Cooke. It was Cooke, claims Zapfee (1969:468) who, 'developed a remarkable classification based upon simple arithmetical formulae for six different "series"' which 'not only represented one of the first clear breaks from the concept of triads, which had largely held since the time of Döbereiner, but it anticipated Newlands' "octaves" in that several of Cooke's series were based upon the number eight'. Here Zapfee identifies Newlands's law of octaves published in 1865 where, with some adjustments, ordering by atomic weight gave a system where elements of similar chemical properties occurred with every eighth element – hence law of *octaves*. The result was a series of vertical columns of elements with similar properties. Newland's arrangement, which received wider coverage than Cooke's earlier attempt, is somewhat dismissed by Peirce,

> No doubt, many a chemist in those days drew up a table more or less like this, but refrained from publishing it, feeling that a great discovery was imminent. An obscure American chemist actually assigned this as a reason for not attaching his name to such a table. Yet this was all, if not more than all, that Newlands did; and his papers, in a very widely circulated journal, made no sensation. (W8:285 1892)

The 'obscure American chemist' mentioned here is Peirce himself, referring to his paper 'The Pairing of the Elements'[15] published in the June 1869 issue of the American edition of *Chemical News*. By the time Newlands was publishing there was a greater agreement on atomic weight values, a result in part due to the first international conference of chemists held in 1860 at Karlsruhe in Germany, and the work of Italian chemist Stanislao Cannizzaro (1826–1910) amongst others. It was Peirce's view that once there was general agreement on atomic weights following the 1860 Karlsruhe congress, chemists would then speculate on the possible relations between chemical behaviour and atomic weight. Writing in this way Peirce proposes the 'penetrating intellect' of Josiah Cooke as the 'principal precursor' of Mendeleev, having arrived at his scheme before atomic weight values became more settled. In ending his article Peirce makes the point that it was Mendeleev who 'alone had the sagacity to discern the true scheme of relationship' (W8:285). In terms of the contemporary debate around the acceptance of the periodic scheme with reference to its ability to accommodate existing data or in making successful predictions, writing some twenty three years after Mendeleev's first publication Peirce shows no preference in praising,

> His [Mendeleev's] wonderfully vivid conception of the scheme, as well as his clear perception of its evidence, [which] is shown by the formal and audacious descriptions he gave of the properties of several elements then undiscovered, but required to fill blank spaces, and by the subsequent triumphant verification of his

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[15] This paper will be considered in chapter two

> predictions, especially of what seemed the most wild and improbable of all—that relating to gallium. (W8:285, 1892)

The *accommodating* aspects of Mendeleev's 'wonderfully vivid conception' are not ranked against the *predictive* and 'subsequently triumphant verification of his predictions'[16]. Nonetheless Peirce is clear that taken in total, 'very few inductions in the whole history of science are worthy of being compared with this as efforts of reason' (W8:285, 1892). To paraphrase Peirce's view, if Dmitri Mendeleev was 'alone' the true sage of the periodic scheme then Josiah Cooke was his prophet.

1.8 Cooke's treatment of crystallography – a case of diagrammatic reasoning

At this point it is worth investigating the resonance between Peirce's formulation of diagrammatic reasoning and his experience of studying chemistry with Cooke – something that has been largely ignored by Peirce scholars. Whilst the theory of iconicity is prominent in much Peirce scholarship, Stjernfelt (2007:89) argues that 'Peirce's general notion of diagram has passed much more unnoticed' even though 'the diagram concept plays a central, not to say *the* central, role in the mature Peirce's semiotics' (emphasis in the original). The concept of a diagram occurs in many of Peirce's writings but it is to his essay 'Prolegomena to an Apology of Pragmatism' (c1906), we encountered earlier on, that I shall refer here. It is this paper, Stjernfelt (2007:89) argues that 'makes clear the crucial part played by the diagram and diagrammatic reasoning in Peirce'. It is here that Peirce describes the process of experimenting with diagrams by using a description drawn from chemistry. It is also recalling the often quoted Eisele's Law: 'Peirce's philosophy and logic can be understood only in the context of his mathematics' (Tursman 1987). Again Peirce picks up on a chemical analogy – a chemist inquiring into the nature of a compounds molecular structure,

> But the object of the chemist's research, that upon which he experiments, and to which the question he puts to Nature relates, is the Molecular Structure, which in all his samples has as complete an identity as it is in the nature of Molecular Structure ever to possess. Accordingly, he does, as you say, experiment upon the Very Object under investigation. (CP 4.530)

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[16] I will return to what has become known as the accommodation/prediction debate (Brush 1996, Scerri and Worrall 2001) around the periodic table in chapter six.

Next Peirce tackles the objection that there might be a difference between a laboratory experiment, where the chemist is in direct contact with the 'very object under investigation', and an experiment on a diagram where there is no direct physical connection with the thing it represents. What links the two - experimenting on a chemical compound and experimenting on a diagram – is that in each case the object of investigation 'is [in] the *form of a relation'* (CP 4.530) (emphasis in the original). Next and seemingly in accord with Eisele's Law, Peirce turns to mathematics to demonstrate that the Object of Investigation 'is the *form of a relation*' and that 'this Form of Relation is the very form of the relation between the two corresponding parts of the diagram' (CP 4.530).

> For example, let ***f***[1] and ***f***[2] be the two distances of the two foci of a lens from the lens. Then,
>
> $$1/\boldsymbol{f}[1] + 1/\boldsymbol{f}[2] = 1/\boldsymbol{f}[o]$$
>
> This equation is a diagram of the form of the relation between the two focal distances and the principal focal distance; and the conventions of algebra (and all diagrams, nay all pictures, depend upon conventions) in conjunction with the writing of the equation, establish a relation between the ***very*** letters ***f***[1], ***f***[2], ***f***[o] regardless of their significance, the form of which relation is the ***Very Same*** as the form of the relation between the three focal distances that these letters denote.
> (CP 4.530) (emphasis in the original)

Taking here from Peirce - molecular structure is the 'very object' of the chemist's investigation; for the mathematician the 'algebraic Diagram presents to our observation the very, identical object of mathematical research'. (CP 4.530). By performing operations on a diagrams – whether molecular formulae or mathematical equations - we are in effect performing experiments on the on the very objects they represent. Notice also a connection here between Cooke and Peirce. Earlier we saw Cooke (1888:101) state that, 'mathematics is the science of quantitative relations wholly independent of their material expression'. This resonates with Peirce, when he describes an equation (here to do with focal lengths) as establishing a relation irrespective of the letters used in its material notation. That said, I am not claiming a direct connection between Peirce's approaches to mathematics and to Cooke, his chemistry tutor. What I do claim is that Peirce's treatment of *relations* owes something to his training as a chemist and is not located wholly within the context of mathematics. Peirce's chemical training – directed by Cooke (in turn inspired by

Liebig through Dumas and Regnault) – brought together the 'form' of *relations* with the practice of chemistry. From a slightly different perspective, chemistry contributed to Peirce's mind-set when dealing with the nature of *relations.*

1.9 Chemistry, diagrams and logical relations

We will see here how Josiah Cooke encouraged his students not to see chemistry as a study of essences but as an inquiry into the relations between its objects. At the very start of his book *Chemical Physics* (1860), Cooke identifies chemistry as an empirical study of the *relations* between substances and the laws that capture these associations. It is Cooke's (1860:3) view that we can have no knowledge of a substance's *essential nature,*

> In regard to the *essential nature* of matter, or of the elements of which it consists, we have no knowledge, but we have observed the properties of almost all known substances, as well elements as compounds, have studied their mutual relations and their action on each other, and have discovered many of the laws which they obey.

For, as Cooke affirms, chemistry has no access to the essences of substances – to things in themselves – it is only possible to come to know the objects it studies by observing their relations as they act on one another. Notwithstanding the Kantian overtones here Cooke makes no reference to this in his text. A study of properties through 'their mutual relations' characterises the way Cooke attempts to engage his students with the practice of crystallography. The crystalline form was not treated as a thing in itself but as a set of triadic relations: the crystalline form under investigation, its diagrammatic representation and the thoughts in the minds of his students.

Harvard's catalogue for 1861-62 includes[17] Cooke's *Chemical Physics* as one of the texts Peirce would have used. It was as previously described, largely a physics text with *chemistry* mentioned only twice within the 'contents' – 'physical and chemical change' and 'physical and chemical properties'. Chapter three of Cooke's *Chemical Physics* deals with the three states of matter and has an extensive section on crystallography. What is of particular note is the approach Cooke takes as he initiates young chemists, such as Peirce, into the various crystallographic systems. Before looking at Cooke's diagrammatic approach to crystal

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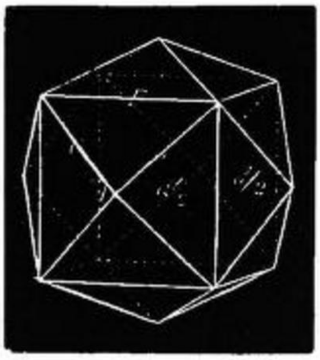
[17] Page 75

structures it is worth examining how Peirce connects thinking and reasoning, using a diagram functioning as an icon, as described in his essay 'On the Algebra of Logic',

> Icons are so completely substituted for their objects as hardly to be distinguished from them. Such are the diagrams of geometry. A diagram, indeed, so far as it has a general signification, is not a pure icon; but in the middle part of our reasoning we forget that abstractness in great measure, and the diagram is for us the very thing. (EP1 226, 1885)

I will show that Peirce was immersed in this form of visual thinking as part of his chemistry training on crystallography. Whilst a mathematical diagram is iconic in being completely substituted for the object it represents, crystallographic diagrams too – if we are willing to suspend in our minds their abstraction from the sample under investigation – also become 'the very thing'. I will show that Cooke's use of crystallographic diagrams encourage the student to reason whereby the diagram becomes indistinguishable from the crystal form it represents. The importance to the practice of science of being able to construct and manipulate a diagram or equation was emphasised by the philosopher and psychologist David Gooding. It is possible to see Cooke attempting to develop in his chemistry students this important skill which Gooding (2010:15) describes as, '[t]he ability to create and manipulate visual representations [which] is a cognitive skill acquired as a scientist becomes an accomplished participant in the methods that define a particular domain'. In this case the 'domain' of study is crystallography.

The section on crystallography begins with Cooke (1860:132) emphasising the need to engage with these diagrams by encouraging his students to reproduce their own representations by 'prepar[ing] models of the more important forms'. He then considers the principal crystal systems starting with holohedral forms of the monometric system. An example of his approach can be seen in the section dealing with the crystallographic form known as the tetrakis-hexahedron. The shape of each crystalline form in this particular system can be described by the ratios of the three values, represented by the letter a, measured along three mutually perpendicular axes (x, y and z). For the tetrakis – hexahedron these ratios are a:ma: ∞. In this example Cooke (1860:134) offers his students (such as Peirce) the following diagram and instruction,

Tetrakis-hexahedron	
6.  $a : ma : \infty a.$	Earlier in the text Cooke deals first with more straightforward crystallographic forms such as the cube and dodecahedron. The tetrakis-hexahedron is intermediate in form between the cube and dodecahedron. The dodecahedron aspect of the structure Cooke (1860:134) states is formed when ‘m=1 [and] the pair of faces meeting at m coincide and the cube is formed as ‘the value of m increases, the solid angle at A becomes more obtuse’ with the four planes meeting at A when m= ∞
Figure 3: Diagram of the tetrakis-hexahedron crystalline form Source: Cooke’s (1860) *Chemical Physics*, page 135	

Having described the tetrakis-hexahedron Cooke suggests that his students repeat the process for themselves on a number of other analogous structures such as the hexakis-octahedron. The responsibility for this Cooke (1860:134) places squarely with Peirce and his fellow students: ‘to trace out these relations, both in the symbols and the forms, is left for an exercise to the student’.

There are three points of interest here in terms of how Peirce is later to deal with diagrams. Firstly Cooke describes the diagrammatic structures in terms of the *relations* between their geometric characteristics. Secondly Cooke defines the internal characteristics of his diagrams in terms of a number of key indicators such as the ratio values expressed as the symbols a, b and c and measured along the x, y and z axes as well as the sizes of the solid angles formed between the various planes. When describing a set of compound crystalline forms Cooke (1860:161) sets out the values for a, b and c, stating that, ‘with the aid of these symbols, the student will easily be able to see the *relations* of the forms without any further description’ (emphasis added). Such key crystallographic factors as these correlate with or point out key relational aspects within the diagram. Sometime later, after his training as a chemist, Peirce would describe such pointers as the indexical aspects of a diagram[18].

Thirdly, to help his students fully engage with the diagrammatic structures, Cooke (1860:132) encourages them to ‘prepare models of the more important forms’ or by

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[18] Indexical signs will be discussed later in chapter four

examining ‘[c]rystals made of wood or of porcelain [which] can be obtained from dealers in philosophical instruments’. Cooke’s emphasis on engagement rather than rote learning of the facts can be seen in the way he encourages his students to experiment on the diagrams in his text. Not all the crystal systems are set out in detail, for as Cooke (1860:140) asserts somewhat confidently, ‘since, after the details already given, the relations of these forms can easily be traced by the student, we need not dwell upon the subject [of the remaining systems]’. In training his students in this way Cooke is striving to develop what Gooding (2004a:278) describes as the skill of ‘visualization [which] involves making and manipulating images that convey novel phenomena, ideas and meanings…[being]…central to the intellectual objectives of almost every area of science’. In this second example from Cooke’s *Chemical Physics* we can see how he develops this skill of ‘visualisation’ in his students. What is interesting here is that later Peirce was to connect our mental processes in a graphic way for he writes that the mind imagines or visualises diagrams to experiment on in order to reason by,

> We form in the imagination some sort of diagrammatic, that is, iconic, representation of the facts, as skeletonized as possible. The impression of the present writer is that with ordinary persons this is always a visual image, or mixed visual and muscular; but this is an opinion not founded on any systematic examination. (CP 2.778, 1902)

We can see how Peirce’s chemistry training involved mental experiments upon diagrams. Here Cooke (1860:121) is approaching reasoning as both a visual and a diagrammatic process by way of introducing his students to a number of fundamental concepts in crystallography such as *crystal, faces and plane angles.*

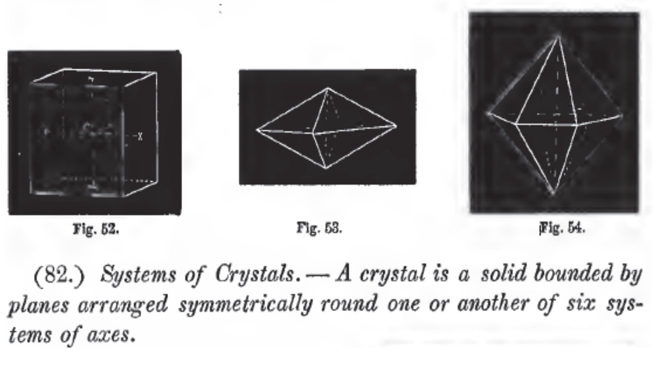

Fig. 52. Fig. 53. Fig. 54.

(82.) *Systems of Crystals.* — *A crystal is a solid bounded by planes arranged symmetrically round one or another of six systems of axes.*

In using geometric diagrams in this way, Cooke offers to the student’s imagination an image that seems to encourage her to merge the representation as printed in the text book with its object itself - the crystalline form found in nature.

Figure 4: Diagrams of crystal systems
Source: Cooke’s (1860) *Chemical Physics,* page 121

Cooke writes in a way that brings the student’s attention to the internal geometric characteristics of the structure without losing sight of the crystal as an object of observation. In the text accompanying the diagram Cooke (1860:121) refers directly to the natural crystalline form - the object - as ‘the faces of the diamond and of some other crystals are at times curved…[although]..made up of a large number of small planes’. He then shifts his focus seamlessly to the diagram’s geometric features by describing ‘the axis of a crystal is a line passing through its centre, round which two or more faces are symmetrically arranged’. Here Cooke invites the student to visualise in his imagination the superimposition of the natural characteristics of the crystal form – the appearance of its faces - with its visual representation in terms of its internal axis. In recalling Peirce’s earlier chemical analogy relating to experimenting on diagrams the effect here is that Cooke’s geometric diagram – his representation - *is,* for the student, the thing itself – the object – the natural crystalline form under investigation. This aspect of Peirce’s training as a chemist encouraged him to engage with the relations established between the natural crystalline form, its representation and his thoughts. In this way Peirce and others came to know the object of their study – the crystalline form itself. By viewing the representation through the lens of Peirce’s chemical practice he was experiencing an iconic form in a way which he later described as,

> So in contemplating a painting, there is a moment when we lose the consciousness that it is not the thing, the distinction of the real and the copy disappears, and it is for the moment a pure dream, – not any particular existence, and yet not general. At that moment we are contemplating an icon. (EP1 226, 1885)

By means of Cooke’s diagramatic approach were Peirce and his fellow students introduced to crystallography. The student is encouraged to set to one side or to suspend the distinction between the crystal object form and the iconic diagram printed in the text. In this way Cooke guides his students in coming to an understanding of the important crystallographic relations under study where, in Peirce’s words, the diagram on the page becomes ‘the very thing’.

1.10 Conclusion

In this chapter I have shown that whilst Liebig’s laboratory method was first introduced at Harvard by Eben Horsford it was Josiah Cooke who, influenced in particular by Dumas and Regnault, fully developed these methods into a highly successful teaching programme. In structuring the curriculum, Cooke was determined that his students would develop problem solving skills and the ability to process numerical data. Such an approach would very likely have appealed to Peirce given his interests and skills in mathematics. In common with other nineteenth century chemists, Cooke framed the subject in terms of the *relations* existing between chemical objects and their physiochemical properties. As a young chemist Peirce would have been immersed in this language of *relations* as a means of making visible the interplay between the world's material elements and its cognitive elements.

Douglas Anderson (1995:32) expresses a view common amongst Peirce scholars that, 'for Peirce, all other sciences depend upon mathematics insofar as it was the model for reasoning… involv[ing] imaginative construction and experimentation in diagrammatic thinking…'. This is another form of what we previously encountered as Eisele's Law. I claim that in this chapter I have laid the foundations to question the exclusive focus on mathematics that has preoccupied Peirce scholars thus far. Furthermore, Peirce's training at Harvard as directed by Josiah Cooke made a substantial contribution to his way of thinking diagrammatically and in terms of *relations.* The way of thinking that was integral to Peirce's study of chemistry at Harvard has so far been largely ignored by scholars in their accounts of the conceptual basis for his later accounts of diagrams.

Chapter Two

Charles Peirce – a nineteenth century chemist

2.1 Introduction

This chapter focusses on Charles Peirce as a nineteenth century chemist. Whilst there are a few papers on Peirce's use of analogies drawn from chemistry in support of his philosophy (Atkins 2010 & 2012, Roberts 1973 and Tursman 1989,) there is very little analysis of the papers he published on the subject of chemistry. To emphasise the breadth of Peirce's interests and achievements Max Fisch[19] asked the following rhetorical question,

> Who is the most original and the most versatile intellect that the Americas have so far produced? The answer "Charles S. Peirce" is uncontested, because any second would be so far behind as not to be worth nominating. [He was] mathematician, astronomer, chemist, geodesist, surveyor, cartographer, metrologist, spectroscopist, engineer, inventor; psychologist, philologist, lexicographer, historian of science, mathematical economist, lifelong student of medicine; book reviewer, dramatist, actor, short story writer; phenomenologist, semiotician, logician, rhetorician and metaphysician.

It was perhaps with such a list in mind that Vincent Colapietro (1996:138) encouraged his readers to 'reflect on the heroic dimension of his [Peirce's] philosophical career'. Although Fisch lists chemistry, this aspect of Peirce's work sits outside of his 'heroic' output being rarely mentioned in the literature. I will show that Fisch's somewhat triumphalist portrait of Peirce as a unique intellect does not necessarily apply to his output as a chemist. An examination of Peirce's published works and research interests, as part of the historiography of nineteenth century chemistry, reveals a more ordinary Charles Peirce – at least as a chemist. Where Peirce is unusual for a nineteenth century chemist is in his willingness to engage in metaphysical speculation. Nineteenth century chemists, claims Bensaude-Vincent (2009:48), were 'not really concerned with understanding the fine structure of matter'. As an example Bensaude-Vincent (2009:48) cites August von Kekulé who offered the six membered hexagonal structure of carbon atoms as the structure of benzene as 'deny[ing] the existence of atoms' and firmly rejecting this 'ontological issue out of chemistry, as belonging to metaphysics'. This is taken from a quotation from Kekulé (1867) which Alan Rocke (2010:225) cites in full as, '[t]he question whether atoms exist or not has but little significance in a chemical point of view: its discussion belongs rather to

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[19] Cited in Brent (1993:2)

metaphysics'. Whilst rejecting the Daltonian notion of the indivisible atom Rocke (2010:226) argues that Kekulé believed that, 'the chemist is perfectly justified in using this empirically supported concept' for although '[c]hemical atoms may well not be irreducible bits of matter, like Dalton's tiny hard spheres; but they behave chemically as if they were'. I will later claim that Peirce's chemistry writings of the early 1860s present him as a metaphysical chemist which, as I will show, was an unusual position for the time and not one found in Peirce scholarship.

In addition to Peirce's position as a chemist I will also explore the connections between Peirce's largely neglected writings in chemistry and his philosophical essays of that same period. Many Peirce scholars acknowledge the influence of Kant on his thinking, particularly his earlier writings. As Cheryl Misak (2004:1) points out 'one of the most important influences on Peirce was Kant', an opinion supported by Gabriele Gava (2008:699) when he states that, [f]rom his own day to ours, the Kantian character of Charles S. Peirce's philosophy has been recognized'. Around the same period of Peirce's chemistry papers he also published his essay 'On a New List of Categories' (hereafter the 'New List'). This paper is for many scholars, according to Mats Bergman (2007b:604), 'the foundational text' for Peirce's theory of signs which, Bergman claims, 'provides a Kant-styled 'derivation' of the basic concepts of the theory of categories and semiotic in one brilliant, albeit dense and often enigmatic package'. In common with other Peirce scholars, Misak (2016:85) is of the opinion that Peirce's own set of metaphysical categories grew out of his reading of Kant's *Critique of Pure Reason* which he had first read 'as a teenager and continued to be immersed in…(in the original German) as an undergraduate at Harvard'.

The year Peirce graduated from Harvard's Lawrence Scientific School coincided with the first paper of his career, published in the *American Journal of Science and Arts*, 'Chemical Theory of Interpenetration' (1863). I will show that this paper also has a Kantian lineage, this time to the *Metaphysical Foundations of Natural Science* (1878) and to Kant's later and unpublished work, the so-called *Opus postumum.* As far as I am aware there is nothing in Peirce scholarship that connects Peirce's writings on chemistry with Kant. Scholars such as Carolyn Eisele and Max Fisch have so far paid little attention to Peirce as a chemist; this project hopes to make an original contribution to this neglected area of Peirce scholarship.

An examination of Peirce's 'Chemical Theory of Interpenetration' (1869) will show in part that his interests were common to other nineteenth century chemists such as Jean-Baptiste Dumas and Jöns Jacob Berzelius as well as his tutor Josiah Cooke. These interests included atomism, the validity of Prout's hypothesis and using atomic weights as a classification scheme for the chemical elements. This paper also reveals something of the younger Peirce's metaphysics as applied to chemistry. In 1869 Peirce publishes in both chemistry and philosophy. In arguing for an orderly arrangement of the chemical elements Peirce deploys inductive reasoning. That same year Peirce publishes a series of three papers which includes a justification for inductive reasoning which denies J.S Mill's defence in terms of the orderliness of nature. I will show that 'philosopher' Peirce's position in opposing Mill's position is not inconsistent with the 'chemist' Peirce in seeking an orderly arrangement of the chemical elements.

2.2 Nineteenth century atomism

Before considering Peirce's paper 'The Chemical Theory of Interpenetration' (1863), it would be useful to say something of the nineteenth century debates around atomism in order to place Peirce's work in context. This also provides a useful starting position for a later examination of Peirce's reception of Prout's hypothesis.

The historian Alan Rocke (1978:225) claims,

> There were two types of atomism in the nineteenth century: the universally, if usually implicitly, accepted chemical atomic theory, which formed the conceptual basis for assigning relative elemental weights and molecular formulas, and the highly controversial physical atomic theory, which made statements about the intimate mechanical nature of substances.

As will be shown later, chemists were often willing to receive Dalton's atomic theory by way of accepting atomic weights as experimentally useful for determining reacting quantities and likely product yields. There was however reluctance by some to embrace physical atomism, thinking this to be irrelevant to their practice, or as Bernadette Bensaude-Vincent and Isabelle Stengers (1996:117) explain, 'why venture into an area inaccessible to experiment to establish the gravimetric proportions of combination'. Using Rocke's (1978) terms, whilst chemists of the early and mid-nineteenth century were comfortable with the 'chemical atom', many regarded the 'physical atom' as a metaphysical speculation, inaccessible to experimental verification and a distraction from their empirical practice. Consider for example Dumas's[20] (1837) observation that, 'if I were master, I would erase

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[20] Cited in Bensaude-Vincent and Stengers (1997:123)

the word ‘atom’ from the science, persuaded that it goes beyond experience; and in chemistry we should never go beyond experience’. Chemists sharing Dumas’s position took an empirical approach to Dalton’s theory whilst rejecting its ontological speculations. Chemical atomism unlike physical atomism avoids any reference to indivisible atoms as the basic building blocks of matter.

It is impossible to capture the subtlety of the debates that took place in such a short space as this chapter affords. The scepticism towards Dalton’s physical atomism can however be appreciated in the Swedish chemist Jacob Berzelius’s[21] judgement of it as ‘imperfect and clogged with difficulties’. As Alan Chalmers (2009:182) explains, Berzelius devised a system of chemical formulae, such as SO^2 for sulphur dioxide, which represents the combining weights of the two elements; such an approach was ‘without a commitment to atoms’. We now examine Dalton’s atomic theory and more of the responses it provoked. A useful source of Dalton’s papers published from manuscripts held originally by the Literary and Philosophical Society of Manchester is Roscoe and Harden’s *A New View of Dalton’s Atomic Theory* (1896). In his lecture notes (13th January, 1810) John Dalton[22] argues there being some point beyond which matter cannot be divided and that the existence of ultimate particles of matter ‘can scarcely be doubted, though they are probably much too small ever to be exhibited by microscopic improvements’. Here Dalton appears to affirm his belief in atoms as real entities. He chooses the word atom over particle or molecule for its expressive power in conveying the property of indivisibility. In a letter to Berzelius (20th September, 1812) Dalton[23] asserts the logic of his theory as ‘the doctrine of definite proportions appears to be *mysterious* unless we adopt the atomic hypothesis’ – then borrowing on the authority of Newton for emphasis he continues – ‘it appears like the *mystical ratios* of Kepler, which Newton so happily elucidated’.

In 1808 Dalton published *A New System of Chemical Philosophy* (Part 1) which contained the now famous Plate IV. The visual impact of this representation of atoms, together with what later became known as molecules, provided powerful support for Dalton’s concept of atomism.

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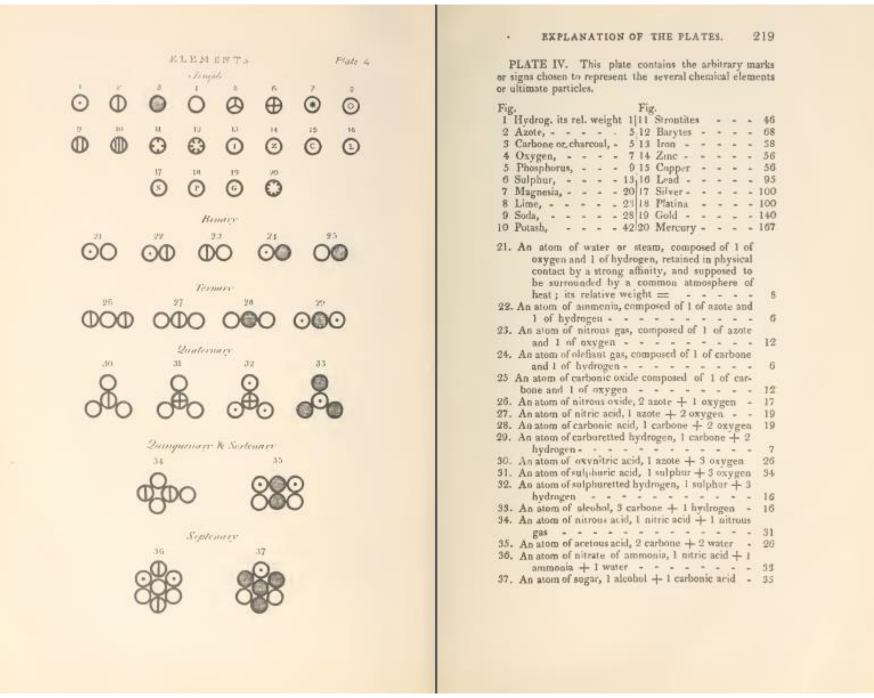
[21] Cited in Chalmers (2009:182)

[22] Cited in Roscoe, H and Harden, A. 1896 *A New View of the Origin of Dalton’s Atomic Theory* page 111

[23] Cited in Roscoe, H and Harden, A. 1896 *A New View of the Origin of Dalton’s Atomic Theory* page 159

Table of atomic weights and accompanying signs – Plate IV



EXPLANATION OF THE PLATES. 219

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.			Fig.		
1	Hydrog. its rel. weight	1	11	Strontites	46
2	Azote,	5	12	Barytes	68
3	Carbone or charcoal,	5	13	Iron	38
4	Oxygen,	7	14	Zinc	56
5	Phosphorus,	9	15	Copper	56
6	Sulphur,	13	16	Lead	95
7	Magnesia,	20	17	Silver	100
8	Lime,	23	18	Platina	100
9	Soda,	28	19	Gold	140
10	Potash,	42	20	Mercury	167

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = - - - - - - 8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen - - - - - - - - - - - 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen - - - - - - - - - - 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen - - - - - - - - - - 6
25 An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen - - - - - - - - - 12
26. An atom of nitrous oxide, 2 azote + 1 oxygen - 17
27. An atom of nitric acid, 1 azote + 2 oxygen - - 19
28. An atom of carbonic acid, 1 carbone + 2 oxygen 19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen - - - - - - - - - - - - - - 7
30. An atom of oxynitric acid, 1 azote + 3 oxygen 26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen - - - - - - - - - - - - - 16
33. An atom of alcohol, 3 carbone + 1 hydrogen - 16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas - - - - - - - - - - - - - - - 31
35. An atom of acetous acid, 2 carbone + 2 water - 26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water - - - - - - - - - 33
37. An atom of sugar, 1 alcohol + 1 carbonic acid - 35

Figure 5: Plate IV
Source: Dalton's (1808) *A New System of Chemical Philosophy, page* 218

The diagrams, Dalton (1808:219) explains, are 'arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles'. The accompanying explanations and atomic weights were intended to be considered together as a single representation which Bernard Cohen (2004:69) describes as 'addressing the ontological status of the entities through their tandem representational format'. The cause of Berzelius's's[24] scepticism is the very realistic and spatial interpretation which he described as 'imagining these elementary bodies in spherical form' – real physical entities.

Another of Dalton's opponents to his atomic theory was Humphrey Davy (1778 – 1829) who in 1812, some four years after Dalton, published *Elements of Chemical Philosophy.* In the letter to Berzelius referred to earlier, Dalton's realist approach to visualising atoms and as exemplified by his table, was justified by his interpretation of the law of definite proportions[25]. In his treatment of this law Davy (1812:64) contests Dalton's interpretation in stating, 'it is not necessary to consider the combining bodies, either as composed of indivisible particles, or even as always united one and one, or one and two, or two and

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[24] Cited in Nye(1993:64)

[25] The French chemist Joseph Proust (1799) first proposed the law of constant composition as a result of his observations that in chemical compound the elements were always present in the same definite proportion by weight

three proportions…numerical expressions ought to relate only to the results of experiments'. Without delving into Davy's own interpretations it can be seen that he has rejected Dalton's diagrams of 'ultimate particles' as depicting real entities – physical atoms. In emphasising this physicality, David Knight (1996:193) describes Dalton's atoms as 'not just chemical atoms, which resist analysis at present but might succumb to more formidable procedures, but genuine physical atoms'. Although, as Rocke (2005:147) states, Davy's opposition to chemical atomism softened, he never accepted Dalton's position 'which seemed to him far too material and hypothetical' – conflicting as it did with his Kantian idealism and a rejection of atoms as material entities. The philosopher Rom Harré (1981:15) argues that Davy's writings involved 'attacks on 'substance' theories of physical action' and that 'true to his Kantian predilections Davy preferred theories based on the assumption of attractive and repulsive forces' such as the atomic theory of Roger Boscovich (1711 – 1787). Interestingly the young Peirce too will be shown to object to – in today's terms - physical atomism, offering a Kantian theory in response. Although a reluctance to accept atomism on Kantian grounds is not surprising for a nineteenth chemist, Peirce's willingness to engage in metaphysical debate in support of his own position perhaps is, as will be shown later.

As well as detractors Dalton also had his supporters, one being Thomas Thomson professor of chemistry at Glasgow University. In his *A system of Chemistry,* Thomson (1810:441) writes 'the hypothesis upon which the whole of Mr Dalton's notions respecting chemical elements is founded, is this: When two elements unite to form a third substance, it is to be presumed that *one* atom of one joins to *one* atom of the other, unless when some reason can be assigned for supposing the contrary', which was followed by a number in Dalton's atomic diagrams.

Problems came for Dalton's physical atomism towards the end of the first decade of the nineteenth century with Gay-Lussac's law of combining gas volumes (1809) as well as a theory put forward independently by Amedeo Avogadro (1811) and André-Marie Ampère (1814), that equal volumes of gases contained the same number of particles under constant conditions. For example, two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam. The problem here is that using Dalton's atomic theory would require the 'indivisible' atom of oxygen to divide in two. It was partly in response to this, explains Alan Chalmers (2009:182), that 'Berzelius (1813, 1815) argued for using formulae in preference to Dalton's diagrams because the latter, in conjunction with a table of 'atomic weights', could capture all that was warranted by experiments on combining weights and volumes without commitment to the atomic hypothesis'. Whilst the epistemic usefulness of the theory was accepted its ontological implications were not.

As discussed in chapter one Peirce was taught chemistry by Josiah Cooke who was much influenced by the French chemists Dumas and Regnault. It is therefore worth examining briefly the position taken towards 'atomism' by these three chemists. Nineteenth century French chemists, argues Bensaude-Vincent (1999:81), 'were reluctant to adopt the atomic theory…. Instead of atomism, the French chemists preferred the language of equivalents because it avoided commitment to a speculative theory of indivisible elementary particles'. This offers a different approach to expressing the relations between the chemical elements and their reacting quantities on the formation of new substances. An example can be seen on examining Regnault's (1853:112) *Elements of Chemistry*, one of the texts Cooke chose to support his course, where it states, '[w]e shall exclusively adopt the notation of equivalents in the present work'. Experiment shows that eight parts by weight of oxygen will combine exactly with one part of hydrogen to form water. From this Regnault (1853:111) argues '[t]he quantities 8 of oxygen and 1 of hydrogen are called *equivalent quantities*, or *chemical equivalents'* (emphasis in the original). On this basis water is represented by the formula HO, a statement of the *relations* between the elements of composition and their combining mass ratios. Such reasoning was common to chemists who took a similar 'equivalentist' position. This is a different approach to the *relations* between the chemical elements to that offered by the use of atomic weights, one that avoids any commitment to the atomic theory.

What Bensaude-Vincent (1999:81) describes as Dumas's (1836) 'solemn condemnation of atoms' was quoted in part earlier and is given here in greater detail,

> On this subject too many hypotheses have already been made; (…) instead of investigating these hypotheses more thoroughly, it would be far better to seek some reliable foundations on which to base more substantial theories. … If I had my way, I should erase the word `atom' from science, in the firm belief that it goes beyond the realm of experiment; and never in chemistry must we go beyond the realm of experiment.

This quotation is often cited as an example of Dumas's positivist attitude in seeking to eliminate all consideration of unobservable entities from physical theory. Bas Van Fraassen (2009:16) suggests caution here before we label Dumas an instrumentalist or empiricist anti-atomist for 'the quotation scandalously omits the sentence just before that ''If I had my way'', which is ''It is my conviction that the equivalents of the chemists—those of Wenzel and of Mitscherlich, which we call atoms—are nothing but molecular groups'. It is Rocke's (1978:261) view, having also pointed out the missing sentence, that Dumas whilst rejecting physical atomism, was 'not expressing a general opposition to chemical atomism'. However, the prevailing view of in France during the time Cooke studied there was one that avoided speculative theory focussing instead on the empirical and descriptive aspects of chemistry. Such an attitude was embodied by the influential French chemist Marcellin Berthelot who, argues Mary Jo Nye (1993:69), was 'an antiatomist and powerful member of the French establishment…[and]… dissuaded students from writing their examinations in the notation of atomic weights and symbols that were used almost everywhere outside France after 1860'. In preference Berthelot required his students to work with equivalent weights which are founded on chemical analysis where, as Nye (1993:69) states, 'atomic weights are based on *physical hypotheses'* (emphasis in the original).

What approach did Peirce's tutor Josiah Cooke take once he returned from France, having attended Dumas's Paris lectures of 1848 and 1851, to take up his post as Erving Professor of chemistry at Harvard? Unsurprisingly perhaps given Cooke's admiration for Dumas and Regnault, his *Chemical Problems and Reactions to Accompany Stöckhardt's Elements of Chemistry* (1857), discussed in the previous chapter, works entirely in equivalents - as does Regnault in *Elements of Chemistry.* There is no mention of the atomic hypothesis. Thus writing the symbol C stands for six parts of carbon, or as Cooke (1857:15) states, '[t]he weight of an element indicated by its symbol is called *one equivalent*; and it is a law of chemistry that elements always combine by equivalents'. Cooke's *Elements of Chemical Physics* (1860) was also used on his course as discussed in chapter one. In the preface Cooke (1860:iv) affirms his subject's empirical foundations and one founded on precise measurement of quantities,

> The history of Chemistry as an exact science may be said to date from Lavoisier, who first used the balance in investigating chemical phenomena, and the progress of the science since his time has been owing, in great measure, to the improvements which have been made in the processes of weighing and measuring small quantities of matter.

We can see here the value Cooke places on the chemical balance as an instrument of chemical inquiry. A successful inquiry is dependent upon the chemist's skilful and accurate work with the chemical balance with a keen appreciation of any sources of error. A keen theoretical knowledge of the principles underlying the processes involved is also essential for, as Cooke (1860:iv) states, an investigator who 'relies on mere empirical rules, will be exposed to constant error'. Nevertheless Cooke (1860:110) is familiar with the notion of atoms as invisible and indivisible particles which he describes as, 'the *atomic theory* as this hypothesis is called'. However, Cooke (1860:110) aligns himself 'with Newton regard[ing] them [atoms] as infinitely small, that is, as mere points, or, as Boscovisch [sic] called them, variable centres of attractive and repulsive forces'. Significantly Cooke (1860:110) prefers Boscovichian atoms where 'matter is purely a manifestation of force'. Peirce differs from his tutor Cooke in being prepared to engage in metaphysical speculations which Cooke, as we will see later, rules as being out of the chemist's court. In *First Principles of Chemical Philosophy* (1868) Cooke (1868:24) offers an account of the atomic theory to explain the loss of identity which occurs when a substance undergoes chemical change as, 'suppos[ing] that the molecules themselves are broken up into still smaller particles, which it calls *atoms'* (emphasis in the original) with the new product being a different arrangement of the original atoms. Cooke (1868:24) explains the word atom is derived from ancient Greek and 'recalls a famous controversy in regard to the infinite divisibility of matter, which for many centuries divided philosophers of the world'; then adding, *[b]ut chemistry does not deal with this metaphysical question'* (emphasis added).

It is here that we shall later see Peirce departing from his tutor by engaging in metaphysical speculation within a paper targeted at chemists and dealing with the atomic theory. Cooke appears not to favour an approach based on the atomic theory and atomic weights although he gives an account of both in his text. As an empirical chemist trained in France he retains a preference for the earlier system of equivalents which, states Cooke (1868:55), have the advantage 'that they are the result of direct experimentation, and are based on no hypothesis in regard to the molecular constitution of matter'. Given that the number of atoms in a particular compound is, states Cooke (1868:30), 'more or less hypothetical' then inevitably this uncertainty 'must extend to the atomic weights of the elements, so far as they rest on such hypothetical conclusions'. Nevertheless Cooke was not hostile to the atomic theory but was cautious of its hypothetical foundations. For example Cooke (1865:31) concludes that atomic weights when accurately determined 'become essential data in all quantitative analytical investigations'.

Thus in sum: Peirce was taught chemistry by Cooke, who admired the largely anti-atomist French chemists Dumas and Regnault and retained a preference for empirically determined equivalent weights and the ‘Boscovich atom’. Cooke believed metaphysics was not the province of chemists but kept an open mind on the developing atomic hypothesis and recognised the empirical value of atomic weights if determined accurately. His student Peirce shared some of his tutor’s views but differed radically in feeling able to mix metaphysics with chemistry.

As we shall see in the coming chapters Peirce was a great admirer of Mendeleev and it is worth looking briefly at the Russian chemist’s position on atomism. Mendeleev’s stance on atomism is more difficult to fix, as will be seen in the very different positions adopted by Eric Scerri (2006) and Robin Hendry (2006) on the matter. Writing in 1872 Mendeleev (1872:44) argues that the concept of atomic weight had acquired such ‘an indestructible solidity’ that it might be expected to ‘remain without change, whatever modifications the theoretical ideas of chemists might undergo’. At the same time Mendeleev acknowledges that the term atomic weight ‘implies the hypothesis of atomic structure of matter’ which he describes as ‘a rather conventional concept’; atoms as a useful working convention rather than an existing physical entity. In a footnote to this Mendeleev (1872:98 n1) adds that ‘by replacing the expression “atomic weight” with “elementary weight” one could, it seems to me, avoid the concept of atoms when speaking of atoms’. Scerri (2006:312) regards Mendeleev as an anti-atomist, citing in support Mendeleev stating, ‘there is a simplicity of representation in atoms, but there is no absolute necessity to have recourse to them…the atomic hypothesis seems to me to be useless’. It is on the basis of such evidence that Scerri (2006:311/2) argues that Mendeleev was rather sceptical of atomistic explanations’ and regarded atoms only as ‘useful fictions’.

It is also possible to find Mendeleev writing in seemingly realist terms about atoms. For example in the 1901 English translation of his seminal text book *The Principles of Chemistry*, Mendeleev (1901a:xi) make the following statements,

> Just as the microscope and telescope enlarge the scope of vision, and discover life in seeming immobility, so chemistry in discovering and striving to discern the life of the invisible world of atoms and molecules and their ultimate limit of divisibility, will clearly introduce new and important problems into our conception of nature.

Also when describing chemical change Mendeleev (1901a:33) writes in a realist manner that likens the reacting atoms to the celestial planets,

> Not only does chemical reaction itself consist of motions, but that in the compound formed (in the molecules) the elements (atoms) forming it are in harmonious stable motion (like the planets) in the solar system.

It is partly on the basis of writings such as these that Robin Hendry (2006:332) disagrees with Scerri's argument that Mendeleev was 'sceptical of atomistic explanations' describing this as 'contestable'. In support of Mendeleev's atomism Hendry (2006:332) quotes from Mendeleev's 1902 pamphlet, *Attempt at a chemical conception of the ether.* Here again Mendeleev offers a seemingly realist account of the atom and one similar to the two mentioned earlier,

> Chemically the atoms may be likened to the heavenly bodies, the stars, sun, planets, satellites, comets & c. The building up of molecules from atoms, and of substances from molecules, is then conceived to resemble the building up of systems, such as the solar system, or that of twin stars or constellations, from these individual bodies. This is not a simple play of words in modern chemistry, nor a mere analogy, but a reality which directs the course of all chemical research, analysis and synthesis.

From just this very brief selection from Mendeleev's writings it is possible to begin to see why scholars such as Scerri and Hendry disagree so strongly on Mendeleev's stance on atomism. It is Hendry's (2006:331) view that, 'Scerri is mistaken to represent Mendeleev as an anti-atomist'. For his part Scerri (2006:312) states 'Hendry has been too quick…in assuming that Mendeleev shared Dalton's belief in the existence of physical atoms'.

To complete this section and by way of contrast to Mendeleev's nuanced position on atomism it is worth giving an example of a more staunchly atomist and of an anti-atomist view. Firstly a clear anti-atomist position: throughout most of his career the physical chemist Wilhelm Ostwald[26] (1853 – 1932) had been an opponent of atomism. As late as 1904, showing that this debate continued through the nineteenth and into the twentieth century, Ostwald (1904:508/9) argued that the mainstays of atomism – stoichiometric laws, and the laws of constant composition, multiple proportions and of combining weights could be,

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[26] In his definition of chemistry as 'the science of the different kinds of matter' (CP 1.259) Peirce cites Ostwald and Mendeleev in claiming this to be 'substantially [their] definition' too.

> [D]educ[ed] from the principles of chemical dynamics [...] mak[ing] the atomic hypothesis unnecessary… put[ting] the theory of the stoichiometrical laws on more secure ground than that furnished by a mere hypothesis.

As an indication of the continuing liveliness of the debate around atomism during the early twentieth century, particularly in Britain, the home of Dalton's atomic theory, Ostwald (1904:509) adds 'I am quite aware that in making this assertion I am stepping on somewhat volcanic ground…among this audience there are only very few who would not at once answer, that they are quite satisfied with the atoms as they are, and that they do not in the least want to change them for any other conception'. In opposing atomism Ostwald offered an interpretation of the laws of chemistry in terms of energy and the recently formed laws of thermodynamics.

A supporting statement on atomism is provided by the Alsatian French chemist Charles Adolphe Wurtz (1817 – 1884), who is described by Alan Rocke (2001:5) as 'the apostle of atomic theory in France' and as Jaime Wisniak [2005:348] notes 'a staunch defender of the atomic theory against the sceptical positivism of [Marcellin] Berthelot.' One of Wurtz's most notable texts was *La Théorie Atomique* (1879) where he developed his theory of atomicity or the valency of the atoms. Towards the end of his book Wurtz (1880:301) sets out his position on atomism in distinctively realist terms,

> Atoms are not material points; they possess a sensible dimension, and doubtless a fixed form; they differ in their relative weights and in the motions with which they are animated. They are indestructible and indivisible by physical and chemical forces, for which they act, in some manner, as points of application.

Set against this context we can now consider Peirce's opposition to atomism in terms of its lack of explanatory power with regards the laws of chemistry and also to Prout's hypothesis.

2.3 'The Chemical Theory of Interpenetration' (1863)

This was one of Peirce's earliest papers written when he was aged twenty-four having just graduated from Harvard's Lawrence Scientific School. It is worth quoting in full Peirce's (1863:78) introduction and then looking to see how this fits with the concerns of other chemists writing at the time, and also with Peirce's later philosophical writings,

> Physicists are now rapidly doing away with all theories which demand peculiar shapes and kinds of matter in favour of those which demand peculiar vibrations. At this day, the arrow shaped particles of the old theory of light seem grotesque. There is a good reason for this tendency. We require an explanation of forces. Now a force is only a mathematical function of a change, and a change in space can only be conceived of a priori as a motion. To explain a thing is to bring it into the realm of our a priori conceptions. Hence, whenever we endeavour to explain any force of nature by means of hypothetical shapes and properties of matter these only help us so far as they are conditions of certain motions. These motions are the real explanation; and if we can succeed in getting the motions without the peculiarities of matter, our hypothesis will be so much the smaller. The object of the present article is to apply this principle to the Atomic Theory.

There are several points worth pursuing here which will be discussed in turn:-

a) The deference to physics in justifying his choice of chemical hypothesis
b) The metaphysical speculations – such as 'a change in space can only be conceived of a priori as a motion' – which rejects Daltonian atomism on the basis of a Kantian dynamical theory of matter[27]
c) The fact that the topics considered were common to nineteenth century chemists of his time – in addition to the atomism mentioned above Peirce also attempts a justification of Prout's hypothesis.

2.3.1 'The Chemical Theory of Interpenetration' (1863) and physics

What is at first striking for a paper on chemistry is that Peirce (1863:78) opens with an appeal to physics and to physicists who he claims, 'are now rapidly doing away with all theories which demand peculiar shapes and kinds of matter in favour of those which demand peculiar vibrations'. This is a reference to a challenge to Newton's corpuscular theory of light by the wave theory of Thomas Young (1773 – 1829) and Augustin-Jean Fresnel (1788 – 1827). It is interesting to contrast Peirce's claim, that physicists favour theories 'which demand peculiar vibrations' with regards to light, with Young's own caution as illustrated in his lecture to the Royal Society of 1801.

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[27] Michael Friedman (2004:xvi) describes Kant's dynamical theory of matter as follows: 'Matter fills the space it occupies by a continuous "balancing" of the two fundamental forces of attraction and repulsion exerted by all the continuum of points in the space in question'. I will return to this formulation later on.

In his Bakerian Lecture 'On the Theory of Light and Colour', delivered to the Royal Society in 1801, Young (1801:16) defends the hypothesis and explains that 'undulations are excited in this ether whenever a body becomes luminous'. Young states that 'I use the word undulation, in preference to vibration, because vibration is generally understood as implying a motion which is continued alternately backwards and forwards, by the combination of the momentum of the body with an accelerating force, which is more or less permanent'. In brief Young prefers undulation which, although a vibratory motion within the transmitting medium, the motion continues only as the effect of repeated transmissions of further undulations from the source. As the historian of science Frank James (1984:47) explains, 'there existed essentially two theories of light during the early nineteenth century: the particulate theory and the wave theory' although we now recognise this to be a simplification 'since there were many varieties of each theory'. Perhaps Peirce in his portrayal of physicists of the 1860s being so ready to dispense with the corpuscular theory is an illustration of James's (1984:47) point that as a supporter of the wave theory Peirce viewed its alternative as having 'faults so fundamental that no distinction between varieties of the same theory was sufficient to placate [his] opposition to that theory'.

In common with the physicists alluded to in the introduction to this paper, Peirce also favoured theories based on vibrations. For example, in an essay written six year later and on the English scientist and historian of science William Whewell (1794 – 1866), Peirce states that the spectroscope's capacity to distinguish between different chemical substances is due to 'the greater or less refrangibility[28] of the heat with which they *vibrate*' arguing that '[d]ifferent chemical substances are therefore bodies of different elasticity and susceptible of different rates of *vibration*' (W2:343 1869, emphasis added). Also when discussing sound and the pitch a particular note makes Peirce states that this 'depends upon the rapidity of the succession of the *vibrations* which reach the ear (W2:197, 1868, emphasis added). In describing the 'arrow shaped particles of the old theory of light' as now seeming 'grotesque' we might view Peirce as a historical actor in accepting the wave theory of light without as James (1984:47) argues, having 'distinguished between different varieties of either theory'. In this way Peirce is adopting an attitude typical of many of physicists and chemists of his time.

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[28] Refrangibility is a capacity for refraction

We can see something more of the early Peirce (1861) privileging physics when he poses the question: 'what is the meaning of this thing? Examples being: 'What makes the rainbow? [and]' What makes the top stand up?'. Questions in this form, Peirce claims, are inquiries belonging to 'physics…[because]…[t]hey are questions of force' (W1:53 1861). Peirce understands force to be present wherever there is matter. He argues that questions relating to different kinds of matter, 'must then treat questions of force…[and]…is therefore a branch of Physics' (W1:53 1861). Peirce illustrates this approach with a question from chemistry: what happens when an acid reacts with an alkali for form a salt? Peirce argues that there 'must be a certain force' which brings about the transformation of an acid and an alkali into a salt (W1:53 1861). Matters of force belong to physics. Thus the answer to the chemist's question 'what makes an acid react with an alkali?' – a question concerned with different kinds of matter – sits within the domain of physics. As we will see in the next section, Peirce's references here to force and physics sit within a Kantian approach to the behaviour of matter.

2.3.2 'The Chemical Theory of Interpenetration' (1863) and metaphysical speculations

In this section I will attempt to show that Peirce's paper, which deals with a chemical theory, is underpinned by Kantian metaphysics. Returning to Peirce's (1863:78) introduction, he claims that 'to explain a thing is to bring it into the realm of our a priori conceptions'; when it comes to the behaviour of matter 'motions are the real explanation'. Moving forces of nature, a priori, contain the principles that enable an explanation of the laws of chemistry. The Kantian connection here can be seen in the *Opus postumum* where Kant (1993:21:) states that 'moving forces must be assumed for the laws of motion that are *a priori* given, which [forces] alone serve for the explanation of the latter, although one cannot prove them'. Kant (1993:21) sets out his dynamic theory of matter as a metaphysical system founded a priori as moving forces and revealed to the observer in the laws of experience.

> In the metaphysical doctrine of nature, matter was only [dealt with] as the movable in space, as it is determinable *a priori;* in physics the moving forces are [dealt with] as experience reveals them; in the transition from metaphysics to physics, however, the movable with its moving forces is arranged in a system of nature, so far as the form of such a system can be constructed in general from these elements, according to the laws of experience.

I will attempt to show how Peirce takes a Kantian approach to the atomic theory, where the moving forces of nature embody a priori the principles of chemistry's laws of experience.

As a philosophical chemist, Peirce's objections to the explanatory power of Dalton's atomism are founded on metaphysics. As has been shown earlier, a concern with the implications of Dalton's atomism was common to other nineteenth century chemists. Nonetheless Peirce's readiness to engage in metaphysical disputation by way of rejecting Dalton's atoms was not typical of chemists of his time. Peirce's approach stands in stark contrast to his tutor Josiah Cooke who, as we saw earlier, dismissed metaphysical speculations as being irrelevant to the study of chemistry. Cooke is an example of a nineteenth century chemist who Mary Jo Nye (1993:71) describes as having, 'a pragmatic epistemology that suited well the practical needs of everyday laboratory life' eschewing metaphysics 'because it presented few useful strategies in the chemical laboratory'. Where other chemists rejected untestable metaphysical speculations as irrelevant to the empirical status of their science, Peirce offers a detailed Kantian explanation for the laws of chemistry in opposition to Dalton's atomism.

The possible relationship between Peirce's writing on chemistry and Kant is not something I believe that has featured in Peirce scholarship. Two of the laws Peirce deals with in detail are the chemical laws of composition and Prout's hypothesis. It is however worth examining Peirce's Kantian metaphysics further so that Peirce's explanations might be better understood. Peirce scholars would generally agree with Gava (2008:699) when he states that, '[f]rom his own day to ours, the Kantian character of Charles S. Peirce's philosophy has been recognised'. A view held by Hookway (2003:184) when he states: 'All would agree that Peirce was much influenced by Kant and that this influence was evident throughout his writings'. There is however nothing in the literature on the relationship between Peirce's Kantianism and his writings in chemistry. In particular, how Kant provides a metaphysical framework that allows the early Peirce (pre 1880) to explain a number of the laws of chemistry. It is this gap in Peirce scholarship that this project, in part, seeks to address.

The title of the paper is given as 'The Chemical Theory of Interpenetration'. Peirce's use of the word *interpenetration* connects his anti-atomism to Kant. In his final major work *Opus postumum* Kant (1993:28) states, 'matter does not consist of simple parts, but each part is, in turn, composite, and atomism is a false doctrine of nature'. This is part of Kant's argument against the theory that matter is composed of impenetrable atoms distributed in empty space. Halfway through his paper Peirce (1863:80) flies his Kantian colours in stating his intention as ‘the facts of chemistry are explicable by the view of Kant, that matter is not absolutely impenetrable and that chemical union consists in the interpenetration of the constituents’. The two theories seem completely incommensurable: where Daltonian atoms are discrete entities, Kant proposes a continuous and dynamical theory of matter. Before looking at how Peirce accounts for the laws of chemistry in terms of *interpenetration*, Kant’s dynamic theory of matter needs closer inspection.

In 1786 Kant published his *Metaphysical Foundations of Natural Science*. In the second chapter on dynamics Kant develops the dynamical theory of matter, which Friedman (2004:xi) describes as ‘the longest and most complicated part’ of the work. The intention here is to set out in summary those parts of Kant’s *Foundations* that help to put Peirce’s later explanations of the laws of chemistry into context. Kant sets out his metaphysical foundations of dynamics as a sequence of propositions. In the first proposition Kant (2004:34) states his view that ‘matter fills a space, not through its mere *existence*, but through a *particular moving force*’ (emphasis in the original). There are for Kant (2004:35) two fundamental forces in nature. The first is the ‘attractive force’ which as a dynamic force draws matter together thereby preventing its separation. The second is the ‘repulsive force’ which is the cause of matter separating. Matter is considered exclusively in terms of these two moving forces which, as Friedman (2004:xvi) explains, ‘fills the space it occupies by a continuous “balancing” of the two fundamental forces of attraction and repulsion exerted by all the continuum of points in the space in question’. In this way these two opposing and dynamic forces are responsible for enabling matter to fill space. These forces are not properties of matter as is rigidity or elasticity.

How then does Peirce’s use of the word *interpenetration* in relation to the theories of chemistry associate this account with Kant’s dynamic theory of mater? The relationship between the two opposing forces of nature is, in Kant’s view, directly connected to material properties such as rigidity, elasticity and density. When discussing *impenetrability*, Kant in *Foundations* (2004:38) distinguishes between two situations. First there is ‘*relative* impenetrability’ where resistance, as with a volume of gas in a cylinder fitted with a piston, increases in proportion to the extent of compression. Secondly there is ‘*absolute* impenetrability’ which rests on ‘the *presupposition* that matter as such is capable of no compression at all’. It is Kant’s (2004:62) view whereby according to the dynamical theory of matter ‘the objects of the outer senses…must be viewed as a moving force’ and the properties of matter are determined by the relationship between the opposing forces of attraction and repulsion. In this case, states Kant (2004:62), ‘the so-called solid or absolute impenetrability is banished from natural science, as an empty concept, and repulsive force is posited in its stead’. All matter is however subject to relative impenetrability. Matter as a result behaves in an elastic manner as repulsive forces resist attempts at compression.

In arguing against the absolute impenetrability of matter within a dynamic structure of moving fundamental forces of attraction and repulsion, Kant (2004:62) holds ‘that space, if it should be necessary, can be assumed to be completely *filled*, and in different degrees, even *without dispersing empty interstices* within matter’ (emphasis in the original). Differing densities are explained by the degree with which space is filled or, as Kant (2004:62) explains, whilst all space is considered to be completely filled it is ‘filled in different measures, whereby empty space at least loses its *necessity*, and is demoted to the value of a hypothesis’. Atomism posits a theory of matter of discrete, indivisible and so impenetrable atoms distributed in empty space. Kant rejects this on two points: that empty space is at the very least not necessary and a rejection of the absolute impenetrability of matter.

As explained above, essential to what Kant in his *Foundations* (2004:62) describes as ‘the mechanical natural philosophy’ of atomism is the ‘*absolute impenetrability* of the primitive matter’ as discrete and separate particles distributed within empty space. Arguments on the corpuscular model explaining for example why the density of lead is greater than sulphur rest, Kant (2004:62) argues, ‘on the apparently unavoidable *necessity* for using *empty spaces on behalf of the specific difference in the density* of matters’ (emphasis in the original). The mechanical model fails for Kant (2004:62) because the empty spaces on which the concept of density is argued are not ‘determinable or discoverable by any experiment’. Empty space is not a possible object of experience and as a result a model of matter as atoms situated in the void is rejected. From an atomistic approach, differences in chemical behaviour can be explained in terms of the varying characteristics of different types of atoms. For Kant the difference in chemical behaviour, as between for example lead and sulphur, is because each element’s fundamental forces of attraction and repulsion are dynamic and combined in different ways. The difference between the dynamic and atomistic theories of matter and Kant’s own preference is summarised by Friedman (2004:xviii) as,

> In general, the “metaphysical-dynamical” approach, which views matter as a true dynamical continuum and eschews absolutely hard elementary corpuscles and

> empty space, is to be preferred [by Kant] to the opposing "mathematical-mechanical" approach, which postulates precisely an interspersing of hard elementary corpuscles and empty space from the very beginning (to explain differences of density) – and, in its extreme form, thereby attempts to dispense with all genuinely dynamical forces originally inherent in matter.

Before taking up Peirce's paper again, where he applies Kant's theory of interpenetration to the laws of chemistry, it would be useful to see the approach Kant takes to explaining chemical change. The examples chosen are not Kant's but are of chemical substances that would have been known at the time. Take for example the effect of dissolving zinc metal in hydrochloric acid[29]. The type of change occurring here is described by Kant (2004:69) as chemical '*insofar as they* [the reactants] *mutually change, even at rest, the combination of their parts through their inherent forces'.* The word 'inherent' is important as it situates the forces involved as intrinsic to the zinc and to the acid. The effect of this change is the dissolution or separation of both the zinc metal and the acid brought about by their inherent and fundamental forces. This is a very different process to the physical separation which occurs when a piece of zinc is sawed mechanically into separate pieces. The saw does not act by way of inherent forces but by the physical action of the hard edge of the serrated blade against the softer zinc. Dissolution by contrast is achieved by reacting zinc with the acid, where each is considered to be completely and uniformly intermingled with the other. This process is described by Kant (2004:69) as '*absolute dissolution*, which can also be called *chemical penetration*.' As we shall see in detail later, Peirce's use of the term *interpenetration* follows similar Kantian lines to be found in his account of dissolution. For, as Kant (2004:69) explains, taking the zinc-acid reaction as an example with the acid as solvent, 'there can be no part of the volume of the solution that would not contain a part of the solvent' and so the acid fills the volume of the reaction liquid as a continuum. The zinc acts as solute which as Kant explains, 'must also fill the whole space constituting the volume of the mixture, as a continuum'. Thus continues Kant, the zinc and acid 'fill one and the same space, and each of them does this completely, they *penetrate* one another' – the *interpenetration* of matter.

Having made the claim for the process of the total dissolution of two substances to be accompanied by their complete and mutual penetration one of another, Kant then describes the process in greater detail. Once the reaction is complete, the volume of the

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[29] Zinc was discovered in 1746 by the German chemist Andreas Marggraf (1709 – 1782) and hydrochloric acid from much earlier times.

zinc in acid product solution is very similar to the sum of their separate individual values – or as Kant (2004:69) observes ‘the matters [zinc and acid] together occupy a space, which accords with the sum of their densities, not outside, but inside one another, that is, through intussusception’. The term *intussusception* is explained by Hein van den Berg (2013:134) as the process whereby ‘the solute and the solvent fill the whole space constituting the volume of the mixture as a continuum’. The process of *intussusception* occurs as the attractive force of the acid solvent overcomes the weaker forces of attraction within the zinc. The result of dissolving zinc in acid produces a product that exists as a continuum brought about by the interpenetration of these two substances. The strength of the dissolving forces at work here is evidenced, Kant (2004:69) argues, in that once two substances have reacted together they ‘can be separated again by no art' – where by *art* Kant is referring to the practice of chemistry. To complete the example, zinc could not be easily recovered from the final product solution.

Having outlined Kant’s dynamical theory of matter we can return to Peirce’s paper to see how he deploys this theory to refute atomism’s ability to explain the laws of chemistry. As we have seen Peirce introduces his paper with references to motion, forces and physics. Following on from this Peirce (1863:78) sets out to show that Dalton’s ‘hypothesis of atoms, in itself explains nothing’. He then lists nine laws that a single successful hypothesis should be able to explain: the laws of equivalence, multiple proportions, combining volumes of gases, volumes of isomorphous crystals, thermal equivalents of the elements, thermal equivalents of isomorphous crystals, Kopp's Law of Boiling points and Prout's Law as modified by Dumas. Particular attention is paid to the laws of proportion which, as we have seen, were foundational to Dalton in the formation of his theory. In denying atomism’s ability to explain the empirical laws of chemical proportion Peirce (1863:78) comments,

> The explanation is that these are the weights of the atoms and that bodies combine atom by atom. But how should we know that they combine atom by atom? This is an addition to the hypothesis.

In extending this point Peirce (1863:80) argues that the law of definite proportion[30] ‘is capable of demonstration without any hypothesis’. Given Peirce’s reference to ‘atom by atom’ it is the suggestion of physical atoms that he is rejecting here. That is to say

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[30] The French chemist Joseph Proust (1799) first proposed the law of constant composition as a result of his observations that in chemical compound the elements were always present in the same definite proportion by weight

establishing that the law of definite proportion, as applied for example to copper oxide, can be demonstrated empirically – in line with Rocke's (2005) and Chalmers's (2009) discussion of chemical atomism. Any reference to physical atomism is in Peirce's view speculative and in addition to the experimental data. There then follows Peirce's explanation of the law of definite proportions where, and in some detail, Peirce draws on Kant's dynamic theory of matter. The argument begins with Peirce (1863:80) stating that 'we can conceive of no event in space which does not consist of a motion' where 'every quality of matter is either motion or some element of the mental analysis of the conception of a body moving in some way or other'.

The action of one body on another as in a chemical reaction is, explains Peirce (1863:80), 'merely one motion modifying a second to produce a third' where motion 'communicates itself from the moving particle to all others which are in communication with that'. This reference to moving particles communicating through their motion resonates with the earlier Kantian metaphysical-dynamical approach where different substances act (in modern terms, react) through the recombination of their respective attractive and repulsive forces. Taking the case of two substances reacting then it is through these forces, inherent in the bodies themselves, that brings about what Peirce (1863:80) describes as a 'homogeneity of quality throughout the two' – or what today would be said to be the products of chemical change. In covering cases where no reaction occurs the Kantian theme is continued, where the lack of change is the result of there being equal forces of attraction and repulsion between the two reacting bodies. It is clear, states Peirce (1863:80), that 'when the force of the acting body equals that of the body acted upon, all the force will be exhausted in preventing the homogeneity' – that is to say no chemical change takes place. It is at this point that Peirce (1863:80) applies the dynamical theory of matter to the law of constant composition:

> Now the same kind of matter under the same dynamical conditions possesses always the same amount of force proportionally to its mass; hence when one kind of matter acts on another through being of a different kind, it can only act on a definite amount of that matter, the dynamical circumstances remaining the same.

Take for example the burning of magnesium in air – a reaction known at Peirce's time - and relate this to his explanation above. The dynamic forces associated with magnesium and oxygen are both different in magnitude and proportional to their respective masses. Magnesium metal burns brightly in air to form what Cooke (1868:115), and very likely

Peirce, knew as ‘magnesic oxide’ – in today’s terms magnesium oxide, MgO. There is a limit to the amount of magnesium able to combine through the process of *intussusception* with a particular quantity of oxygen whereby the sum total of dynamic attractive forces exceeds the net forces of repulsion. This being the case the reacting mass ratios of each element will remain constant and the resulting magnesium oxide will have fixed proportions of each element (MgO). No recourse to atomism is needed.

I would argue that in setting out his arguments to his ‘Chemical Theory of Interpenetration’, Peirce adopts a Kantian approach. We have seen how Peirce acknowledges the need for explanations to fall within ‘our a priori conceptions’. Furthermore and seemingly in accord with Kant above, Peirce (1863:78) suggests that in order to account for a concept such as the atomic theory, arguments based on the ‘properties of matter’ – such as the chemical law of multiple proportions – are only useful ‘so far as they are conditions of certain motions’. It is, Peirce continues, ‘[t]hese motions [that] are the real explanation’. In conclusion Peirce states that, ‘[t]he object of the present article is to apply this principle to the Atomic Theory’. This echoes Kant who states that ‘the moveable with its moving forces is arranged in a system of nature’ which become manifest ‘according to the laws of experience’.

2.3.3 ‘The Chemical Theory of Interpenetration’ (1863) and Prout’s Hypothesis

In this third and final section we will see that in seeking to justify Prout’s hypothesis Peirce is joining a debate then common to other historical actors of nineteenth century chemistry. Peirce (1863:81) explains Prout’s Law as follows: ‘If we suppose, with the metaphysicians, that all the kinds of matter are derived from one…all the equivalents of the elements will be multiples of that of the original matter’. Peirce’s attempts to demonstrate the validity of Prout’s Law as modified by Dumas will be taken up later in this section. Nineteenth century chemists had, argues Bernadette Bensaude-Vincent (1986:5), ‘two alternative strategies to cope with the multitude of elements [being discovered]’ One was Prout’s hypothesis which sought to reduce the multitude of individual elements into aggregates of a single element or primary matter. The second, argues Bensaude-Vincent (1986:6), supported as did Mendeleev that, ‘elements were actually individual, and that they would never be divided or converted into another element’. Supporters of Prout’s hypothesis included: in Britain, Thomas Thompson, the French chemist Jean-Baptiste Dumas and the Swiss chemist Jean Charles Galissard de Marignac. The hypothesis became an issue of debate amongst nineteenth century chemists and came under attack, argues Bensaude-Vincent (1986:6), ‘when more accurate experiments brought undesirable, non-integral values for atomic weights'. In America Ralf Hamerla (2006:173) states that Josiah Cooke and his student Theodor Richards (later awarded America's first Nobel Prize for chemistry), who both investigated atomic weight values in the early 1860s, 'eventually concluded that Prout's hypothesis had to be viewed as valid until better analytic techniques could determine otherwise'. Prout's hypothesis was something that concerned chemists both in Europe and in America. The balance of the debate is captured by Hamerla (2006:157) when he states that, [w]hile there were vocal opponents of Prout's hypothesis, by the second half of the nineteenth century a majority of scientists accepted it as correct'.

In this section we see Peirce, as a nineteenth century chemist, engaging in the debate around Prout's hypothesis. Yet again, rather than dismissing metaphysics as not falling within the context of chemistry – as his tutor Cooke did – Peirce engaged in an empirical inquiry into the dispute around Prout's hypothesis, at the same time framing his explanations within a wider metaphysical framework. Before looking at what Peirce has to say on Prout's hypothesis it is worth looking at some of the issues surrounding this hypothesis at the time by way of historical context.

The English physician William Prout (1785-1850) measured the specific gravities of a wide range of substances and found these to be generally integral multiples of hydrogen at one unit. As a result Prout (1816:29) stated that `if the views we have ventured to advance be correct, we may almost consider the πρώτη ΰλη[31] of the ancients to be realized in hydrogen'. This has become known as Prout's law or hypothesis and can be stated as 'the atomic weights of the elements are integer multiples of that of hydrogen'. As Otto Benfey (2006:104) explains, Prout's proposal 'led to much fruitful research throughout the 19th century and later to some ingenious speculations as to why atomic weights deviated from integral values'. As techniques for determining atomic weights improved and values were re-calculated, some elements were found to have non-integral values and so were seemingly in conflict with Prout's hypothesis. Chemists began to take sides, as Hans-Werner Schütt (2006:243) explains, 'alongside Berzelius, chemists like Jean Servais Stas (1813–1891) rejected Prout's hypothesis on analytical grounds, while chemists such as Thomas Thomson (1773–1852) and Dumas tended to support it'. Later it will be shown that Peirce, in common with other chemists of his time, also took an empirical approach to the verification of Prout's hypothesis. Two years after Prout published his hypothesis, the Swedish chemist Jöns Berzelius determined independently the atomic weights of forty-five

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[31] πρώτη ΰλη translates from the Greek as *prote hyle* (sometimes described as prime matter) from which the term protyle is derived.

elements. A stumbling block for Berzelius was the non-integral values for elements such as chlorine (35.47). These values, explains A A Matyshev (2005:1269), 'were inconsistent with the Prout hypothesis'; therefore Berzelius rejected it.

To place Peirce's approach in context it is worth considering in brief the contribution to the debate around Prout's hypothesis made by other nineteenth century chemists. For example the Belgian analytical chemist Jean Servais Stas (1813 - 1891), later to be shown as one of Peirce's sources of atomic weight values, also tested Prout's hypothesis. As we will see, Stas, in common with Peirce, selects only those elements showing the greatest stability and agreement in their atomic weights. Writing three years before Peirce, Stas (1860:45) chooses nitrogen, chlorine, sulphur, potassium sodium, lead and silver because he explains 'they are the best known, form the stablest compounds, and because generally they have been regarded as obeying Prout's law'. In describing his technique Stas (1860:40) states that he has exercised the most 'efficacious control' of his methods and ensured sufficient repeats for each value 'so that the probability in favour of their exactness becomes very great'. Somewhat differently to Peirce who as we will see finds in favour of Prout's Law, Stas (1860:45) comes to the following view,

> I conclude then by saying: as long as we hold to experiment for determining the laws which regulate matter, we must consider Prout's law as a pure illusion, and regard the un-decomposable bodies of our globe as distinct entities having no simple relation by weight to one another.

The Swiss chemist Jean Charles Galissard de Marignac (1817 – 1894) in response to Stas's paper, whilst praising the thoroughness and accuracy of his method, rejects his conclusion. Stas, and as we shall see later Peirce, tested Prout's hypothesis by seeking a common divisor for the atomic weights. Marignac takes a different approach in suggesting that a number of the laws of chemistry, such as Gay-Lussac's law of gaseous volumes, have been shown to be inexact when subjected to particularly precise measurements. Such laws are none the less useful to chemists in calculating quantities to degree of precision that they find acceptable for practical purposes. From this perspective of practice Marignac (1860:57), believes that for Prout's hypothesis too, 'even if it is not rigorously confirmed by experience, it none the less appears to express the ratios between the atomic weights of the elements with sufficient accuracy for the practical calculations of chemistry…'. In his concluding paragraph Marignac offers the following comment to chemists such as Stas, and later Peirce, who favour the 'common divisor' approach to testing Prout's hypothesis.

Firstly Marignac (1860:58) reminds his readers of the fundamental principle of 'the unity of matter' that prompted Prout's formulation of his law and also of 'all the more or less brilliant conceptions which have been based on this principle'. Secondly the fruitfulness of Prout's hypothesis is in Marignac's (1860:58) opinion 'altogether independent of the magnitude of the unit which serves as common divisor to the atomic weights of the elements…whether this weight be that of a single atom of hydrogen, or of a half or a quarter atom or whether it be an infinitely smaller fraction, say a hundredth or a thousandth…'Marignac (1860:58) takes the view that Prout's hypothesis may not imply a common divisor for every element's atomic weight because the 'primordial atoms' of primary matter are grouped together as 'chemical atoms' and 'obey[ing] the law of universal attraction' in such a way 'that the weight of each group might not be exactly the sum of the weights of the primordial atoms composing it'. With this argument Marignac sought to save Prout's hypothesis.

In reviewing the points described above it can be seen that the dispute surrounding Prout's hypothesis was centred on how the changing atomic weight data over time fitted the possibility of a common divisor. In 1859 and six years before Peirce's paper, Dumas published a list of the atomic weights for thirty five elements showing values that were either whole multiples of 1, 0.5, or 0.25 - for example, C = 6, Cl = 35.5, Cu=32.75. On the basis of this evidence Dumas proposed a modification of Prout's original hypotheses where atoms were composed of primary units of matter of mass 0.25 (with H=1). The primary units could no longer be thought of as hydrogen atoms. Later in this section we will see Peirce also working from Dumas's modification of Prout's hypothesis.

As atomic weights were determined with ever increasing accuracy no common divisor could be found with Prout's hypothesis becoming ever more difficult to defend. In his third paper (1871) and two years after the first publication of his periodic system, Mendeleev[32] expresses this point as follows,

> Everybody knows the fate of Prout's hypothesis, viz., that the atomic weights of the elements are integer multiples of that of hydrogen. There could have been no doubt whatsoever that this hypothesis overstated the facts, after exact investigations had shown that there are atomic weights which contain fractions, and after Stas has shown that there are no rational fractions among them, despite

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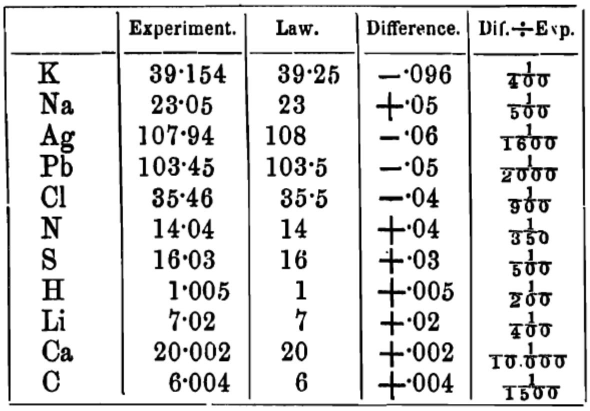
[32] Cited in Sambursky (1969:106)

> Marignac's[33] splendid critical remarks in support of the hypothesis. It seems to me that there are no sufficient reasons in favour of accepting this hypothesis.

Without going into further details of this debate the attempts to salvage Prout’s Hypothesis are captured by (1917:298) by Alexander Scott in his 1917 presidential address to the Royal Society of Chemistry,

> As the determinations of atomic weights increased in accuracy doubts began likewise to grow in strength as to the validity of “Prout’s law,” as it was not unfrequently styled. Marignac’s modification to take 0.5 of the hydrogen unit as a common divisor would not fit all cases; even reducing this to half, that is, 0.25, as Dumas proposed, was not enough to bring all into line.

Peirce also adopts an empirical approach to show the validity of Prout’s Law. In making his calculations Peirce (1863:79) decides that ‘the only atomic weights which have been determined with sufficient accuracy to test the law, besides those of Stas, are the following’ and lists with others Berzelius, Dumas and Liebig. In making his calculations as shown in the table below Peirce (1863:79) is attempting to use the most accurate and reliable data available to him at the time.



	Experiment.	Law.	Difference.	Dif.÷Exp.
K	39·154	39·25	−·096	$\frac{1}{400}$
Na	23·05	23	+·05	$\frac{1}{500}$
Ag	107·94	108	−·06	$\frac{1}{1600}$
Pb	103·45	103·5	−·05	$\frac{1}{2000}$
Cl	35·46	35·5	−·04	$\frac{1}{900}$
N	14·04	14	+·04	$\frac{1}{350}$
S	16·03	16	+·03	$\frac{1}{500}$
H	1·005	1	+·005	$\frac{1}{200}$
Li	7·02	7	+·02	$\frac{1}{400}$
Ca	20·002	20	+·002	$\frac{1}{10.000}$
C	6·004	6	+·004	$\frac{1}{1500}$

Peirce lists the experimental atomic weights and the atomic weights expected from Dumas’s modification of Prout’s Law. To test the agreement Peirce calculates the difference between the two values and then expresses this as a fraction of experimental value. In conclusion Peirce (1863:79) affirms his belief in Prout’s law in stating that, although ‘*K* is an unexplained anomaly’ nonetheless ‘the probability is still in favour of the law’.

Figure 6: Testing Prout’s Law as modified by Dumas
Source: Peirce’s (1863) ‘The Chemical Theory of Interpenetration’*,* page 79

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[33] Marignac’s ‘splendid critical remarks’ will be taken up later in this chapter.

A close examination of Peirce's results and conclusions yields a number of curious points. Firstly the entry for silver (Ag) in the final column has been wrongly calculated (or misprinted) with the correct value being 1/1800 and not 1/1600 as Peirce states in error. Secondly Peirce's identification of potassium (K) as the sole anomaly is seemingly not consistent with his results. Potassium is identified on the evidence of the greatest difference (0.096) between its atomic weight as experimentally determined and the value in accord with Prout's hypothesis. Another measure of agreement between the two values would be to express the difference as a fraction or as a percentage of the accepted experimental value – what today would be regarded as the experimental error. In the final column of the table Peirce makes a similar calculation of error which he expresses as a fraction of the accepted experimental value for the atomic weight. On this basis if potassium (K) is identified as anomalous with a value of 1/400, then so too should any element with a value equal or greater than this. Looking at the table this would give the following elements as anomalous: K, N, H and Li – that is to say four of Peirce's original set of eleven elements. This casts doubt on Peirce's (1863:79) conclusion of the data being 'in favour of the [Prout's] law'. The results corrected for silver and including a column for the percentage error given by the atomic weight in accord with Prout's hypothesis are given below:

Element	**Difference between experimental atomic weight and that in agreement with Prout's hypothesis expressed as a fraction of the experimental value**	**Percentage error**
H	1/200	**0.50**
N	1/350	**0.29**
K	1/400	**0.25**
Li	1/400	**0.25**
Na	1/500	0.20
S	1/500	0.20
Cl	1/900	0.11
C	1/1500	0.07
Ag	1/1800 (corrected value)	0.06
Pb	1/2000	0.05
Ca	1/10 000	0.01

Elements with deviations from Prout's hypothesis that are equal or greater to the value for potassium (K)

Figure 7: Differences between atomic weights determined experimentally and values in accord with Prout's hypothesis (modified by Dumas)

Peirce (1863:79) states himself as satisfied of the validity of Prout's hypothesis as modified by Dumas although his reasons for identifying potassium as the sole anomaly are puzzling,

> *K* is an unexplained anomaly, but the probability of only one difference out of thirteen being greater than 0.25/4 is 0.0000087, while the effect of the residual influence which carries *K* out of this limit is only 1/12000 of the atomic weight.

Firstly it is not clear what Peirce means by 'only one difference out of thirteen' as his table contains a total of eleven elements. His method for evaluating the evidence given in his table does not address the three other elements – hydrogen, nitrogen and lithium - where the difference between the experimental atomic weight and the value based on Prout's hypothesis is equal or greater than that for potassium.

Having claimed to have demonstrated the validity of Dumas's variant of Prout's hypothesis, Peirce (1863:79) contends that this 'must probably be capable of a common explanation with the rest 'of the other laws of chemistry' whilst claiming that 'it is clear that the atomic hypothesis can never explain it'. In rejecting atomism as an explanation for the laws of chemical composition and for Prout's hypothesis, Peirce (1863:81) claims that, in accord with Kant, 'matter is not absolutely impenetrable and that chemical union consists in the interpenetration of the constituents'. From this Kantian perspective Peirce (1863:81) argues that, 'if we suppose, with the metaphysicians, that all the kinds of matter are derived from one' then the atomic weights of the elements 'will be multiples of the original matter' and it is 'this explains Prout's Law'. In sum: Peirce's chemical theory of interpenetration, which draws on Kant's dynamical theory of matter, holds that matter is not completely impenetrable. Prout's Law is explained on the basis that Peirce's 'original matter' condenses to produce the chemical elements with atomic weights that are integer multiples of that original matter.

In this section we have seen Peirce take a typically empirical approach to testing the validity of Prout's hypothesis and confirming Dumas's common divisor for the atomic weights having a value of 0.25. I would argue that in seeking to justify Prout's hypothesis the 'younger' Peirce showed a research interest that was common to other chemists of his period. His approach was conventional in that he used mathematical methods to justify a common divisor to the atomic weights of those elements where there was good agreement on their individual values. His method was typically empirical for a chemist in using atomic weight data gained through the experience of making observations during the course of experimentation.

Where Peirce differs however, is in his readiness to frame his empirically derived conclusions within a wider metaphysical framework. In this case Prout's law is explained by a dynamical theory of matter. Other chemists of his period were far less interested in relating their chemical knowledge to any underlying metaphysical scheme – with Peirce's tutor Josiah Cooke being one typical example. Peirce's second chemistry paper published six years later in 1869 again shows Peirce immersed in another common concern of nineteenth century chemistry but this time without the metaphysical speculations of the paper just discussed. These are not issues that have featured in Peirce scholarship so far.

2.4 'The Pairing of the Elements' (1869) – classifying the elements according to their atomic weights

In this section I examine Peirce's research interest in developing a system for classifying and grouping the chemical elements according to atomic weight is common to nineteenth century chemistry. In this respect Peirce's interest is again main-stream for the period. In fact, as has already been discussed in chapter one, Peirce's interests were also shared by his tutor Josiah Cooke.

In February 1869 Dmitri Mendeleev published the first edition of his periodic table. In September of the same year The Scientific American[34] reported, 'Mr Charles S Peirce, of Cambridge, had greatly added to the illustration of the fact [elements that had corresponding or closely approximating atomic weights were related in physical properties] of pairing by representing in a diagram the elements in positions determined by ordinates representing the atomic numbers'. The arrangement of the chemical elements that Peirce achieved is described by Nathan Houser (1982:xx) as going 'far in Mendeleev's direction, before Mendeleev's announcement of the [periodic] law' and before Mendeleev's work 'became known in Western Europe and America'. Here again Peirce's chemical researches mirror the concerns of other researches in both North America and in Europe. This is a diagrammatic representation of Peirce's arrangement from his paper 'The Pairing of the Elements' published in Chemical News 1869:

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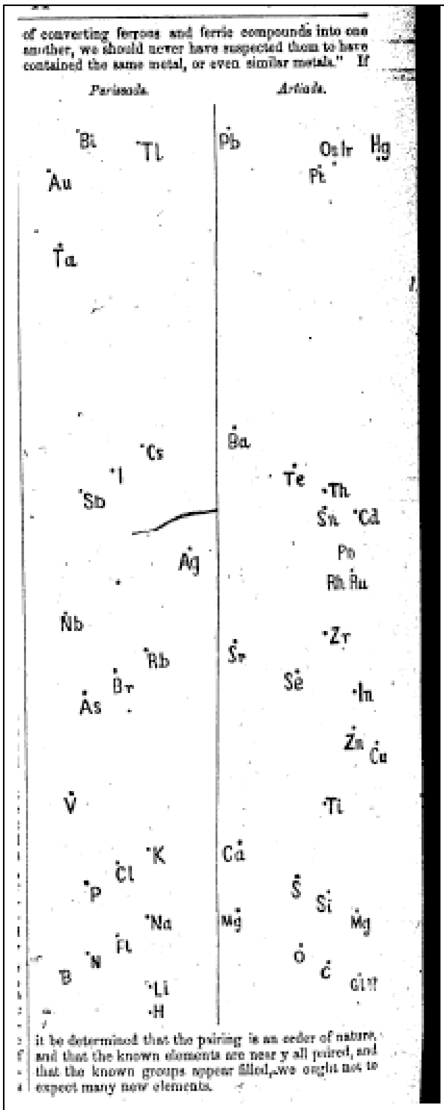
[34] *Scientific American* **(21)** (1869:162**)**



of converting ferrous and ferric compounds into one another, we should never have suspected them to have contained the same metal, or even similar metals." If

it be determined that the pairing is an order of nature, and that the known elements are nearly all paired, and that the known groups appear filled, we ought not to expect many new elements.

Here Peirce's (1869:340) table divides the elements into two columns: perissads and artiads. Using modern nomenclature perissads are elements with odd-numbered valencies where artiads have even-numbered valencies. Josiah Cooke (1874:59) defines the terms as follows: 'atoms like those of sulphur, whose quantivalance is always even, are called artiads, while those like nitrogen, whose quantivalence is always odd, are called perissads'. The terms are derrived empirically from a quantative study of sulphur and nitrogen and their compounds. The elements are arranged in height order by atomic weights. Elements belonging to what Peirce (1869:340) describes as 'series' and later to be known as groups appear as vertical columns. Collected under the perissads are the monovalent metals Li, Na, K, Rb and Cs and under the artiads the bivalent metals Mg, Ca, Sr, Ba. Peirce (1869:340) notes the pattern of 'parallel shelving lines' but more importantly the 'correspondence between the series of artiads and perissads which have the highest atomic weights – that is to say, Na, K, Rb, Cs, Tl, on the one hand, and Mg, Ca, Sr, Ba, Pb, on the other'. By arranging the elements by atomic weight Peirce has achieved a 'pairing of the elements' with similar properties. Taking for example Peirce's series of what will later be known as the group I and II metals, Na is paired with Mg, K with Ca and so on. Peirce notes their chemical similarity in that 'they form strong bases and peroxides, but no suboxides or acids'. The paper includes other similar connections between say what is now known as the halogens (group VII) and group VI - F pairs with O, Cl with S and so on. This particular 'pairing' brings elements of similar properties together, Peirce notes, in that they 'unite in simple proportions' with the metals mentioned above and 'form strong acids with oxygen, but never bases'.

Figure 8: Peirce's arrangement of the chemical elements
Source: Peirce's (1869) 'The Pairing of the Elements', page 340

Commenting on Mendeleev's original paper (1869) on the periodic law Eric Scerri and John Worrall (2001:414) state, 'very similar ideas were being developed independently by others in 1869 and indeed earlier Lothar Meyer, for example, had essentially the same table; and other periodic tables with some differences to Mendeleev's but with much overlap, were, as is well known, developed by Hinrich, Odling, de Chancourtois and Newlands'. For example in 1863 the English chemist John Newlands organised fifty-six elements into eleven groups according to their physical properties. A year later Newlands published a version of the periodic table where the chemistry of every eighth element was similar – his so-called law of octaves. A second example is the German chemist Julius Lothar Meyer who five years before Mendeleev produced a table comprising twenty eight elements organised by valence.

In common with Mendeleev and other earlier workers on the classification of the chemical elements, Peirce too recognised the organisational power of atomic weights order to reveal groups of elements with similar chemical behaviour. Also worth noting is that whilst Peirce (1869:340) writes of 'resemblances between elements', he does not frame his account in terms of the *relations* to be found in Mendeleev and in Cooke. This is perhaps because whilst some intriguing patterns emerge (such as the pairing of Na and Mg) Peirce (1869:339) describes 'the regularity observable' as 'certainly a very rude one'. As noted earlier, Peirce orders around sixty elements into two series: artiads and perissads, with a close correspondence between a number of elements belonging to the two series. Whilst Peirce regards his system as rather rudimentary in form, Helge Kragh (2010:100) notes that '[i]n fact, the correspondence amounted to a classification of groups of elements which in some cases were the same as those proposed by Mendeleev the same year. Furthermore Kragh (2010:100) argues that, 'although Peirce's "pairing" scheme of elements has not attracted attention among historians of chemistry, it clearly has a place in the history of the periodic system'. To my knowledge Peirce's scheme does not feature in the recent standard texts on the periodic table (e.g Scerri 2007, 2011). Here again we see Peirce engaged in a research programme common to other nineteenth century chemists. The extent of regularity that Peirce has uncovered in this brief paper is insufficient to justify the detailing of *relations*[35] between the chemical elements. It is worth now however pursuing an occasion that same year (1869) Peirce connects *regularity, orderliness* and the possible existence of *relations.*

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[35] The role of *relations* in the writings of Peirce and Mendeleev will be considered in detail in chapter four.

2.5 The relationship between Peirce's chemistry and his philosophical writings of the same period

Towards the end of the 1860s Peirce published three essays in the *Journal of Speculative Philosophy* which Bergman (2007a:53) describes as, 'a stinging criticism of Cartesian thought … advocat[ing] a semiotic theory of cognition that denied the privileged status of individual intuitions while affirming the dynamic and ultimately social nature of knowledge'. In 1869, the year Peirce is also writing on the possibility of an orderly arrangement among the chemical elements, the second of his anti-sceptical, anti-Cartesian essays, 'Grounds of Validity of the Laws of Logic: Further Consequences of Four Incapacities' is published. A section of this essay is concerned with hypothesis formation and inductive inference where Peirce states: 'All probable inference, whether induction or hypothesis, is inference from the parts to the whole. It is essentially the same, therefore, as statistical inference' (EP1:78, 1869).

Returning to Peirce's 'Pairing of the Elements' (1869) we can see Peirce applying inductive thinking when he discusses his arrangements of the chemical elements. For example, Peirce (1869:339) notes that in order to arrive at his diagrammatic arrangement he has, 'put the different elements at heights representing their atomic weights, and those of one series in columns together' – the series being families of elements with similar physiochemical properties. Here Peirce uses inductive reasoning to build his series by 'infer[ing]' from the parts' – the individual atomic weights and knowledge of each element's series – 'to the whole' as shown by 'The Pairing of the Elements'. In so doing Peirce has managed to project a degree of order onto the approximately sixty chemical elements that fall within his scheme. Interestingly though, in his essay 'Further Consequences' (1869) Peirce rejects any justification of induction on the inherent orderliness of nature when he states that such an explanation 'will not do' for 'nature is not regular' (EP1:75, 1869).

Before pursuing Peirce's claim any further it is worth exploring first what he understands here by the term *relations.* By way of clarification Peirce describes a hypothetical event where a man in China buys a cow shortly after a Greenlander sneezes. Although Peirce writes of these two events as a state of *relations,* they are he explains 'not connected with any regularity whatever', stating further that 'such relations [are] infinitely more frequent than those which are regular' (EP1:75, 1869). Thus for Peirce the term *relations* can be used to associate frequent ('regular') events such as a Greenlander sneezing with the possibility of having contracted the cold virus. There are also incidental or irregular relations such as the purchase of a cow in China with a person sneezing many thousands of miles away in

Greenland. These points are emphasised by Peirce when he again picks up the themes of *orderliness, regularity* and *relations*,

> The orderliness of the universe, therefore, if it exists, must consist in the large *proportion* of relations which present a regularity to those which are quite irregular. But this proportion in the actual universe is, as we have seen, as small as it can be; and, therefore, the orderliness of the universe is as little as that of any arrangement whatever. (EP1:76, 1869)

Note here the two points already encountered. Firstly Peirce implies that regularity is not always required in order for a relation to exist. Secondly, the most common relations are those that present as irregular; our experience of orderliness presents as that proportion of relations that are regular. A third point to note is that Peirce emphasises the dominance of irregular relations in nature in stating, 'it is true that the special laws and regularities are innumerable; but nobody thinks of the irregularities, which are infinitely more frequent' (EP1:75, 1869). Regularities where they exist are therefore something of a surprise and worthy of further inquiry in search of an explanation – which Peirce attempts in his *Paring of the Elements* in searching for a degree of order among the chemical elements.

It is possible to connect further aspects of Peirce's *Further Consequences of Four Incapacities* – his philosophy - with his paper investigating the possible orderliness amongst the chemical elements – his chemistry – both written in 1869. In *Further Consequences* Peirce makes the perhaps surprising statement for a chemist, who is at the same time publishing on a possible orderly arrangement of the chemical elements, that even if there were orderliness in nature, 'it never could be discovered'(EP1:76, 1869). The reason, explains Peirce, is that should such orderliness exist, 'it would belong to things either collectively or distributively'. Where orderliness belongs to a set or system of things collectively, the difficulty Peirce explains is that, 'a system can only be known by seeing some considerable proportion of the whole' (EP1:75, 1869). It is difficult to justify projecting a degree of discovered orderliness onto the whole of nature as there is no way of knowing how large a proportion of nature the discovered order relates to. In describing his arrangements of the chemical elements Peirce echoes the earlier point on 'collective order'. In 'The Pairing of the Elements'*,* Peirce (1869:339) explains that his proposal of a degree of regularity shown by the 'pairing of the elements' is limited in reach in that he is dealing with 'only sixty elementary substances, out of the myriads which there might probably be', and so we ought not to expect a 'more accurate classification of them' than he is presenting. Thus the chemist's claim of discovering orderliness among the chemical elements is necessarily limited by knowing only a few examples from the 'myriad' of total possibilities. For, as Peirce (1869:339) explains, how accurate would a classification of the animal kingdom be 'if only sixty animals were known'.

The second kind of order which Peirce claims in *Further Consequences of Four Incapacities* is described as *distributive*, that is 'belonged to all things only by belonging to each thing' where the difficulty here lies in that 'a character can only be known by comparing something which has it with something which has it not' (EP1:76, 1869). This form of orderliness or regularity also resonates with Peirce's paper on the chemical elements. A degree of order is established by grouping the elements according to their atomic weights. The groupings are confirmed by the presence of chemical characteristics that are held in common. For example Peirce (1869:340) relates the monovalent metals (perissads) Na, K, Rb, Cs and Tl to the divalent (artiads) Mg, Ca, Sr, Ba and Pb in that they 'form strong bases and peroxides, but no suboxides or acids'. All elements outside these two sets of metals – part of Peirce's evidence for the 'pairing of the elements' – do not possess these particular properties. Peirce also compares the two groups F, Cl, Br and I with O, S, Se and Te in that they 'form strong acids with oxygen, but never bases'. Again the chemical character of these elements is known by comparing a property they all possess with the remaining elements that do not. The process here is one of taking a sub-set of the total known elements deciding on a quality that brings them into relation with one another, qualities that are not present in the remaining elements. Connecting Peirce's 1869 papers on chemistry and inductive logic, it would seem that in order to justify his groupings or 'pairings of the elements' Peirce claims the existence of a degree of distributive order. He achieves this by comparing the chemical properties common to a particular set of 'pairs of elements' (*something which has it*) with the remaining elements where this property is absent (*something which has with it not*).

So what are we to make of the seeming contradiction between Peirce's claim for having discovered some order among the chemical elements – albeit an imperfect one – and his philosophical claim that if order existed in nature it could not be discovered? [36] Does Peirce's practice as a chemist conflict with his early philosophical writings on inductive reasoning? The target of Peirce's arguments on the nature of order within the universe is J.S Mill, who as Peirce states 'explains the validity of induction by the uniformity of nature'

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[36] I am grateful to Mats Bergman in helping me to clarify my thoughts in this section

(EP1:77, 1869). Peirce does not believe that ‘the validity of induction and hypothesis [are] dependent on a particular constitution of the universe’ (EP1:76, 1869) – upon how the universe happens to be. In the universe as we experience it, whilst inductive arguments can on occasion fail, Peirce maintains, ‘all that can be said is that in the long run they prove approximately correct’ (EP1:76, 1869). On a broader point, Peirce argues that inductive inference is both fallible and ultimately self-correcting when he argues that, ‘it cannot be said that we know an inductive conclusion to be true, however loosely we state it; we only know that by accepting inductive conclusions, in the long run our errors balance one another’ (EP1:79, 1869).

Would Peirce at this time deny the discoverability of regularities in the world? I think not. Then how is it that an inquirer from Peirce’s perspective, by reasoning inductively, is able to seemingly discover a degree of order in the world – such as Peirce’s arrangements of the chemical elements? Some insight is given later in *Further Consequences* (1869), where Peirce offers an account of induction within a realist framework,

> The other question relative to the validity of induction, is why men are not fated always to light upon those inductions which are highly deceptive. The explanation of the former branch of the problem we have seen to be that there is something real. Now, since if there is anything real, then (on account of this reality consisting in the ultimate agreement of all men, and on account of the fact that reasoning from parts to whole, is the only kind of synthetic reasoning which men possess) it follows necessarily that a sufficiently long succession of inferences from parts to whole will lead men to a knowledge of it, so that in that case they cannot be fated on the whole to be thoroughly unlucky in their inductions. (EP1:79, 1869)

In his paper ‘The Pairing of the Elements’ and by inductive reasoning – ‘the only kind of synthetic reasoning which men possess’ – Peirce offers his arrangement as a contribution to the nineteenth century inquiry into the chemical elements. The hope is that in the longer term chemists will eventually gain the knowledge they are seeking, as ‘they cannot be fated on the whole to be thoroughly unlucky in their inductions’. Peirce (1869:339) acknowledges that his own inductions have achieved a somewhat imperfect knowledge when he states, ‘[t]he regularity observable is certainly a very rude one’. Perhaps we might regard Mendeleev, who like Peirce also published his arrangement in 1869, as being luckier in his inductions.

2.6 Conclusion

As a nineteenth century chemist Peirce was not unusual in that he shared both interests and empirical methods in common with many of his contemporaries. In this chapter whilst not wishing to challenge Fisch's view of Peirce as 'most original and versatile intellect', I have highlighted that as a chemist, Peirce operated within the boundaries of what Thomas Kuhn (1996) described as *normal science*[37]. Where Peirce differed was in his ready willingness to engage with the metaphysical issues that many chemists, including his tutor Josiah Cooke, chose to ignore. During the 1860s most scholars agree that Peirce almost 'outsources' his metaphysics from Kant when forming his philosophical position. What I believe is an addition to this scholarship is my claim that Peirce's Kantian metaphysics emerges in his chemistry.

Of significance is that in 1869 Peirce, by employing inductive reasoning, argues for an orderly arrangement of the chemical elements. That same year Peirce publishes a series of three papers which includes a justification for inductive reasoning which denies J.S Mill's defence in terms of the orderliness of nature. I would argue that Peirce does not deny the discoverability of regularities in the world; rather the insufficiency of such an appeal to order to justify inductive reasoning. As we have seen Peirce's justification turns on the likelihood that in the longer term inquirers – such as chemists seeking a ordered system for the chemical elements – would be 'fated' on occasion to be successful in their inductions, inductive reasoning being, at least at this stage in Peirce's philosophy, the only form of 'synthetic reasoning' inquirers possess.

I believe this is an addition to Peirce scholarship where there is little discussion of his chemistry papers of 1863 and 1869 or their relation to his philosophical writings of the time.

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[37] Kuhn (1996:10) states: 'Normal science means research firmly based upon one or more past scientific achievements, achievements that some particular scientific community acknowledges for a time as supplying the foundation for its further practice.

Chapter Three

Dmitri Mendeleev and Charles Peirce – the *relations* between chemists, chemistry and philosophy

3.1 Introduction

So far, in chapter one I tried to show that Peirce's study of chemistry under Josiah Cooke, with an emphasis on mathematics and the use of diagrams paved the way to Peirce's subsequent research in chemistry and allied well with Peirce's later treatment of diagrams as a way of visualizing relations. In chapter two I discussed examples of Peirce's own researches into chemistry. In this chapter I will further explore Peirce's work in chemistry, on the nature of *relations*, and his use of diagrams to create knowledge and to foster understanding.

This is relevant to this project for two reasons. Firstly I will argue that the concept of *relations* was important not only to Peirce but also to the Russian chemist Dmitri Mendeleev. This will establish some important common ground between these two philosopher chemists, ahead of chapter four, where Peirce's formulation of iconicity will be applied to Mendeleev's periodic table. Secondly, I will show that Peirce had an abiding interest in Mendeleev's periodic table long after its first publication in 1869. The periodic table, and the associated concept of chemical valency, will be shown to have provided Peirce with a particular mind-set when developing his phenomenology. This will involve an exploration into the late Peirce (1903) phenomenology; however it is not intended to be an exegesis on Peirce's phenomenology which can be found for example in Parker (1998) as well as Rosensohn (1974&1977).

Richard Atkins (2010) sets out the differences between Peirce's *formal* categories (Firstness, Secondness and Thirdness) and his *material* categories by appealing to the relations between Peirce and Mendeleev. In particular Atkins (2010:101) characterises Peirce's 1908 re-characterisation of the relationship between his *formal* and *material* categories as Peirce's '*Mendeleevian Model of Formal and Material Categories'.* This project makes no attempt to deal with Peirce's system of categories. My focus will be on how Peirce's chemical mind-set contributed to define some key aspects of his phenomenology, broadly construed. Chemical valency is founded on the bonding relations between the chemical elements; the periodic table on their physio-chemical relations. Both afforded Peirce with ways of exploring his formulation of phenomenology diagrammatically. This too will provide an important insight into Peirce's use of diagrams to generate knowledge in the minds of his readers, ahead of the next chapter dealing with iconic diagrams.

Why is the concept of *relations* of relevance to chemistry? The philosopher of chemistry Joachim Schummer (1998:135) argues that 'chemistry at the core is a science of peculiar relations'; chemists such as Peirce and Mendeleev are not measuring, comparing and cataloguing isolated chemical objects but, as Schummer (1998:135) states, the 'dynamic relations between objects [which] constitute the basic set of chemical knowledge'. When writing of Robert Bunsen (1811–1899) and Gustav Kirchhoff (1824–1887), who in 1860 and by using novel spectroscopic methods, discovered the two alkali metals caesium and rubidium, Peirce states that they 'not only discovered these elements, but studied them so well…that they are now among those whose chemical *relations* are the best understood' (W2:286, 1869 emphasis added).

In a series of papers written in 1879 and published in *Chemical News*, Mendeleev (1879:243) emphasised the importance of establishing causal *relations* as a means of gathering new knowledge – he writes, 'the principal end of modern chemistry is to extend our knowledge of the *relations* between the composition, the reactions, and the qualities of simple and compound bodies, on the one hand; and, on the other hand, the intrinsic qualities of elements which are contained in them; so as to be able to deduce from the known character of an element all the properties of all its compounds'(emphasis added). Mendeleev is concerned with the relations between the chemical elements of composition and the properties of their compounds. Peirce, in forming his position on phenomenology, sought to reveal and identify the most the most universal elements of experience, then, 'to draw up a catalogue of categories…to make out the characteristics of each category, and to show the *relations* of each to the other' (CP 5.43 1903, emphasis added). Where Mendeleev is dealing with the relations between the material elements of chemical composition, Peirce is as we shall see concerned with the relations between the conceptual elements of experience.

The literature has accounts of the origins of Peirce's phenomenology (Rosensohn 1974), the methodology of Peirce's phenomenology (Rosenthal 1997) as well as the relationship between Peirce's phenomenology and his three metaphysical categories of Firstness, Secondness and Thirdness (Misak 2004). Richard Atkins (2010 & 2012) uses the framework of Mendeleev's periodic table to analyse Peirce's categories. There is, however, very little on how Peirce uses his knowledge and understanding of chemistry and of Mendeleev's periodic table to explicate the ‘difficult work’ of ‘disentanglement’ of human thoughts that is the work of the phenomenologist. I will argue that elucidating Peirce’s use of chemistry affords a useful insight into his phenomenology, a view largely ignored in the literature.

Before going any further it is worth setting out a brief description of Peirce’s phenomenology or phaneroscopy as he later termed it. In 1902, states Thomas Short (2007:60), Peirce ‘presented an ‘architectonic’ ordering of the sciences, within which he announced a new science, of phenomenology’. In first using the term phenomenology, Short (2007:61) states, Peirce initially ‘referred to Hegel…[and]… in 1904 he switched to ‘phaneroscopy’ whilst also substituting the term ‘phaneron’ for phenomenon. Peirce sets out his position on phaneroscopy in 1904, and as part of his Adirondack Summer School Lecture (1904),

> Phaneroscopy is the description of the phaneron; and by the phaneron I mean the collective total of all that is in any way or in any sense present to the mind, quite regardless of whether it corresponds to any real thing or not. (CP 1.284, 1905)

On another occasion, explaining how we might approach the totality of our consciousness at any one instant, Peirce invites his reader ‘to join me in a little survey of the Phaneron…in order to discover what different forms of indecomposable elements it contains’ (EP2:362, 1906). By using the term ‘indecomposable element’ – which he rejects as ‘pleonastic’- Peirce uses the term ‘element’ as it is ‘the only being a constituent of the Phaneron has’, and ‘indecomposable’ because each element ‘of the collective total’ of our consciousness is ‘incapable of being separated by logical analysis into parts’ (EP2:362, 1906). The ‘indecomposable’ nature of the cognitive elements of the phaneron is analogous to the irreducibility of the chemists’ atoms. By using the term ‘indecomposable elements’ in his ‘little survey of the phaneron’ Peirce meant, states Gava (2011:238), ‘those features of our thought that could not be reduced to simpler concepts without losing their proper meaning’.

By 1903 philosophy is described by Peirce as having three sub-divisions: phenomenology, normative science (aesthetics, ethics, and logic) and metaphysics[38]. In his 1903 lectures on pragmatism, Peirce describes the practice of phenomenology as, ‘simply to open our mental eyes and look well at the phenomenon and say what are the characteristics that are

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[38] This is an example of Peirce’s later writings (1903)

never wanting in it, whether that phenomenon be something that outward experience forces upon our attention, or whether it be the wildest of dreams, or whether it be the most abstract and general of the conclusion of science'. No judgements as to causes or reasons are required, but only states Peirce the, 'artist's observational power is what is most wanted in the study of phenomenology' (CP 5.41 1903). Thus in terms of the methodology, Peirce writes that the phaneroscopist, 'does not undertake, but sedulously avoids, hypothetical explanations of any sort…[but]…simply scrutinizes the direct appearances, and endeavours to combine minute accuracy with the broadest possible generalization' (CP 1.287, 1904). Thus the method of the phaneroscopist, argues Sandra Rosenthal (1997:77), 'does not make judgements concerning the reality that is observed'. A similar view is taken by Short (2007:67) when he states that the phaneroscopist should note appearances but, 'not judge their veracity'. The acritical method of the phaneroscopist, argues André De Tienne (2004:15), is similar to the study of mathematics*,* ′in the sense that it does not make assertions: the results of its observations are recorded in descriptive propositions, the truth of which is not its business to assess'.

My purpose in this chapter is not to contest these views. I will argue that an additional and valuable insight is afforded by viewing Peirce's phenomenology, or phaneroscopy, through the lens of chemistry. To show how the concept of chemical valency and the structure of Mendeleev's periodic table offered Peirce (himself a chemist) a framework to explore phenomenological relations diagrammatically. There is little in the literature exploring these possibilities. The philosopher of chemistry Jaap van Brakel (2012:26), in his analysis of Peirce's formulation of phenomenology argues that,

> He [Peirce] based his phenomenology or phaneroscopy, which he also called "phanerochemy", chemistry of appearances, or chemistry of thought, on an analogy with chemical elements and compounds…Still it cannot be said that Peirce gave a central place to chemistry in the scheme of things.

In justifying his rejection of a 'central place' for chemistry in Peirce's phenomenology, van Brakel (2012:26) refers us to a much earlier writing (1861) where Peirce states, '[w]e must be satisfied with the Natural History of the chemical Elementary bodies without as yet explaining their physics'. Unfortunately van Brakel offers no explanation as to why this very early example of Peirce's writings on chemistry leads him to reject chemistry as playing a 'central place' in his phenomenology. Perhaps the objection lies in Peirce suggesting that although the properties or 'Natural History' of the chemical elements can be determined they cannot be explained on a more fundamental level – 'their physics'. What van Brakel omits is the sentence immediately following on from his quotation where Peirce states, '[w]e must not assume they [the chemical Elementary bodies] do not exist because we cannot explain them' (W1:54, 1861). As has been shown in chapter two, some two years later in his paper 'The Chemical Theory of Interpenetration' (1863), Peirce offers an explanation of the behaviour of atoms – 'their physics' – based on a Kantian model of forces. Whilst van Brakel makes the connection between chemistry and Peirce's phenomenology, he denies it any significant impact. In this chapter I will disagree with van Brakel and argue that chemistry – the periodic table, valency and their capacity to facilitate diagrammatic reasoning – offered Peirce a conceptual framework to set out his position.

I should like to make one other point on phaneroscopy before moving on to Peirce and Mendeleev's common interest in the nature of *relations.* As we have seen, Peirce describes the phaneron to 'mean the collective total of all that is in any way or in any sense present to the mind, quite regardless of whether it corresponds to any real thing or not' (CP 1.284, 1905). What does the study of the phaneron – phaneroscopy – entail? Phaneroscopy, states Short (2007:68), 'observes, describes and analyses the phaneron'. Then having observed, described and analysed, we are in a position to, as Peirce describes, determine the 'broadest categories of phanerons there are' and then to 'enumerate the principal subdivisions of those categories' (CP 1.286, 1904). On this basis, argues Robert Marty (1982:169), Peirce 'assigns to phaneroscopy two tasks: the first is analytical and yields the formal elements; the second is taxonomic and bears a close resemblance to the methods of the naturalist'. There are parallels here with chemistry and the attempt by Peirce – and as we shall see Mendeleev - to systemise the chemical elements according to their atomic weights. Their first task is analytical whereby the chemical elements and their atomic weights are identified. Secondly, and similar to the biologist's taxonomy of assigning and naming groups of organisms on the basis of their shared characteristics, is the chemist's organisation of the chemical elements into groups within their scheme.

3.2 Mendeleev and Peirce on *relations*

Both Peirce and Mendeleev published their systems for the chemical elements in 1869. Before examining the approach Mendeleev and Peirce took to *relations* I should like to point out that each worked independently of the other. In his extensive research into the reception of Mendeleev's periodic law into America Stephen Brush (1996:609) notes that 'no American or British textbooks mentioned the periodic law at all until after the discovery of gallium' – which was in 1875 and six years after Peirce had published.

If Peirce had not read Mendeleev's work in a formal publication were they perhaps in direct contact with one another? This author has found no evidence to suggest that Peirce and Mendeleev met or corresponded at any time during their careers. The correspondence hosted by Indiana University-Purdue University Indianapolis as the *Peirce Edition Project* records over eight hundred of Peirce's correspondents but makes no mention of Mendeleev. A search of Peirce's correspondence preserved in the Houghton Library at Harvard University and registered in the Robin catalogue also makes no reference to Mendeleev.

In their essay 'Charles Peirce's First Visit to Europe, 1870-71' Jaime Nubiola and Sara Barrena (2009:101) were able to 'identify 17 surviving letters of Peirce's first trip to Europe' – Mendeleev is not mentioned. There is also no suggestion that Peirce travelled to Russia to meet Mendeleev. Peirce's first visit to Europe lasted ten months (June 1870 – March 1871) and was close to the time when both he and Mendeleev had published on the organisation of the chemical elements by atomic weight. There was one other occasion when the two might have met. In June 1876 Mendeleev visited America for one month to make a study of oil production processes. Before leaving America, Mendeleev, by now a well-known chemist, visited the Centennial Exposition held in Philadelphia. Many prominent American and overseas scientists also attended. Seemingly reluctant to take full advantage of this situation, Mendeleev appears to have kept a very low profile - Henry Leicester (1957:332) describes him as having 'avoided contact with most of his fellow chemists'. Even had Mendeleev shown a greater willingness to socialise, he would not have encountered Peirce who was then away in Europe. This trip was part of Peirce's work on the earth's magnetic field for The U. S. Coast and Geodetic Survey. He departed from America in April 1876 to return four months later in August. It would seem likely therefore that Peirce's interest in chemistry during the mid to late 1860's was independent of Mendeleev's work.

To recap on Brush's point: American literature made no mention of Mendeleev until after the discovery of Gallium in 1875; US chemists such as Josiah Cooke and his student Peirce were therefore working independently of Mendeleev in attempting to classify the elements according to atomic weight. Scerri (2007:104/5) claims that whilst Mendeleev 'steadfastly maintained in all subsequent writings that he did not see any of the systems developed by the five other discoverers of the periodic system, namely, De Chancourtois, Odling, Newlands, Hinrichs, and Lothar Meyer' nonetheless 'he repeatedly acknowledged his debts to some earlier pioneers of the system, including Peter Kremers, *Josiah Cooke*, Max

Pettenkofer, Alexandre Dumas, and Ernst Lenssen' (emphasis added). For example in his Faraday Lecture of 1889, Mendeleev (1889:637) explained that prior to his work and during the period 1860-70 and the decade before it had become evident that 'the relations between the atomic weights of analogous elements were governed by some general and simple laws'. Mendeleev credits Josiah Cooke along with others such as Dumas for their work in this field. The American historian of science Bernard Cohen (1959:672) states that Cooke 'can fairly be described as the first [American] university chemist to do truly distinguished work in the field of chemistry'. In support of Cohen's claim for Cooke as a nineteenth century pioneer of American chemistry Brush (1996) notes that during 1876 to 1885 some American chemists regarded Mendeleev's successful predictions of gallium and scandium as offering significant support for the periodic law. As an example Brush (1996:611) cites Cooke who, 'in a textbook published in 1881 and reprinted several times', asserted that 'the power of such a working theory to predict the order of undiscovered phenomena [as in the case of gallium] is a good criterion of its validity'. The book Brush refers to here is Cooke's *Principles of Chemical Philosophy* first printed in 1881 and reprinted 1885. In the earlier chapters I showed how Peirce and Cooke shared an interest in seeking a means of ordering the chemical elements; one framed in terms of *relations*. We will now see how Mendeleev too framed his inquiry into the chemical elements in terms of *relations*.

On June 4th, 1889, some twenty years after the first publication of his periodic table, Mendeleev delivered the Faraday Lecture at the Royal Institution before the Fellows of the Chemical Society. Early on in the lecture Mendeleev (1889:636) recalled a statement he made as part of his address to the Russian Chemical Society some twenty years earlier and which he also included in his *Principles of Chemistry.* The following statement illustrates the importance of *relations* to Mendeleev.

> The aim of this communication will be fully attained if I succeed in drawing the attention of investigators to those *relations* which exist between the atomic weights of dissimilar elements, which, as far as I know, have hitherto been almost completely neglected. I believe that the solution of some of the most important problems of our science lies in researches of this kind. (emphasis added)

Mendeleev believed that his periodic law, capturing as it does the regularity of the relationship between the elements, the formulae of their compounds and their physiochemical properties, as a function of atomic weight, offered a powerful investigative framework to his fellow chemists. Consider now Peirce's reflections of 1896 – over thirty years after his early chemistry papers – on what sets the true scientific chemist apart from all who would call themselves 'a chemist',

> The genuine scientific chemist cares just as much to learn about erbium[39] -- the extreme rarity of which renders it commercially unimportant -- as he does about iron. He is more eager to learn about erbium if the knowledge of it would do more to complete his conception of the Periodic Law, which expresses the mutual *relations* of the elements. (CP 1.145, 1896, emphasis added)

Note here the acknowledgement of *relations* as a foundational issue for Mendeleev and for Peirce, both in the realms of chemistry and the chemical elements. It is also worth recording Peirce's appreciation of the significance of Mendeleev's periodic law as well as identifying the dilemma around the correct positioning of the rare earth elements within Mendeleev's scheme. For Peirce, as will be shown, is much concerned with the nature of relations in developing his phenomenology, and regards chemists as not interested in delving into the physical properties of individual substances any more than is necessary to 'identify them and to make out their constitutional *relations*'(CP 1.260, emphasis added). The single physical property defining the 'constitutional relations' between the chemical elements was identified by Mendeleev (1879:273) as atomic weight, for he states that, 'the nature of the elements depends above all on the their mass, and it considers this function to be periodic'. One piece of advice Peirce offers the chemist engaged in an inquiry is that, 'you must train yourself to the analysis of *relations*' (CP 1.345, emphasis added). Both Peirce and Mendeleev are here united in their understanding of the importance of *relations.*

The importance of an analysis of relations to chemical inquiry can be seen in later writings by Mendeleev. In the very first footnote to volume one of his *Principles of Chemistry,* Mendeleev (1901a, Vol 1:1) emphasises *relations* when making a number of observations on the right conduct of scientific investigations. Such investigative inquiries should, he argues, include, 'framing hypotheses or propositions as to the actual cause and true nature of the *relation* between that studied (measured or observed) and that which is known or the categories of time, space, &c.'. For hypotheses that build into theories, these too, Mendeleev (1901a, Vol 1:1) argues, should 'account for the nature of the properties of that

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[39] A rare earth element

studied in its *relations* with things already known and with those conditions or categories among which it exists' (emphasis added). Mendeleev applies these principles when considering Lavoisier's work on the oxidation of mercury to mercury oxide and as a way of gaining an insight into the term element. For it is the chemical element that serves for Mendeleev (1901a Vol1:22) as, 'the starting point, and is taken as the primary conception on which all other substances are built up'. True to his footnote on the conduct of inquiry, Mendeleev accounts for mercury oxide in terms of '*relations* with things already known and with those conditions or categories among which it exists' – the free elements mercury and oxygen and their relations to the material but invisible components of mercury oxide:

> Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, which, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is contained in mercury oxide ; it only contains the substance of these elements, just as steam only contains the substance of ice, but not ice itself, or as corn contains the substance of the seed, but not the seed itself.

An element, Mendeleev (1901a Vol1:23) continues, can only be consciously recognised in its action with another and in the uniqueness of the compound formed,

> The existence of an element may be recognised without knowing it in the uncombined state, but only from an investigation of its combinations, and from the knowledge that it gives, under all possible conditions, substances which are unlike other known combinations of substances.

Here again is a case of *relations* – this time between the nature and properties of the free elements mercury and oxygen and their compound mercury oxide, which is unlike other compounds given by these elements – such as mercury sulphide or copper oxide. Hendry (2005:43) stresses the importance of the abstractness of the concept of the chemical element as the result of chemistry being concerned with explaining chemical changes, such as the oxidation of mercury, and so 'a system of the elements should contain substances that can survive change in phase or state of chemical combination'. In sum: Mendeleev demonstrates the importance of *relations* to his underlying rationale - his elemental hypothesis was formed around investigative inquiries into the nature of compounds such as mercury oxide and framed in terms of the *relations* with known properties and the existing categories.

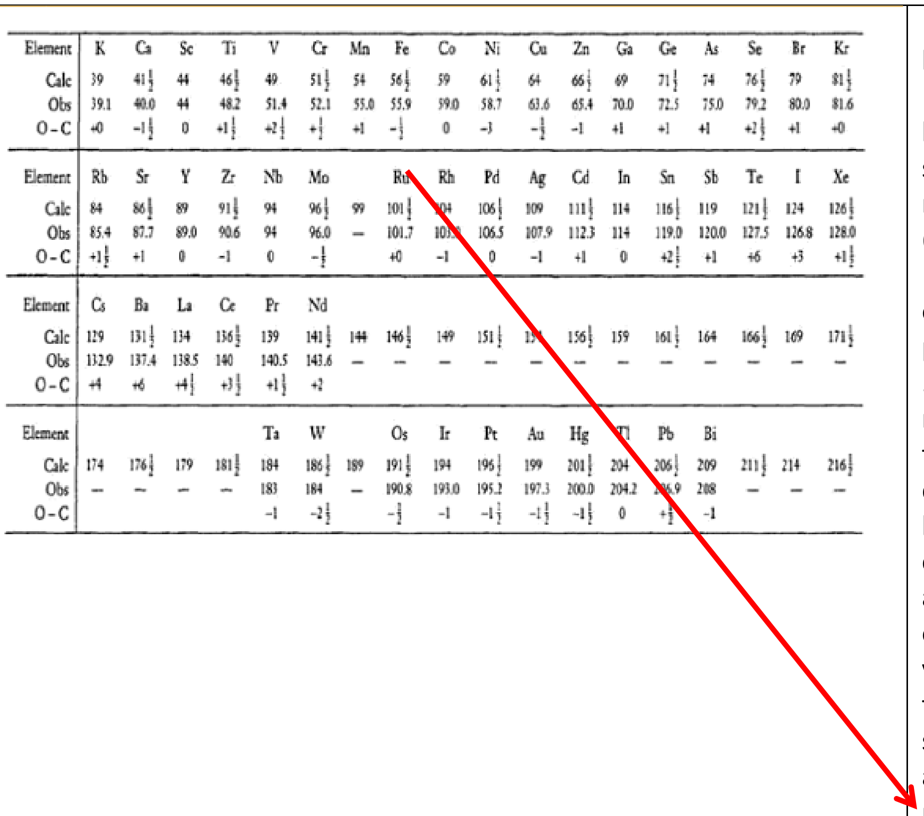
Having established a concept of *element*, Mendeleev uses this to reject the ancient notion of primary matter. Here too *relations* were important to his argument. Whilst Mendeleev's position as an atomist is disputed (see chapter two) he rejected Prout's hypothesis (1810) of atoms as an aggregation of primary matter (as hydrogen atoms). Having proposed the periodic relationship between an element's atomic weight and its physiochemical properties, Mendeleev (1904:227) states, 'no general relation is possible between things unless they have some individual character in them'. Earlier Mendeleev (1901a Vol I: 221) argued that, 'the conception of the individuality of the parts of matter exhibited in chemical elements is alone necessary and certain.' Returning to the Faraday Lecture, Mendeleev (1889:640) describes chemical atoms as being 'best described as chemical individuals' whilst noting that 'the Latin word 'individual' is merely a translation of the Greek word 'atom''. The theory of primary matter arose, he explains, to deal with an issue of relations. Early thinkers as well as those of the nineteenth century such as William Prout and his supporters took up the idea of a common formative material – primary matter – because, states Mendeleev (1889:645), 'they were not able to evolve the conception of any other possible unity in order to connect the multifarious *relations* of matter'(emphasis added). Whilst arguing that science has established a unity of forces and such unity exists in many areas of science, Mendeleev (1889:645) argues that in connecting with the many different types of relations of matter, 'we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere'. The chemical elements are examples of individuals where diversity exists.

3.3 Peirce's Reception of Mendeleev's Periodic Table

The interest Peirce had in Mendeleev's work and its value in underpinning philosophical work can be seen in his essay 'On the Logic of Drawing History from Ancient Documents' (1901). This essay is particularly illustrative of Peirce's reception of Mendeleev. Written in 1901 we can see how the mature Peirce draws on Mendeleev to illustrate some of the key elements of what he takes to be 'the method of science'. So this text is important in two ways: firstly because it tells us how the mature Peirce continues to work on chemistry, especially Mendeleev, and secondly because he sees also Mendeleev's work as an example of the logic of science at work, which lends more substance to his philosophical arguments.

Peirce sets out economic ways of hypothesis testing and is typically wide-ranging. One of its important themes is what he describes as, 'the reasonings of science' (EP2:106). Here Peirce includes induction as a way by which hypotheses are tested and abduction which he describes as, 'the first step of scientific reasoning, as induction is the concluding step' (EP2:106). Thus, by abductive reasoning a scientist seeks a hypothesis and then collects corroborative facts by reasoning inductively. The process of abduction, responsible as it is for all new truths, is also described by Peirce as 'nothing but guessing' (EP2:107). Whilst Peirce also extols the scientist to be, 'animated by that hope concerning the problem we have in hand' (EP2:107) two questions arise: how many guesses are to be made before the correct hypothesis is hit on and is there an efficient way of going about this process? A possible hypothesis must be capable of being tested experimentally as well as explaining the surprising facts that prompted the initial inquiry. Given the great intellectual and financial investment in hypotheses testing, and bearing in mind that the whole process has been initiated by the chance nature of abductive reasoning, Peirce, with his background as an experimental chemist, recognises the need for 'the consideration of economy' (EP2:107) when selecting a particular hypothesis, for the often protracted and costly process of experimental verification. He first identifies three factors upon which his notion of economy in this context is dependent: 'cost; the value of the thing proposed, in itself; and its effect upon other projects' (EP2:107). Thus inexpensive experimental procedures should be given precedence in gathering data which by inductive reasoning might put the hypothesis to the test. Secondly the scientific inquirer, by both instinct and reasoning, needs some measure of their expectations of their chosen hypothesis as being true, considering 'what will happen if the hypothesis breaks down' (EP2:109), for new hypotheses rarely turn out to be entirely satisfactory. But just before completing what Peirce describes as, 'all the elements of merit of an hypothesis' (EP2:111), he adds one more 'economic' consideration which he likens to the billiard player's 'good leave' where the situation on the table is left in a favourable position after a shot has been played. Transferring Peirce's analogy from the billiard room to the laboratory, a particular hypothesis might not accommodate all the known facts but be a useful 'leaving point' on the path of inquiry to something more complete. It is here that Peirce draws on Mendeleev's periodic table by way of example.

Peirce uses Mendeleev's periodic table to illustrate an economic method of hypothesis testing in seeking to, 'find some mathematical relation between the atomic weight and the succession of chemical elements according to Mendeleef's system' (EP2:110). In passing, Peirce (EP2:110) is of the opinion that although Mendeleev was successful in his predictions of gallium, germanium and scandium, the non-discovery of hecamagnesium leads him to the view that, 'the time has yet to come when it is worthwhile' to look for an exact mathematical relationship. By taking Mendeleev's table, which Peirce describes as, 'a first rough approximation to the truth' (EP2:111), and starting with potassium (atomic weight 39), he looks at the effect of increasing the atomic weight of each consecutive element by 2½ units. He then calculates the difference between the observed and calculated values, setting out his results in the table below (EP2:112):



Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Calc	39	41½	44	46½	49	51½	54	56½	59	61½	64	66½	69	71½	74	76½	79	81½
Obs	39.1	40.0	44	48.2	51.4	52.1	55.0	55.9	59.0	58.7	63.6	65.4	70.0	72.5	75.0	79.2	80.0	81.6
O−C	+0	−1½	0	+1½	+2½	+½	+1	−½	0	−3	−½	−1	+1	+1	+1	+2½	+1	+0
Element	Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Calc	84	86½	89	91½	94	96½	99	101½	104	106½	109	111½	114	116½	119	121½	124	126½
Obs	85.4	87.7	89.0	90.6	94	96.0	—	101.7	103.0	106.5	107.9	112.3	114	119.0	120.0	127.5	126.8	128.0
O−C	+1½	+1	0	−1	0	−½		+0	−1	0	−1	+1	0	+2½	+1	+6	+3	+1½
Element	Cs	Ba	La	Ce	Pr	Nd												
Calc	129	131½	134	136½	139	141½	144	146½	149	151½	154	156½	159	161½	164	166½	169	171½
Obs	132.9	137.4	138.5	140	140.5	143.6	—	—	—	—	—	—	—	—	—	—	—	—
O−C	+4	+6	+4½	+3½	+1½	+2												
Element					Ta	W		Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			
Calc	174	176½	179	181½	184	186½	189	191½	194	196½	199	201½	204	206½	209	211½	214	216½
Obs	—	—	—	—	183	184	—	190.8	193.0	195.2	197.3	200.0	204.2	206.9	208	—	—	—
O−C					−1	−2½		−½	−1	−1½	−1½	−1½	0	+½	−1			

In forming his table, Peirce has left sixteen spaces after neodymium (Nd) for Mendeleev's other predictions[40]. He also notes that the difference between the calculated and observed values start to become significant after ruthenium (Ru).

Figure 9: Peirce's attempt to find a mathematical relation between the atomic weight and the succession of chemical elements according to Mendeleev's system
Source: *The Essential Peirce, Volume 1*, page 112

Now what is Peirce up to here? Firstly he is making the point that such simple calculations are an economic way of hypothesis testing – in this case the existence of an exact mathematical relationship between an element's position in the periodic table and its atomic weight – there isn't one. As Peirce explains, whilst his table might be 'of little service to chemistry' he has provided, 'a tolerable illustration of the point of logic we have under consideration to compare the numbers required by this hypothesis with the numbers found' (EP2:111). Secondly the data shows some agreement with the suggestion of there being some truth in Mendeleev's system – a good 'leaving position' in search of a more exact hypothesis. But Peirce – the chemist - doesn't leave it here and further exploits his data for additional meaning. Relatively large differences between his calculated and the observed values for atomic weights might imply a contaminated sample. Inquiry is

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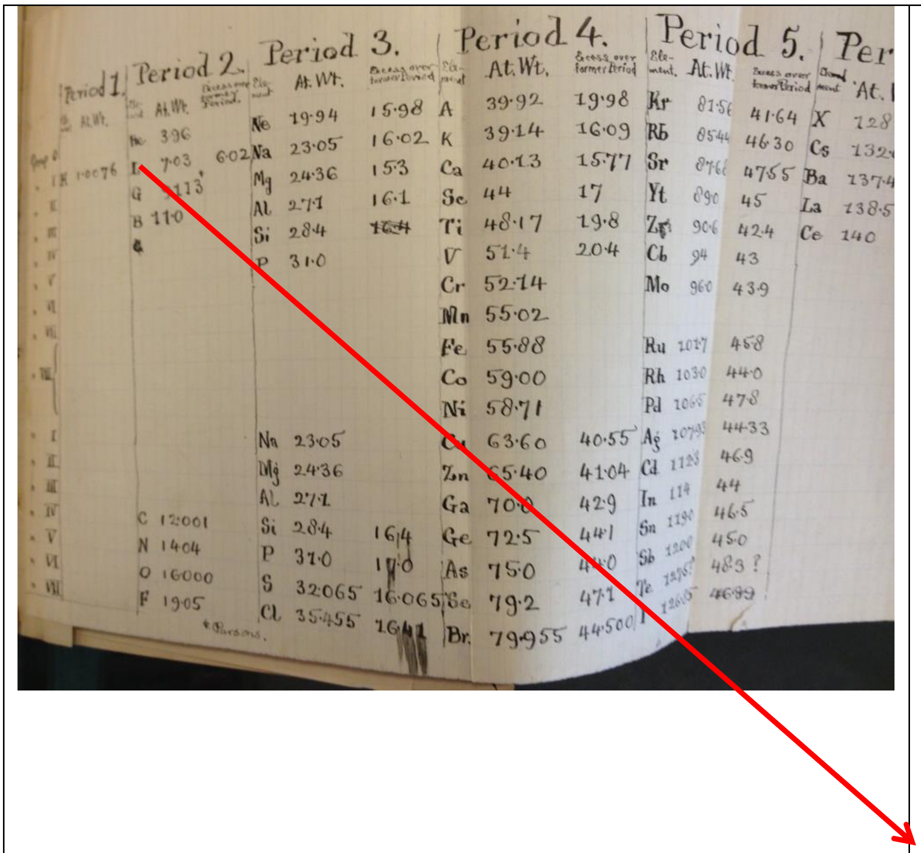
[40] It has now been shown that there are twelve elements not sixteen – which include the eleven elements of the lanthanide series

prompted by such surprising results and Peirce notes that these differences are particularly significant – surprisingly high - at a value of six for both tellurium and barium. It is these two elements, Peirce advises, that we should look to as ‘admixtures of substances of higher atomic weight’ (EP2:111). Inquiries had proved, in Peirce’s view, inconclusive for tellurium but there was perhaps some evidence for barium being contaminated as he described. This foray into the periodic table was mainly to illustrate an aspect of economy in hypothesis selection and Peirce draws this to a close with the comment that Mendeleev’s arrangement ‘is itself in considerable doubt’ (EP2:111). Notice too how Peirce when dealing with a largely philosophical issue takes time to speculate on matters of chemistry.

Peirce’s continuing interest in the periodic table shown by his search for an exact relationship between the atomic weights of the elements as arranged by Mendeleev is shown in one of his unpublished manuscripts *A Treatise on Discovery* (MS 693). This MS includes the noble gas radon which, discovered in 1900, dates the MS to be of this date or later. Here Peirce explores the relations existing between the atomic weights of successive elements within the periodic table. These numerical relationships resonate with those used in his essay ‘On the Logic of Drawing History from Ancient Documents’ (1901). They also match similar calculations carried out by Mendeleev – and discussed later.



Group	Period 1. El.	At. Wt.	Period 2. Ele-ment	At. Wt.	Excess over former Period.	Period 3. Ele-ment	At. Wt.	Excess over former Period	Period 4. Ele-ment	At. Wt.	Excess over former Period	Period 5. Ele-ment.	At. Wt.	Excess over former Period	Per Ele-ment	At.
Group 0			He	3·96		Ne	19·94	15·98	A	39·92	19·98	Kr	81·56	41·64	X	128
I	H	1·0076	Li	7·03	6·02	Na	23·05	16·02	K	39·14	16·09	Rb	85·44	46·30	Cs	132
II			G	9·113*		Mg	24·36	15·3	Ca	40·13	15·77	Sr	87·66	47·55	Ba	137·4
III			B	11·0		Al	27·1	16·1	Sc	44	17	Yt	89·0	45	La	138·5
IV			~~C~~			Si	28·4	~~16·4~~	Ti	48·17	19·8	Zr	90·6	42·4	Ce	140
V						P	31·0		V	51·4	20·4	Cb	94	43		
VI									Cr	52·14		Mo	96·0	43·9		
VII									Mn	55·02						
VIII									Fe	55·88		Ru	101·7	45·8		
									Co	59·00		Rh	103·0	44·0		
									Ni	58·71		Pd	106·5	47·8		
I						Na	23·05		Cu	63·60	40·55	Ag	107·93	44·33		
II						Mg	24·36		Zn	65·40	41·04	Cd	112·3	46·9		
III						Al	27·1		Ga	70·0	42·9	In	114	44		
IV			C	12·001		Si	28·4	16·4	Ge	72·5	44·1	Sn	119·0	46·5		
V			N	14·04		P	31·0	17·0	As	75·0	44·0	Sb	120·0	45·0		
VI			O	16·000		S	32·065	16·065	Se	79·2	47·1	Te	127·5?	48·3 ?		
VII			F	19·05		Cl	35·455	16·41	Br	79·955	44·500	I	126·85	46·99		

*Parsons.

Peirce takes Mendeleev's system of groups arranged horizontally and periods set out vertically. He then looks for a numerical relationship in the differences of atomic weight between adjacent elements in the same period. For example in group 1:-

Li(7.03) and Na(23.05)

Difference = 16.02

Na(23.05) and K(39.14)

Difference = 16.09.

K(39.14) and Rb(85.44)

Difference = 46.3

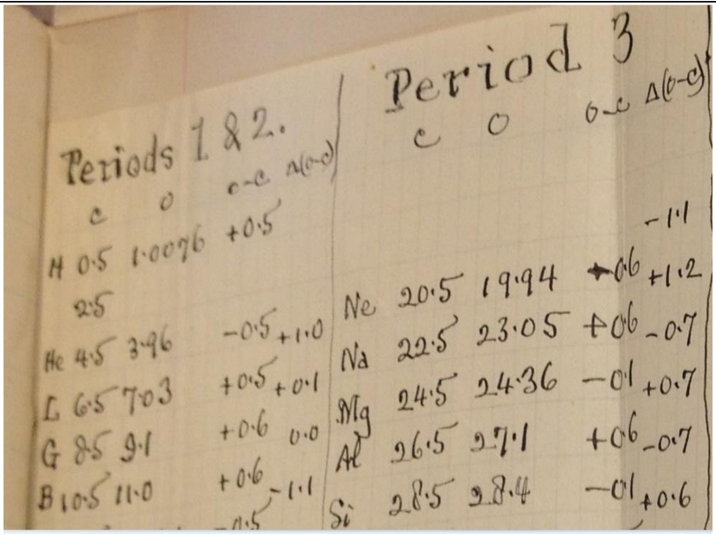
Figure 10: Peirce's investigation into the atomic weights of the elements when arranged by periods
Source: Peirce's *A Treatise on Discovery* (MS 693:436 c1900)

Here we see Peirce examining the relation between each element's position in the periodic table and successive differences in atomic weight. Whilst there are general increases across a period and within a group of elements, there is no exact numerical pattern. In performing these many calculations, it is tempting to cast Peirce, the master of mathematical logic, as being frustrated by this lack of numerical exactness. In this same manuscript, Peirce praises Mendeleev's work as 'one of the most admirable generalisations that the whole history of science can boast' (MS 693:432, c1900). What are Peirce's motives here? As a chemist he might be expected to be interested in Mendeleev's arrangement, being the most successful attempt then known at a systemisation of the chemical elements. As can be seen from the earlier quotation, Peirce appreciates Mendeleev's contribution to chemistry. But more than this, we will see that Peirce, with an understanding of how Mendeleev's scheme is founded upon the relations between the chemical elements, later uses this as an analogy for the relational aspects of his phenomenology. On examining the functional relations between the chemical elements of the periodic table, Peirce concludes, 'the evidence seems to be that such functions are not of an exact mathematical nature. Indeed, wherever we look, we meet with the appearance of an *imperfect regularity'* (MS 693:435, c1900, emphasis in the original).

Following this Peirce investigates the effect of imposing an arithmetic progression on to successive atomic weights and using a method similar to that in 'On the Logic of Drawing History from Ancient Documents' (1901):

> But in order to show the *relations* between the numbers of the same sort, in their sequence in the periods, I give another table, which compares the succession of atomic weights with that of an arithmetical series of constant difference 2½ , except below the number corresponding to Argon, where the difference is 2. I have differenced the column of *plus* or *minus* excesses of the atomic weight over the successive numbers of these two arithmetical series; because the regularly alternating values of these differences in some place and their constancy in others, brings out in another way the imperfections… (MS 693:440, c1900, emphasis in the original)

The effect of Peirce’s experimenting on the data is shown below,



Periods 1 & 2.

	c	o	o-c	Δ(o-c)
H	0·5	1·0076	+0·5	
	2·5			
He	4·5	3·96	−0·5	+1·0
L	6·5	7·03	+0·5	+0·1
G	8·5	9·1	+0·6	0·0
B	10·5	11·0	+0·6	−1·1
			−0·5	

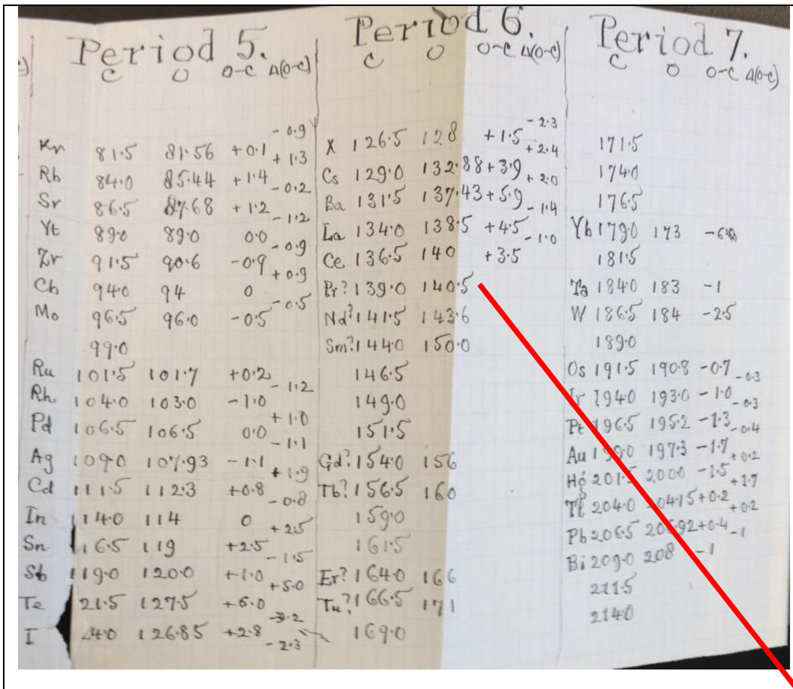
Period 3

	c	o	o-c	Δ(o-c)
				−1·1
Ne	20·5	19·94	+0·6	+1·2
Na	22·5	23·05	+0·6	−0·7
Mg	24·5	24·36	−0·1	+0·7
Al	26·5	27·1	+0·6	−0·7
Si	28·5	28·4	−0·1	+0·6

Here Peirce shows the experimentally determined or observed values for the atomic weights of a number of elements preceding argon, recorded as O. He also assigns his calculated atomic weight (as C) to hydrogen, the lightest element, at 0.5. The second element helium is given a calculated value of 4.5. The calculated values for subsequent elements are assigned by adding 2 to the element before. The differences between the calculated and observed values are shown under (O-C). Differences between successive values of (O-C) are shown under Δ(O-C).

Figure 11: Peirce’s calculations on the difference between an element’s experimentally determined atomic weight and one based regular incremental changes from H = 0.5
Source: Peirce’s *A Treatise on Discovery* (MS 693:442, c1900)

It is also interesting to note that ‘the chemist’ Peirce was troubled by the thorny issue of the correct positioning of the rare earth elements which, as we shall see, was also a concern for Mendeleev. Over thirty years since graduating, Peirce continues to retain an investigative interest in chemistry:



Period 5.

	c	o	o-c	Δ(o-c)
Kr	81·5	81·56	+0·1	-0·9 +1·3
Rb	84·0	85·44	+1·4	-0·2
Sr	86·5	87·68	+1·2	-1·2
Yt	89·0	89·0	0·0	-0·9
Zr	91·5	90·6	-0·9	+0·9
Cb	94·0	94	0	-0·5
Mo	96·5	96·0	-0·5	
	99·0			
Ru	101·5	101·7	+0·2	-1·2
Rh	104·0	103·0	-1·0	+1·0
Pd	106·5	106·5	0·0	-1·1
Ag	109·0	107·93	-1·1	+1·9
Cd	111·5	112·3	+0·8	-0·8
In	114·0	114	0	+2·5
Sn	116·5	119	+2·5	-1·5
Sb	119·0	120·0	+1·0	+5·0
Te	121·5	127·5	+6·0	-3·2
I	124·0	126·85	+2·8	-2·3

Period 6.

	c	o	o-c	Δ(o-c)
X	126·5	128	+1·5	-2·3 +2·4
Cs	129·0	132·88	+3·9	+2·0
Ba	131·5	137·43	+5·9	-1·4
La	134·0	138·5	+4·5	-1·0
Ce	136·5	140	+3·5	
Pr?	139·0	140·5		
Nd?	141·5	143·6		
Sm?	144·0	150·0		
	146·5			
	149·0			
	151·5			
Gd?	154·0	156		
Tb?	156·5	160		
	159·0			
	161·5			
Er?	164·0	166		
Tu?	166·5	171		
	169·0			

Period 7.

	c	o	o-c	Δ(o-c)
	171·5			
	174·0			
	176·5			
Yb	179·0	173	-6·0	
	181·5			
Ta	184·0	183	-1	
W	186·5	184	-2·5	
	189·0			
Os	191·5	190·8	-0·7	-0·3
Ir	194·0	193·0	-1·0	-0·3
Pt	196·5	195·2	-1·3	-0·4
Au	1[illegible]0	197·3	-1·7	+0·2
Hg	201[illegible]	200·0	-1·5	+1·7
Tl	204·0	[illegible]04·15	+0·2	+0·2
Pb	206·5	20[illegible]92	+0·4	-1
Bi	209·0	208	-1	
	211·5			
	214·0			

Peirce states, 'it hardly seems as if these elements [rare earth elements] and others could find places in the table. It would be rash, in the existing ignorance of the physical properties of these bodies, to attempt to place them in the table' (MS 693:438).

Note too how Peirce shows question marks against the rare earths Pr, Nd, Sm, Er and Tm. (omitted from some forms of Mendeleev's own table)

Figure 12:The rare earth elements
Source: Peirce's *A Treatise on Discovery* (MS 693:438, c1900)

Interestingly Mendeleev, in his paper 'The Periodic Law of the Chemical Elements' (1880) and published in *The Chemical News*, also performed calculations similar to Peirce. In common with Peirce, Mendeleev cites *relations* but has rather more to say on there being no exact mathematical sequencing. In calculating atomic weight differences in a manner similar to Peirce, Mendeleev (1880:301) notes the following differences: 'Na-Li=16, as also K-Na=16 but Mg-Be=14.6; on the other hand Ti—Si=20, V-P=20, Pt-Pd=91, Au-Ag=89, Hg-Cd=88, Pb-Sn=89, Bi-Sb=86'. In coming to a view on these differences in values Mendeleev evokes *relations* when he writes, 'it is difficult to admit that the gradual diminution of the differences is only a matter of chance. We ought rather to see that the *relations* between Pt and Pd is not altogether the same as that between Bi and Sb and therefore the differences cannot be the same'.

Modern theory holds that the elements are ordered in atomic number sequence – in order of increasing numbers of nuclear protons. The ordering of the elements was tracked by Mendeleev indirectly, through changes in atomic weight, where an element's value is often dependent upon the distribution of a number of different isotopes. Both Peirce and Mendeleev were not tracking the property that we now accept as governing the ordering of the periodic table. It is left to Mendeleev to speculate on why these *relations* between the elements' atomic weights are not predictable with any exactness. Whilst the elements possess properties that show a periodic relation to their atomic weights, Mendeleev (1880:301) writes,

> We do not really know anything of the just mentioned relation, except the periodic property; and even this one is not properly understood. It is therefore impossible to determine exactly the amount of the separations, any more than we can correct positively the magnitude of atomic weights. We can only determine limits, certainly very near together, between which the amount of the atomic weight of an element should be.

Earlier, in 1871, and working within the limitations he describes above, Mendeleev published a list of predictions as follows[41], which are described by Scerri (2007:132) as being accurate to 'an astonishing degree'.

Element	**Atomic Weight (Predicted)**	**Atomic Weight (Measured)**	**Year of Discovery**
Gallium (eka-aluminium)	68	69.2	1875
Scandium (eka-boron)	44	44	1879
Germanium (eka-silicon)	72	72.32	1886

Whilst Mendeleev seems content working on the approximate relations – within certain 'limits' - between neighbouring elements and their atomic weights, Peirce searches for a more exact relation. As we have seen Peirce is puzzled by Mendeleev's arrangement for its lack of mathematical exactness; his response is to perform his own calculations. Peirce's

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[41] From Scerri (2007:132-139)

approach here resonates with some central ideas of his mature philosophy, so that in one sense his own work with chemistry is at once indicative of his interest in the subject and a way of testing his core philosophical ideas. A couple of years before completing MS 693 (c 1900), Peirce published *The First Rule of Logic,* the fourth in a series of lectures he delivered at Harvard in 1898, where he states, '[the] first, and in one sense [the] sole, rule of reason [is] that in order to learn you must desire to learn, and in so desiring not be satisfied with what you already incline to think . . .' (EP2:48, 1898). We see in MS 693 Peirce as a chemist practising his 'sole rule of reason' which Amy McLaughlin (2014:229) argues for as, 'reasoning [that] must be predicated on a desire to learn, i.e. a desire to find out something not known, which is a manifestation of one's dissatisfaction with the present state of one's beliefs'. Through engaging with Mendeleev's periodic table, Peirce had a 'desire to learn' the exact mathematical relations underlying Mendeleev's arrangement of the chemical elements; he was dissatisfied with the seeming absence of mathematical exactness. Earlier we saw how Peirce commented on the 'appearance of an imperfect regularity [of atomic weights]' and how 'perplexed' he was by this. Such 'dissatisfaction' was the motivation behind Peirce's 'desire to learn'. Peirce reworked Mendeleev's periodic table many times (e.g MSS 693& 1039) provoked in part by doubts raised by the seeming lack of mathematical exactness to Mendeleev's scheme. In his essay 'The Fixation of Belief' (1877) Peirce famously states: 'The irritation of doubt causes a struggle to attain a state of belief. I shall term this struggle *inquiry…*' (EP1:114, emphasis in the original). Thus for Peirce, claims McLaughlin (2011:356), '[d]oubt is the promoter of inquiry and only occurs with the presentation of some surprising stimulus' – in this case the periodic table's lack of mathematical exactness.

According to Peirce, inquiry ends on the removal of doubt, the 'sole object of inquiry being the settlement of opinion' (EP1:115). I have found no evidence to suggest that Peirce's doubts were assuaged. In comparing Mendeleev's periodic law as well as Grimm's law[42] with the mathematical exact formulation of Newton's laws, Peirce lays emphasis on their lack of precision when he states that these 'are not laws in the sense in which the association of ideas and the three laws of motion are laws. They are not satisfactory for a minute. They are nothing that can blend with our metaphysics; they are not of a universal kind; and they are not precise' (CP 7.84 c1896). Also in *The Fixation of Belief* Peirce analyses four possible methods of inquiry in order to argue for one as the most suitable for settling

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[42] According to Emonds (1977:108) 'Grimm's Law expresses the principal sound changes in the Indo-European (IE) stop consonant system that differentiated Germanic from other branches of the IE language family'.

opinion; a consideration of these methods sits outside the scope of this thesis but can be found in McLaughlin (2011) and Misak (1991).

What this section has tried to demonstrate is that Peirce's interest in the *relations* between the chemical elements and their atomic weights was one he shared with Mendeleev. The study of chemistry continued from Peirce's graduate studies of chemistry and the publication of 'The Pairing of the Elements' (1863) and into his later life. Also we have seen something of Mendeleev's work on the periodic table as an introduction to the later chapters of this project. At the time Peirce was writing on the periodic table he was also formulating his phenomenology. His essay on 'On the Logic of Drawing History from Ancient Documents' is dated 1901 and his MS 693 described above is also likely to be from the early 1900s. As we have seen earlier Peirce's phenomenology dates from 1902, which he later renamed phaneroscopy. In describing the scale of the task of the phenomenologist Peirce writes,

> The work of discovery of the phenomenologist, and most difficult work it is, consists in disentangling, or drawing out, from human thought, certain threads that run through it, and in showing what marks each has that distinguishes it from every other. (NEM: 196, 1904)

As stated earlier, the literature has accounts of the origins of Peirce's phenomenology, the methodology of a Peircean phenomenologist – or phaneroscopist, and the relationship of phenomenology to Peirce's three metaphysical categories of Firstness, Secondness and Thirdness. There is very little on how Peirce uses his knowledge and understanding of valency and of Mendeleev's periodic table to explicate the 'difficult work' of 'disentanglement' of human thoughts that is the work of the phenomenologist. I believe that recognising and understanding the connections with chemistry offers an additional insight into Peirce's phenomenology.

3.4 Phaneroscopy and the Periodic Table

Having earlier set out some of the principles of Peirce's phaneroscopy I will now show how he uses his knowledge and understanding of Mendeleev's periodic table to illustrate his thinking. The connection with chemistry is made by Peirce who had considered using the term 'phanerochemistry' as well as 'phanerology' and 'phenoscopy' as alternative neologisms for phenomenology. These terms, states Stjernfelt (2007:143) were used 'from around 1905', nevertheless, as Stjernfelt explains, Peirce returns to phaneroscopy in the

Adirondack lectures of 1905 as well as for ''Phaneroscopy (phan)', intended for the *Monist*, January 1907'. Before exploring the connections to chemistry it is worth restating a couple of Peirce's statements on phaneroscopy made earlier:

> Phaneroscopy is the description of the phaneron; and by the phaneron I mean the collective total of all that is in any way or in any sense present to the mind, quite regardless of whether it corresponds to any real thing or not. (CP 1.284, 1905)

The method of surveying the phaneron is, as we have noted, 'simply to open our mental eyes and look well at the phenomenon and say what are the characteristics that are never wanting in it' (EP2:147, 1903). The skills needed are, states Peirce, firstly 'seeing what stares one in the face, secondly the skill 'of the artist who sees for example the apparent colours of nature as they appear and thirdly 'the generalizing power of the mathematician' (EP2:147/8, 1903). The job of the phaneroscopist is to note appearances but to come to no conclusions and to make no assessments, the purpose of observing the phaneron being 'to discover what different forms of indecomposable elements it contains' (EP2:362, 1906). This emphasis on 'forms' is also made a year earlier when Peirce states that, '[s]o far as I have developed this science of phaneroscopy, it is occupied with the formal elements of the phaneron' (CP 1.284, 1905). The use of 'form' and 'formal' is an appeal to Aristotle, by whom, Peirce claims, '[t]he distinction of matter and form was first made' (CP 6.354, 1902). Aristotle introduces 'matter', claims Thomas Ainsworth (2016), 'to account for changes in the natural world' and appeals to 'form' as 'what unifies some matter into a single object'.

In the coming section I will consider 'The Basis of Pragmaticism in Phaneroscopy' (1905), where Peirce privileges considerations of 'form' above those of 'matter': 'because it is universally admitted, in all sorts of inquiries, that the most important divisions are divisions according to form, and not according to qualities of matter' (EP2:362, 1905). It is not until 1907 that Peirce takes up possible material differences in the 'indecomposable' elements of the phaneron. In describing distinctions according to form, Peirce anticipates his reader's puzzlement in how, 'distinction of form is possible among indecomposable elements' (EP2:362). To explain this important point Peirce draws on the analogous concept of valencies from chemistry – a concept that had been used to great effect in the 1860s in developing a successful theory of the structural relations within organic chemistry. Around the time Peirce is formulating his phenomenology he also writes on the chemical concept of valency. In MS 1041 (c1905) Peirce states that valency in the chemical sense 'was brought to human cognisance by the genius of Sir Edward Frankland'. I will show how Peirce uses the chemical concept of valency to elucidate phaneroscopy. Before this it is worth first looking at the development of valency within the confines of chemistry. This is important because it shows how chemists use diagrams to develop the concept of valency. With his training in chemistry, Peirce uses a similar diagrammatic approach to account for aspects of his phenomenology.

3.5 Nineteenth century chemical valency and graphical formulae

Writing in 1852 on what was then the novel chemistry of organometallic compounds, Edward Frankland (1852:440), observing the sequence of formulae NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3 and $AsCl_3$, as well as NO_5, NH_4O, NH_4I, PO_5 and PH_4I, writes,

> Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining-power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms.

Frankland's 'combining power' as well as the term 'atomicity' were both used during the 1860s with the term valence coming into use towards the end of the decade. As the historian of science Alan Rocke (2010:48) explains, 'by the late 1850s this phenomenon had become known as 'atomicity', then by about 1870 as 'valence''. A detailed examination of the development of valency is beyond the scope of this chapter, for as Rocke (2010:48) states, 'these developments were complex' since 'not only did a host of protagonists participate in the story', many of the chemists involved 'did not always clearly understand, or in many cases were not even immediately aware of' the work of others working in the field at that same time.

Early nineteenth century chemists began to identify substances with identical empirical formulae[43] but surprisingly different properties. One such example is urea and ammonium cyanate, both with the empirical formula $C_2N_2H_4$. It was Berzelius who introduced the term isomer[44] to accommodate this and other examples, such as fulminic acid and cyanic acid (CNOH). It was however to Dalton's Atomic Theory, and to his visual representations in

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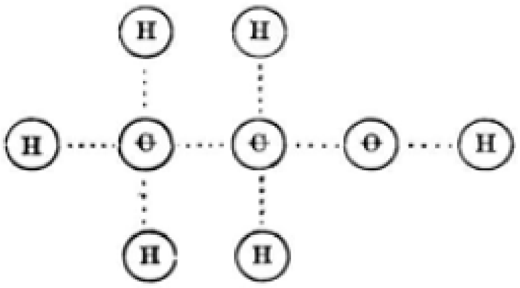
[43] The empirical formula is the simple whole number ratio of different elements present in a chemical compound

[44] Isomer (from the Greek *isos* meaning equal and *meros* meaning part) are chemical compounds with the same number of each type of atom but with different properties.

particular, that by the mid-1840s chemists such as Leopold Gmelin (1788 – 1853) and others, turned to inquire into isomerism by model building and diagrammatic representations – or graphical formulae. During the early 1860s the Scottish physician and chemist Alexander Crum Brown's (1838 – 1922) MD thesis *On the Theory of Chemical Combination*, represented the alcohol (today, ethanol C_2H_5OH) molecule using the following graphical formula,



The dotted lines connecting the various atoms are described by Crum Brown (1861:16) as 'lines of force'. There is no mention of the term *bond* although this representation is one of the earliest attempts to set out the connective relations between the individual atoms forming a compound. Other substances such as water and ammonia were similarly represented.

Figure 13:The graphical formula for alcohol (ethanol)
Source: Crum Brown's MD thesis (1861) *On the Theory of Chemical Combination*, page 16

In 1864 (the year after Peirce's graduation in chemistry) Crum Brown published a paper on isomeric compounds where the dotted lines were replaced by a single and continuous line with double bonds also being depicted. Take for example Crum Brown's (1864:233) representation of succinic acid ($C_4H_6O_4$) which he describes as a 'graphic notation' depicting the 'constitutional formula' or the 'graphic formula':

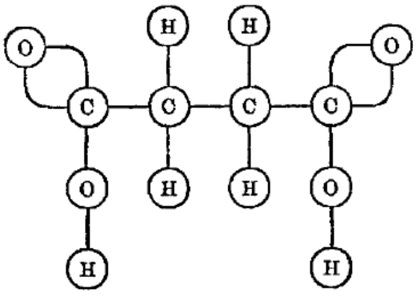
 succinic acid ($C_4H_6O_4$)	Notice the C to O double bond. The term ‘bond’ or ‘valency’ has yet to appear in the literature. The solid lines are described by Crum Brown (1864:241) as the ‘chemical force’ exerted by the individual atoms and the number of what, today, would be regarded as bonds, as the number of ‘equivalents’ of an atom.

Figure 14: The graphical formula for succinic acid
Source: Crum Brown’s (1864) *On the Theory of Isomeric Compounds*, page 241

These graphic formulae are not offered as realistic depictions and should not, explains Crum Brown (1864:232), ‘be mistaken for a representation of the physical position of the atom[s]’ shown.

In 1866 the English chemist Edward Frankland (1825 – 1899) published *Lecture Notes for Chemical Students: Embracing Mineral and Organic Chemistry* which Christopher Ritter (2001:41) argues ‘more than any other early venue in which they appeared…helped install Crum Brown's formulas in chemical practice’. In his introduction Frankland (1866:v) states, ‘I have extensively adopted the graphic notation of Crum Brown, which appears to me to possess several important advantages over that first proposed by [August] Kekulé’.

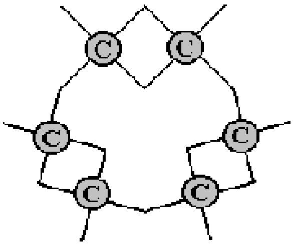
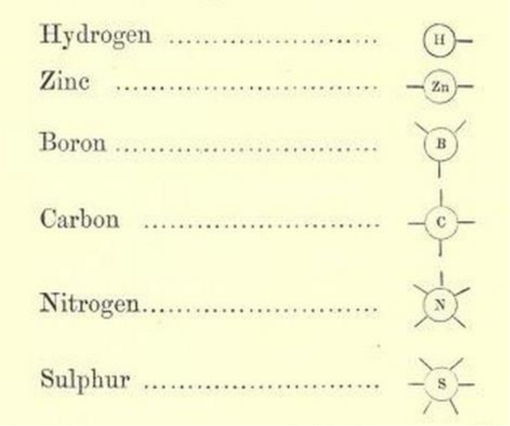
	In 1865 August Kekulé (1865:108) published his ‘sausage formulae’ for benzene in the *Bulletin de la Société Chimique de France.* In the terminology of the time Kekulé suggested that benzene contained a six carbon nucleus (black dots) arranged as a closed chain with alternating single and double bonds, shown by the short vertical black lines. The arrows represent the valences left over at the ends of the chain. Connecting these ‘left over’ bonds closes the chain. There is no attempt to depict the special distributions of the atoms concerned.
 Benzene C_6H_6	This is Kekulé’s representation of the benzene molecule, published in *Lehrbuch der organischen Chemie* in 1866 and the year Frankland used Crum Brown’s graphic formulas in his *Lecture Notes for Chemical Students.* Notice that whilst the alternating single and double bonds between the carbon atoms are shown all six hydrogen atoms are omitted.

Figure 15: Kekulé’s representations of the benzene molecules

In particular Frankland (1866:v) notes that Crum Brown’s graphic formulae ‘affords [a] most valuable aid to the teacher in rendering intelligible the constitution of chemical compounds’

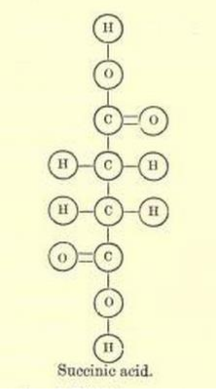


By using these diagrams Frankland (1866:18) states that the elements may be ‘graphically represented showing ‘point[s] of attachment or bonds’ whereby atoms might combine together. Note the emphasis Frankland gives to the term bond which enters the literature in place of Crum Brown’s ‘lines of [chemical] force’. Nevertheless Frankland (1866:25) cautions on the use of the term, stating these are ‘but crude symbols of bonds of union’ in that ‘no such material connections’ exist between the atoms preferring to regard ‘their nature much more like those [forces] which connect the members of our solar system’.

Figure 16: Frankland’s graphical representations of atoms showing bonds,
Source: Frankland’s (1866) *Lecture Notes for Chemical Students: Embracing Mineral and Organic Chemistry*, page 18

The structures Frankland (1866:24) depicts are described as graphic notations, which he explains are a ‘method of symbolic notation’ and one ‘founded almost entirely on the doctrine of atomicity, and consist in representing graphically, the mode in which every bond in a chemical compound is disposed of’. So here we see representations of chemical objects being described in terms of a form of graph. The term valence has yet to enter the literature with Frankland (1866:19) describing the ‘combining power of the elementary atoms’ as ‘their atomicity or atom-fixing power’. Using the diagram above, the atomicity of hydrogen would be one and carbon would be four.

By using this form of notation Frankland (1866:346) represents the graphical formula for succinic acid ($C_4H_6O_4$) as shown,



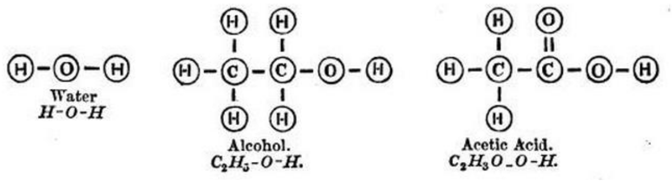
Note the similarity to Crum Brown’s representation shown earlier. The molecule is drawn in a slightly different orientation but the bonding between the individual atoms is clear to see.

The guiding principle in drawing graphic formulae is explained by Frankland (1886:18) as, ‘no element, either alone or in combination, can exist with any of its bonds disconnected’. The atoms must be arranged so that the bonds of each element are fully deployed in connecting to the other atoms within the molecule.

Figure 17: Frankland’s graphic formula for succinic acid.
Source: Frankland’s (1866) *Lecture Notes for Chemical Students: Embracing Mineral and Organic Chemistry,* page 346

Repeating Crum Brown's earlier caution against excessive realism, Mary Jo Nye (1993:69) records Frankland as opposing a realist view of the atoms shown in the graphical formulae when he states 'I neither believe in atoms themselves, nor do I believe in the existence of centres of forces, so that I do not think I can be fairly charged with this very crude notion'.

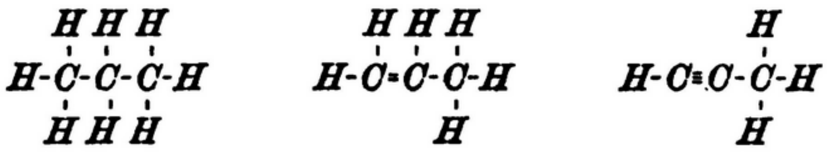
Graphical formulae also travelled to America and were available to chemists such as Peirce and to his Harvard tutor Josiah Cooke. Take for example this example from Cooke's *The First Principles of Chemical Philosophy* (1868)



This system of graphic formulae Cooke (1868:75) describes as being 'frequently used in works of modern chemistry'. The conventions applied here are exactly the same as for the examples seen from Crum Brown and Frankland.

Figure 18: Cooke's graphical formulae for water, alcohol and acetic acid
Source: Cooke's (1868) *The First Principles of Chemical Philosophy,* page 75

By 1885 Cooke's text shows the following modification to the way graphic formulae are being reproduced,



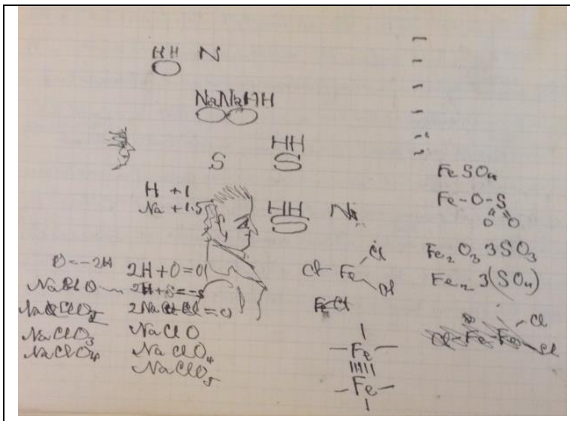
Notice now that the circles depicting the atoms have disappeared. Each element is represented by its symbol. The types of bonds connecting the elements remain clearly visible.

Figure 19: Cooke's graphical formulae for the hydrocarbons propane, propene and propine
Source: Cooke's (1868) *The First Principles of Chemical Philosophy*, page 56

During the early 1900s, the period when Peirce was formulating his phaneroscopy, he was also writing on chemical valency. For example, the following comes from MS 1038 (c1900) and reads a little like a text book. Peirce defines such terms as substance, an elementary substance, chemical compound, atomic weight and valency as shown below,

> The number of atoms of hydrogen to which an atom is thus equivalent is termed its “valency”. The valency of hydrogen is 1. Some chemists consider the valency of an element to be fixed; but the more general opinion is that it is variable. An atom of valency 1 is called a “monad”, of valency 2 a “dyad”, etc. up to “octad”. In graphs or diagrams showing the constitution of compounds, the direct *relations* of combination between two atoms are represented by lines called “bonds”. Every monad has one bond; every dyad, 2, etc. (MS 1038:4, c1900, emphasis added)

In addition to discussing the term valency Peirce describes a chemical ‘graph’ as a ‘diagram’ showing the constitution of compounds. Notice, too, Peirce’s use of *relations* in describing how atoms ‘bond’ or combinine together. In the following extract from MS 1041 Peirce can be seen using graphical formulae to speculate on the likely arrangement of atoms within two compounds of iron – one trivalent ($FeCl_3$) and the other potentially octavalent – thereby supporting the point he made earlier on the general opinion of chemists that valency is ‘variable’. Before progressing further it is worth making a point about the concept of valency that will prove important to Peirce but up to now remained rather implicit. Valency captures the possibility of relations between atoms. Knowing for example the valency of chlorine to be one and phosphorous to be three or five gives the possibility of two chlorides as: PCl_3 and PCl_5. Later in the chapter I hope to show how the chemical concept of valency provided Peirce with a means of expressing the possibility of a relational framework necessary to thought - providing a structure for concepts.

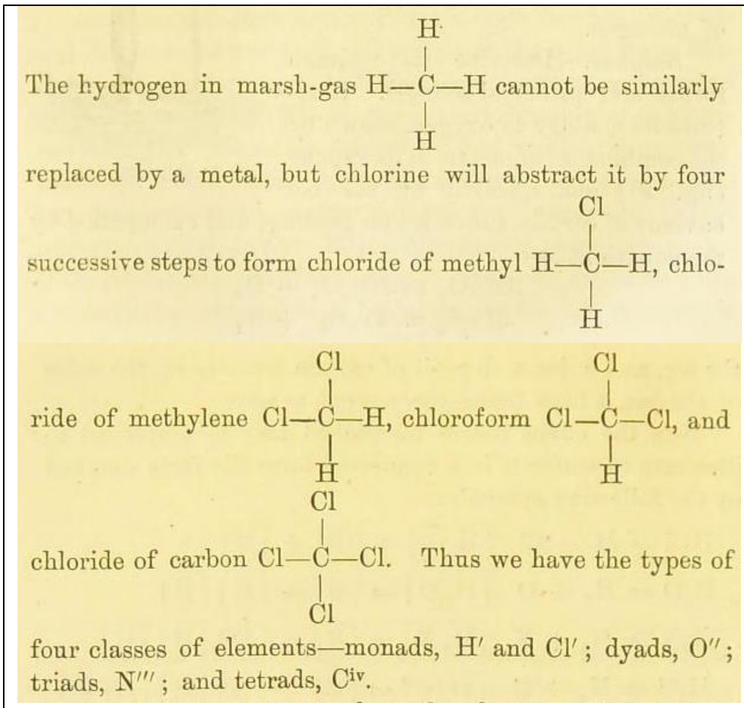


In this extract Peirce's doodle – a characteristic of his manuscripts – shows the graphical formulae of two compounds of iron. As a child Peirce describes himself as 'nourishing his mind with chemistry [and] devoured Frankland's memoirs with avidity'. (MSS 1041, c1905)

Peirce too is of 'the general opinion…that valency can be 'variable'' as he shows iron here to have valencies of both three and eight.

Figure 20: Peirce's sketches showing iron as being both trivalent and octavalent,
Source: Peirce's MS 1041, c1905

I will also show how Peirce uses chemical graphs and valency and to explaining away the seemingly contradictory position of the 'indecomposable elements' of the phaneron having differences of form. Later and in chapter four, when examining Peirce's theory of iconicity, we shall see how chemists use such diagrams to generate novel knowledge. A couple of years after writing these manuscripts Peirce writes, 'I do not think I ever reflect in words: I employ visual diagrams, firstly, because this way of thinking is my natural language of self-communion, and secondly, because I am convinced that it is the best system for the purpose' (MS 619: 8, 1909). This example, from Frankland's *How to Teach Chemistry'* (1875), is an example of where visual diagrams are used to encourage the reader to think and reason about the reaction between marsh gas (today, methane) and chlorine gas. The concept of valency provides Frankland with a visual and diagrammatic means of reasoning as well as expressing the possible bonding relations between the atoms involved.



The hydrogen in marsh-gas $\begin{array}{c}\mathrm{H}\\ \vert\\ \mathrm{H{-}C{-}H}\\ \vert\\ \mathrm{H}\end{array}$ cannot be similarly replaced by a metal, but chlorine will abstract it by four successive steps to form chloride of methyl $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{H{-}C{-}H}\\ \vert\\ \mathrm{H}\end{array}$, chloride of methylene $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{Cl{-}C{-}H}\\ \vert\\ \mathrm{H}\end{array}$, chloroform $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{Cl{-}C{-}Cl}\\ \vert\\ \mathrm{H}\end{array}$, and chloride of carbon $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{Cl{-}C{-}Cl}\\ \vert\\ \mathrm{Cl}\end{array}$. Thus we have the types of four classes of elements—monads, H' and Cl'; dyads, O''; triads, N'''; and tetrads, C^{iv}.

In describing the experiment Frankland (1875:54/5) states how when marsh gas and chlorine are ignited together in the absence of sunlight 'fumes of hydrochloric acid will rise into the air and a dense deposit of carbon remains on the sides of the jar, a little being thrown out as soot'. However, in encouraging his students to think about the course of the reaction where the hydrogen atoms are replaced successively by atoms of chlorine, Frankland (1875:56) states that, 'the replicability of hydrogen in [marsh gas] should be clearly enforced, and illustrated by [the] glyptic symbols' – that is to say the diagrammatic representations of the substances shown. Notice too Frankland's use of the valency terms monad', dyad, and triad as previously seen in Peirce.

Figure 21: Frankland's graphical formulae showing the course of reaction between marsh gas (methane) and chlorine
Source: Frankland's (1875) *How to Teach Chemistry*, page 56

It is perhaps not surprising to see Peirce so consumed with the writings of Frankland, a chemist who, like Peirce, valued diagrammatic representations and their capacity to reveal new knowledge to the reader. In chapter two I argued that Cooke's pedagogical method of employing diagrams fostered Peirce's own predilection for diagrammatic thinking. We see here another possible influence on Peirce in Frankland's own methods, a chemist who we saw earlier Peirce described as having nourished his mind as a child with chemistry. Here we see Peirce's curiosity in chemistry continuing into his later writings in terms of graphical formulae and the associated concept of valency. In *The Logic of Relatives* Peirce writes on the topic of valency whilst at the same time mentioning chemical graphs,

> But when chemists became convinced of the doctrine of valency, that is, that every element has a fixed number of loose ends, and when they consequently began to write graphs for compounds, it seems to have been assumed that this necessitated an abandonment of the position that atoms and radicles [sic] combine by opposition of characters, which had further been weakened by the refutation of some mistaken arguments in its favour. (CP 3.471, 1897)

Notice how Peirce laments the demise of the electrochemical-dualist theory of oppositely charged radicals that formed a part of his own undergraduate studies.

Evidence that the term valency crossed to America is given by Peirce's chemistry tutor, Josiah Cooke, who uses Hofmann's notion of *quantivalence.* As Cooke (1868:56) explains, taking 'the hydrogen atom as our standard of reference, the atoms of different elements are called *uni*valent, *bi*valent, *tri*valent, or *quadri*valent' depending upon whether they are '*equi*valent to one, two, three of four atoms of hydrogen (emphasis in the original). In an earlier series of lectures to the Royal College of Chemistry, Hofmann (1866:168) objects to the 'vague and rather barbarous expression, *atomicity'* because of its suggestion of the physical existence of atoms which he stresses, 'should be assiduously avoided. It is on this basis that Hofmann (1866:169) states his preference for 'escap[ing] this evil by substituting the expression *quantivalence* for *atomicity'* (emphasis in the original). Here we encounter again the objections discussed earlier that some nineteenth century chemists had to the notion of physical atomism. In time, explains Mary Jo Nye (1993:80), quantivalence was 'shortened to valence (*Valenz*) by Kekulé and by Hermann Wichelhaus'. In passing reference to his earlier work on organometallic compounds Frankland (1878:78) brings together the four terms relating to an element's ability to chemically combine in stating, 'the combining value of the elementary atoms, which was first discovered in compounds of certain metals with organic radicals, is termed their *atomicity, equivalence, valency,* or *atom-fixing power'.*

Valency features also in key passages of Mendeleev. In the first edition of his *Principles of Chemistry*, Mendeleev organised the first four chapters according to the valencies of the elements: hydrogen, oxygen, nitrogen and carbon with valencies of 1, 2, 3 and 4 respectively. The valency of an element defines the relations of combination it is able to establish with another element. Taking the elements from Mendeleev's first four chapters above,

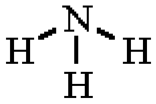
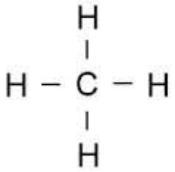
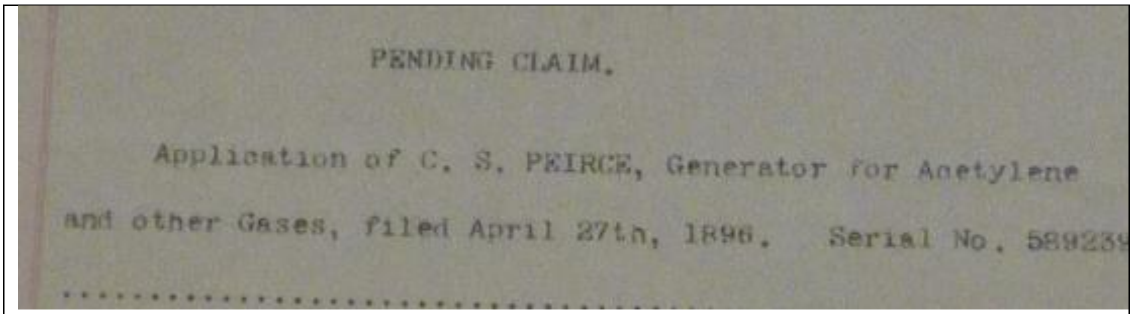
Element	**H**	**O**	**N**	**C**
Valency and number of single bonds	1	2	3	4
Structure of the hydride formed				
Name of hydride	Hydrogen	Water	Ammonia	Methane (marsh gas)

Figure 22: Diagrams illustrating the valencies of hydrogen, oxygen, nitrogen and carbon atoms

By way of explanation, oxygen with a valency of two fulfils its possibility of forming two single bonds by combining with two monovalent atoms of hydrogen to form water, as H_2O. Similar argument can be applied to the formation of the other hydrides shown in figure 22. Carbon dioxide (not shown) involves fulfilling the possibility of carbon forming four bonds and oxygen two as follows: O=C=O.

3.6 Peirce's use of valency to as a means of explaining his phenomenology

As we shall see Peirce made use of both chemical diagrams and of the chemical concept of valency in setting out his formulation of phenomenology and which he styled as phaneroscopy. In this section I will explore the question: what does valency do for Peirce's phaneroscopy? Before this I should like to demonstrate Peirce's facility in drawing out chemical structures which follow the rules of valency. Take for example this series of sketches from MS 1031 (c 1896) on the reactive and combustible gas acetylene, C_2H_2. In his biography of Peirce, Brent (1993:251) states that Peirce was at one time engaged in, ‘a sophisticated design to produce cheap domestic lighting from acetylene gas’ – something Peirce was to record a claim for:



PENDING CLAIM.

Application of C. S. PEIRCE, Generator for Acetylene and other Gases, filed April 27th, 1896. Serial No. 58923

....

Figure 23: A record of the claim Peirce made in 1896 for the design of a generator to generate acetylene and other gases
Source: Houghton Library, Harvard University, USA

This is an image taken from the ‘acetylene’ MS 1031 to which I have added a number of annotations. Note that there is also a doodle of a man’s head – such additions are common to Peirce’s manuscripts[45].

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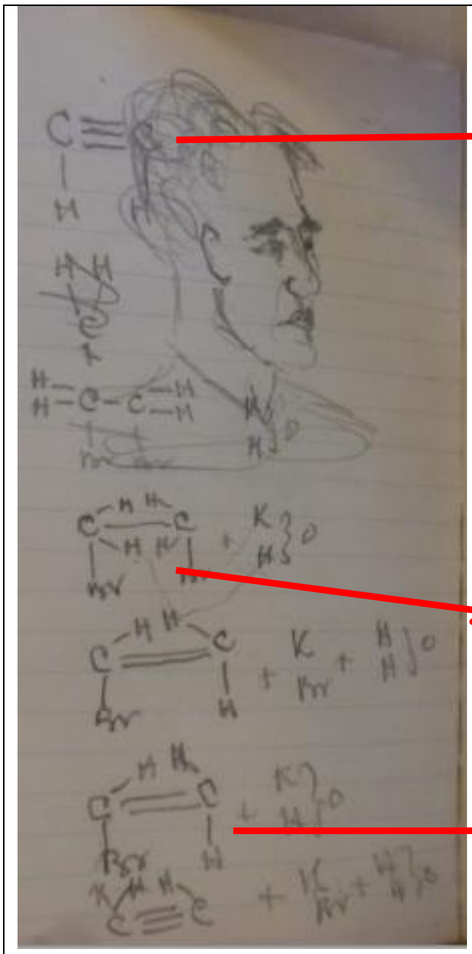
[45] It is worth recalling Peirce’s position on the atom when viewing his chemical diagrams. Writing in 1892 Peirce states that ‘we are logically bound to adopt the Boscovichian idea that an atom is simply a distribution of component potential energy throughout space (this distribution being absolutely rigid) combined with inertia’ (CP W8:167). And again in 1898, Peirce states ‘each object occupies a single point of space, so that matter must consist of Boscovichian atomicules’ (CP 6.82)



A possible schematic outline for the production of acetylene from (in today’s terms) dibromoethane.

Acetylene molecule showing the triple bond between the two carbon atoms and the two single carbon to hydrogen bonds. The diagram satisfies the valency of carbon being four and hydrogen one.

There now appears a two-step sequence of molecular diagrams which appear to suggest how (in today’s terms) dibromoethane might be converted to acetylene.

Step 1: Bromoethane which on eliminating a single HBr molecule yields bromoethene. Note there is a double bond between the two carbon atoms of bromoethene.

Step 2: Bromoethene yields acetylene on the elimination of a second HBr molecule. The presence of ‘K’ suggests the use of a potassium reagent to effect the reaction – possibly potassium hydroxide.

Figure 24: A schematic outline for the production of acetylene.
Source: Peirce’s MS 1031 (c 1896)

Whilst providing another example to Peirce’s continuing interest in chemistry these diagrams show how, as a chemist, Peirce understood the power of chemical diagrams to visualise the relations between the various atoms with a molecular structure - *relations* governed by the rules of chemical valency. In being able to visualise such relations Peirce was able to speculate on a possible synthetic route for acetylene – a gas with great commercial potential as a source of domestic lighting.

To return to the question posed earlier: what does valency do for phaneroscopy? The chemical elements in Peirce’s chemical diagrams relating to acetylene are characterised by their valencies. Carbon with a valency of four is – as Peirce’s sketches show - able to form molecules with carbon to carbon triple, double and single bonds. Bromine and hydrogen, each with a valency of one, is able to form only single bonds to carbon atoms. Peirce is able to propose a possible synthetic route to acetylene based on these particular valency relations between the chemical elements. Whilst each atom might be thought to be indestructible new substances can be postulated on the basis of a rearrangement of these bonding relations and governed by the rules of valency. I will attempt to show how Peirce transposes these chemical concepts to provide part of the conceptual framework for his phaneroscopy.

The conceptual elements of Peirce's phaneroscopy will be shown to be characterised by the number of connections or bonds they are able to form – their *valency*. These conceptual elements are incapable of being reduced to simpler forms – what Peirce describes as 'indecomposable'. Similarly elements such as carbon, hydrogen and bromine as depicted in Peirce's 'acetylene sequence', are non-decomposable and yet able to form bonds one with another, governed by their valencies. The chemical concept of valency might be viewed as the machinery or mechanism of the conceptual framework that connects the concepts of Peirce's phaneroscopy in order to bring it coherence and meaning.

Returning to the essay 'The Basis of Pragmaticism in Phaneroscopy' (1905), here Peirce suggests to his readers that, '[a] doubt may, however, arise whether any distinction of form is possible' when considering the 'indecomposable elements' of the phaneron (EP2:363). Peirce now falls back on his preferred mode of diagrammatic thinking within the context of chemistry to offer an explanation in terms of valencies. One of several compounds he chooses is marsh gas where four single valent – or monad - hydrogen atoms, are bonded to a single four-valent – or tetrad – carbon atom. Given what we have seen of Peirce's practice of sketching out the structures of chemical substances and his admiration for Frankland's formulation of valency it seems likely that he had the following diagrammatic representation of marsh gas in mind. Furthermore the editor's note to this paper explains that 'Peirce's "planar" representation of methane has been retained [in the text]' (EP2:542 n3). That is to say Peirce's original manuscript pictured a similar planar diagram for the methane (CH_4) molecule.

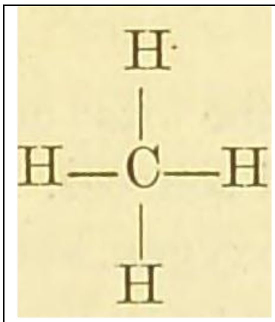
	In considering marsh gas Peirce (EP2:363) makes the point that atoms such as carbon are ‘quite indecomposable and homogeneous’ and differ from other atoms not ‘in *internal* form but in *external* form (emphasis in the original). The external form Peirce refers to here is the valency of the element concerned. Here carbon is tetradic with a valency of four. The elements of the phaneron are ‘indecomposable’ by analogy to the ‘internal form’ of the indivisible chemical elements. Nonetheless ‘distinctions of form’ exist in their ability to establish *relations* – analogous to the tetradic carbon atom’s capacity for forming four bonds with four monadic hydrogen atoms. In pursuing his explanation, Peirce (EP2:363) makes the point that boron ‘is a triad’ and able to bond with three hydrogen atoms to give BH_3.

Figure 25: Peirce’s explanation of distinctions of form within the indecomposable elements of the phaneron

Boron and carbon are both indivisible elements although their atoms demonstrate ‘distinctions of form’ in their ability to form relations with differing numbers of hydrogen atoms. Peirce makes a similar case for dyadic (bivalent) elements such as magnesium, and monovalent (monads) elements such as lithium. To complete the sequence of valencies from four to one Peirce (EP2:363) includes the noble gases helium, neon, argon, krypton and xenon which he describes as, ‘medads, not entering into atomic combination at all’.

In his invitation to his readers to ‘join me in a little survey of the Phaneron’ (EP2:362), Peirce is encouraging us, argues Gava (2011:239), to focus on the ‘formal relational structure[s] without which human thought would not be what it is’. I would argue that Peirce uses the chemical concept of valency as the machinery for phaneroscopy’s relational framework, to bring coherence and meaning to its conceptual framework. Gava (2011:239) argues that Peirce, ‘[b]y analysing thought and experience as they are manifest in human practices, phenomenology, or phaneroscopy, aims to abstract that structure of concepts that is necessary to account for those human practices.’ I would suggest that the chemical concept of valency aided Peirce in abstracting the formal relational structures at play in human thought. Peirce argues that if, ‘the Phaneron were to consist entirely of elements altogether uncombined mentally…[then]…we should have no idea of a Phaneron…[However]…if there is a Phaneron, the idea of combination is an indecomposable element of it' (EP2:364). As we have seen earlier, Peirce argues that the phaneron's indecomposable elements have differences in external form that are analogous to the valencies of the chemical elements. This analogy conveys the crucial importance of the 'idea of combination' to Peirce's phenomenology. Returning to Peirce's work on acetylene, we note that this molecule exists only because two atoms of carbon and two atoms of hydrogen were able to combine in a relation governed by their valencies. The molecule of acetylene is formed by atoms establishing a relation determined by differences in their external form.

Writing two years later and in 1907, Peirce again emphasises that 'distinctions and classifications founded upon form are, with very rare exceptions, more important to the scientific comprehension of the behaviour of things than distinctions and classifications founded upon matter' (CP 5.469). Here again Peirce draws on the concept of valency and Mendeleev's periodic table to illustrate this important point,

> Mendeléeff's classification of the chemical elements, with which all educated men are, by this time, familiar, affords neat illustrations of this, since the distinctions between what he calls "groups," that is to say, the different vertical columns of his table, consists in the elements of one such "group" entering into different forms of combination with hydrogen and with oxygen from those of another group; or as we usually say, their *valencies* differ; while the distinctions between what he calls the "series," that is, the different horizontal rows of the table, consist in the less formal, more material circumstance that their atoms have, the elements of one "series," greater masses than those of the other. Now everybody who has the least acquaintance with chemistry knows that, while elements in different horizontal rows but the same vertical column always exhibit certain marked physical differences, their chemical behaviours at corresponding temperatures are quite similar; and all the major distinctions of chemical behaviour between different elements are due to their belonging to different vertical columns of the table.
> (CP 5.469, 1907, emphasis in the original).

The point Peirce is making through his extended analogy with Mendeleev's scheme can be seen by referring to a copy of the periodic table[46] of that period (1905):

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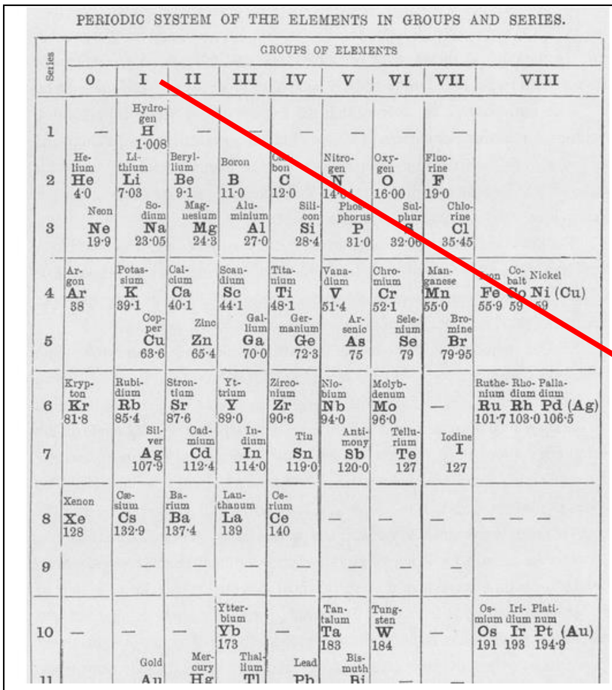
[46] Taken from Chapter 15 of Mendeleev's *Principles of Chemistry* 3rd Edition (1905) and reprinted in Jensen (2002:275)



PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES.

Series	0	I	II	III	IV	V	VI	VII	VIII
	GROUPS OF ELEMENTS								
1	—	Hydrogen H 1·008	—	—	—	—	—	—	
2	Helium He 4·0	Lithium Li 7·03	Beryllium Be 9·1	Boron B 11·0	Carbon C 12·0	Nitrogen N 14·04	Oxygen O 16·00	Fluorine F 19·0	
3	Neon Ne 19·9	Sodium Na 23·05	Magnesium Mg 24·3	Aluminium Al 27·0	Silicon Si 28·4	Phosphorus P 31·0	Sulphur S 32·06	Chlorine Cl 35·45	
4	Argon Ar 38	Potassium K 39·1	Calcium Ca 40·1	Scandium Sc 44·1	Titanium Ti 48·1	Vanadium V 51·4	Chromium Cr 52·1	Manganese Mn 55·0	Iron Cobalt Nickel Fe Co Ni (Cu) 55·9 59 59
5		Copper Cu 63·6	Zinc Zn 65·4	Gallium Ga 70·0	Germanium Ge 72·3	Arsenic As 75	Selenium Se 79	Bromine Br 79·95	
6	Krypton Kr 81·8	Rubidium Rb 85·4	Strontium Sr 87·6	Yttrium Y 89·0	Zirconium Zr 90·6	Niobium Nb 94·0	Molybdenum Mo 96·0	—	Ruthenium Rhodium Palladium Ru Rh Pd (Ag) 101·7 103·0 106·5
7		Silver Ag 107·9	Cadmium Cd 112·4	Indium In 114·0	Tin Sn 119·0	Antimony Sb 120·0	Tellurium Te 127	Iodine I 127	
8	Xenon Xe 128	Cæsium Cs 132·9	Barium Ba 137·4	Lanthanum La 139	Cerium Ce 140	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Ytterbium Yb 173	—	Tantalum Ta 183	Tungsten W 184	—	Osmium Iridium Platinum Os Ir Pt (Au) 191 193 194·9
11		Gold Au	Mercury Hg	Thallium Tl	Lead Pb	Bismuth Bi	—	—	

Peirce likens the more important behaviour based on 'form' to the valencies of the various groups – illustrated by the number of chlorine atoms an element is combined with, for example,

Group I: LiCl, NaCl,

Group II: $MgCl_2$, $CaCl_2$

Horizontal rows (periods or series) demonstrate the 'less formal, more material circumstances' shown by the atoms. For example, He, Li, Be, B, C…. and Ar, K, Ca, Sc, Ti…, being analogous to classifications based on matter.

Figure 26: Peirce's explanation of distinctions founded upon form compared to those founded on matter
Source: Jensen's (2002) *Mendeleev and the Periodic Law,* page 275

The elements of group I are all very reactive metals where the elements of group 0 are unreactive gasses. The vertical groups within Mendeleev's scheme capture the most significant relations between the elements and are likened by Peirce to differences in form. The horizontal rows are less significant in terms of the relations between the elements – likened to differences of matter. Both Peirce and Mendeleev constructed systems which were founded upon the *relations* between their constitutional elements. In setting out his phaneroscopy Peirce likens classifications based on form to the relations between Mendeleev's groups of elements where particular combinations are related to the valencies of the elements concerned. Classifications based on matter Peirce likens to the relations between elements with a particular row of Mendeleev's table.

3.7 Conclusion

The connection between Mendeleev and Peirce in this respect is perhaps captured by the artist Paul Klee (1920:7) in his opening to his essay 'Creative Confessions' with the statement, '[a]rt does not reproduce the visible; rather, it makes visible'. Both Mendeleev and Peirce were committed to making visible the relations existing between the compositional elements of the world. In Mendeleev's case these were the non-decomposable chemical elements of the material world; for Peirce the indecomposable elements of thought concerning everything that is real or imagined and which informed his phenomenology or phaneroscopy. From a nineteenth century perspective a material substance can be reduced only as far as its chemical elements of composition. From the perspective of Peirce's phaneroscopy our thoughts of things real and imagined can be condensed only as far as a set of irreducible conceptual elements. The works of these two philosopher-chemists – Mendeleev and Peirce - were not concerned with 'reproducing the visible' but with making clear the *relations* between the world's material elements and between its cognitive elements. In this respect they were both concerned with the process of 'making visible'.

In this chapter I have argued that Mendeleev and Peirce, with their respective focus on the world's material elements and its cognitive elements, are both dealing with the latent *relations* that lie behind observable phenomena. Furthermore I believe I have shown the importance of Peirce's continuing involvement with chemistry to the structure of the conceptual relations at play in phaneroscopy. The chemical concept of valency and Mendeleev's periodic table each has the capacity to depict relations diagrammatically. I would argue that Peirce puts this diagrammatic facility, within the context of chemistry, to work in an attempt to generate in the minds of his readers knowledge of the relations at work in his phenomenology. Diagrams pick out and enhance the intelligibility of those relations, whether between the conceptual elements of the phaneron or the chemical elements of some molecular structure such as acetylene. In one of the few references in the literature to chemistry and this aspect of Peirce's thought, André De Tienne (2004:12), asks his reader to 'mind the importance of the chemical analogy, as this explains why Peirce was for a while tempted to call his new science by the name of 'phanerochemy' for 'it was with the eyes of the trained chemist and mathematician that he [Peirce] wanted to observe the phaneron'. Why mathematicians and chemists? I would suggest that the mathematician brings to phaneroscopy what Peirce describes as a 'generalizing power' (EP2:147/8, 1903), recording observations as acritical descriptive propositions. The chemist is skilled in observing, recording and depicting relations in diagrammatic form.

Chapter Four

Dmitri Mendeleev’s inquiry into the chemical elements and Peirce’s theory of iconicity

4.1 Introduction

In the earlier chapters I have argued that in pursuing chemistry Peirce immersed himself in a subject, founded on the nature of *relations* and visualised in diagrammatic form. In chapter three I showed that Peirce and Mendeleev were connected through their common interest in seeking an ordered system for the chemical elements; again one founded on *relations.* By using the diagrammatic representation of Mendeleev’s periodic table, as well as the spatial-relational associations of chemical valency, Peirce created a diagrammatic pathway to an understanding of phaneroscopy. Diagrammatic representations taken from chemistry were used by Peirce to create knowledge. In this chapter I will build on these arguments and explore Peirce’s notion of iconicity and the iconic diagram. Having argued that Peirce’s philosophy was in part developed through chemistry, I will now argue that this relationship is bi-directional; Peirce’s theory of iconicity offers an interpretative framework for viewing Mendeleev’s inquiry into the chemical elements and his periodic table.

To begin with I will give a statement of Peirce’s three orders of signs and then introduce iconicity by taking Chiara Ambrosio’s (2014:256) claim that ‘Peirce characterized iconic *representations* as the dynamic constituents of scientific inquiry’. In seeking to capture the essence of Peirce’s iconicity, Ambrosio (2014:256) cites Hookway (2003:102): ‘[t]he key of iconicity is not perceived resemblance between the sign and what it signifies but rather *the possibility of making new discoveries about the object of a sign through observing features of the sign itself’* (emphasis added). The epistemic fruitfulness that Hookway claims for iconic signs will first be illustrated by an examination of nineteenth century chemical graphs. By interacting with diagrammatic forms of chemical structures chemists gained knowledge of the objects they represented. A diagram is a sign which, states Stjernfelt (2007:29), is a ‘special icon providing the condition of possibility for general and rigorous thought’. This examination of chemical graphs will enable aspects of iconicity to be introduced ahead of a more detailed treatment within the context of Mendeleev’s early periodic table.

Peirce's notion of iconicity in relation to the periodic table considered as a particular case of diagram also casts light on the broader issue of representation in science, for as Callender and Cohen (2006:67) argue, '[t]here are now a variety of different accounts of how scientific models represent and, of course, the usual philosophical squabbling over which one is right'. I will show that Peirce and Mendeleev can contribute, as historical actors with precise views on the matter, to elucidate some of the terms of this debate. Also and ahead of a consideration of the early periodic table as an iconic sign I will consider Ursula Klein's (2001) case study from chemistry of Berzelian formulae as 'paper tools'. I will argue that Klein missed an opportunity by rejecting Peirce's iconicity as an interpretative framework for part of her study. This will also serve as an opportunity to further explore iconicity ahead of the section on Mendeleev's periodic table.

4.2 Peirce's three orders of signs

In his essay 'What is a Sign?' (1894), Peirce gives three orders of signs,

> There are three kinds of signs. Firstly, there are likenesses, or **icons**; which serve to convey ideas of the things they represent simply by imitating them. Secondly, there are indications, or **indices**; which show something about things, on account of their being physically connected with them…Thirdly, there are **symbols**, or general signs, which have become associated with their meanings by usage. Such are most words, and phrases, and speeches, and books, and libraries. (EP2:5, emphasis added)

We will first take Peirce's formulation of a symbol and an index before moving to a more detailed treatment of iconicity. Consider potassium, an example of a chemical object, represented as an agreed convention by the symbol K. For as Peirce states a symbol, such as K, is a sign 'because it is used and understood as such' (CP 2.307). Thus KCl is understood to represent the salt potassium chloride – Cl being the conventional symbol for chlorine. A symbol such as K or Cl represents their respective objects as an agreed social convention.

The bright lilac flame that forms when potassium is placed in water would be indexical of potassium. There is a causal connection between this soft reactive metal and the lilac flame – for Peirce states an index 'signifies its object solely by virtue of being really connected with it' (CP 3.360). The flame test is a common laboratory procedure for detecting potassium compounds. A lilac flame then, has an indexical quality in that it draws the chemist's attention to the presence of potassium.

Iconicity has been traditionally more problematic to define, precisely because Peirce often characterises it as a resemblance or likeness. For example Catherine Legg (2013:8) states that defining the icon in terms of resemblance ‘immediately raises sceptical concerns in the minds of many. “Resemblance is cheap”, it is thought. Anything can be argued to resemble any other thing in some respect. For instance, a photograph of Richard Nixon might be thought to resemble other objects qua male (e.g. Brad Pitt)’. I will offer a detailed analysis of iconicity, drawing on chemical examples, in the next section.

4.3 Examples of iconicity in chemistry

This next section develops Hookway’s claim for the epistemic fruitfulness of iconicity from the perspective of nineteenth century graphical formulae, diagrams chemists construct to gain new information on their objects of study. Sami Paavola (2011:297) argues that,

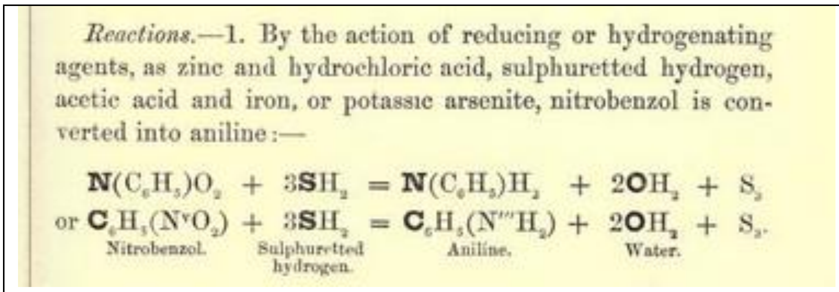
> From the Peircean point of view, diagrams should be the heart of all reasoning. They are central in trying to understand the creative character of reasoning, especially because they are *iconic* signs. (emphasis in the original).

The chemist Edward Frankland – previously discussed in chapter three – uses diagrams to create in his student reader knowledge of the change in structural relations to the reactant and product molecules during the course of a reaction. What we will see in Frankland’s use of chemical graphs is Hookway’s earlier connection of the possibility of making new discoveries ‘through observing features of the sign itself’, the epistemic fruitfulness of an iconic diagram. Our first introduction to Peirce’s writings on iconicity connects the icon with epistemic fruitfulness:

> A great distinguishing property of the Icon is that by the direct observation of it other truths concerning its object can be discovered than those which suffice to determine its construction’. (CP 2.279, c1895).

Also relevant to any treatment of iconic diagrams are two further statements from Peirce. Firstly Peirce states that ‘[a] diagram is mainly an icon, and an icon of intelligible relations’ (CP 4.531, 1906). Secondly, from a Peircean perspective ‘[d]iagrams do not necessarily resemble their objects in looks, but only in respect to the relations of their parts (EP 2: 13, 1895). I will develop these points in the next section.

Let us now turn to this example from Frankland’s text *Lecture Notes for Chemistry Students* where he discusses the conversion of nitrobenzol to aniline:



Reactions.—1. By the action of reducing or hydrogenating agents, as zinc and hydrochloric acid, sulphuretted hydrogen, acetic acid and iron, or potassic arsenite, nitrobenzol is converted into aniline:—

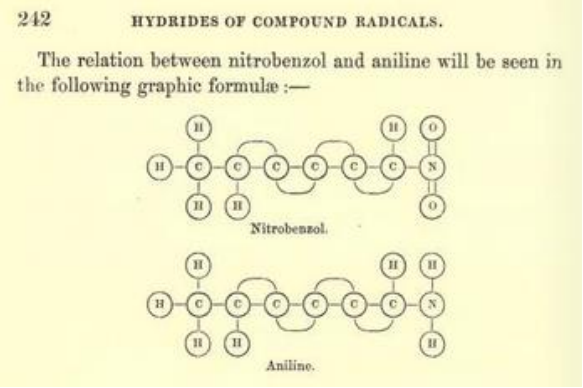
$$\mathbf{N}(C_6H_5)O_2 + 3\mathbf{S}H_2 = \mathbf{N}(C_6H_5)H_2 + 2\mathbf{O}H_2 + S_2$$

$$\text{or } \underset{\text{Nitrobenzol.}}{\mathbf{C}_6H_5(N^{v}O_2)} + \underset{\text{Sulphuretted hydrogen.}}{3\mathbf{S}H_2} = \underset{\text{Aniline.}}{\mathbf{C}_6H_5(N'''H_2)} + \underset{\text{Water.}}{2\mathbf{O}H_2} + S_2.$$

Frankland describes how nitrobenzol is reduced to aniline by the action of sulphuretted hydrogen (H_2S). This equation depicts the formulae for the reactants and products as well as their reacting ratios.

Figure 27: The chemical reduction of nitrobenzol to aniline
Source: Frankland's *Lecture Notes for Chemical Students: Embracing Mineral and Organic Chemistry* (1866) page 241

No information on the bonding relations between the atoms within reactants or the products is given by the formulae depicted above. These representations are of little use to the student chemist interested in which arrangement of atoms on the reactant molecule has been affected by the sulphureted hydrogen (H_2S) in forming aniline. To show the different structural relations between the starting material nitrobenzol and the final product aniline, Frankland immediately includes this next diagram:



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The relation between nitrobenzol and aniline will be seen in the following graphic formulæ:—

These two graphical formulae Frankland notes, display 'the *relation* between nitrobenzol and aniline' (emphasis added). Earlier in the text there is a caution against interpreting the diagrams as a representation of the actual spatial arrangement of the atoms for each compound. Frankland (1866:25) also makes the point that chemical graphs 'are intended to represent neither the shape of the molecules, nor the relative position of the constituent atoms' but 'serve only to show the definite disposal of the bonds' between the different atoms involved.

Figure 28: graphical formulae of nitrobenzol and aniline
Source: Frankland's (1866) *Lecture Notes for Chemical Students: Embracing Mineral and Organic Chemistry*, page 242

It is possible to relate Frankland's graphical formulae for nitrobenzol and aniline to the earlier points relating to a Peircean concept a diagram as an iconic sign. The number and type of each atom present in association with its valency form the basis of the 'intelligible relations' at play. Both nitrobenzol and aniline each have six atoms of carbon and one of nitrogen. In addition nitrobenzol has five hydrogen and two oxygen atoms, whilst aniline has seven hydrogen atoms. The bonding relations between the atoms composing aniline and nitrobenzol are controlled by the rules of chemical valency:-

Atom	Valency	Number of single bonds
C	4	4
N	3 or 5	3 or 5
O	2	2
H	1	1

These particular aspects of the relations underpinning the interpretation of the two chemical graphs make sense of a number of common structural features, as well as some differences between the two structures. Following Frankland's statement (figure 28) that these graphical formulae illustrate the disposal of bonds between the atoms concerned we can assume that both nitrobenzol and aniline have five C—H single bonds and four C=C double bonds. A point of difference is that nitrobenzol has two N=O bonds which are replaced in aniline by two N—H bonds. Frankland (figure 28), in stressing that the chemical graphs do not depict the shape of each molecule but the distribution of bonds between the atoms, echoes Peirce's point that an iconic diagram does not resemble its object in looks. I believe the iconicity of these two chemical graphs is demonstrated in the way they are central to the reasoning process involved in revealing new knowledge.

To begin with the chemist has to physically construct - draw out on paper - the two chemical graphs on the basis of the relations described earlier. It is then possible to use the two chemical diagrams in order to infer something of the nature of the chemical change that occurs when nitrobenzol is converted into aniline by the action of zinc and hydrochloric acid. Firstly, the reaction proceeds by the reduction of nitrobenzol's $-NO_2$ group to form an $-NH_2$ group on the product aniline. Secondly, it is possible to reason that the valency of nitrogen alters during the reaction from being pentavalent in nitrobenzol to trivalent in aniline.

Another example of experimenting on an iconic graphical formula to 'discover unnoticed and hidden relations among the parts' – here a molecule's atoms of construction – can be seen in this problem on isomers taken from Crum Brown's paper 'On the Theory of Isomeric Compounds' (1865). By reasoning with diagrams Crum Brown is able to show that fumaric and maleic acids ($C_4H_4O_4$) can be represented by a single graphical formula and thus are *absolute isomers.* In coming to this conclusion he relies on the explanatory power of the concept of atomicity or valency.

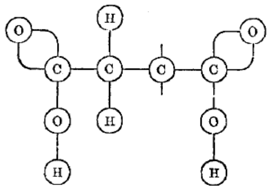
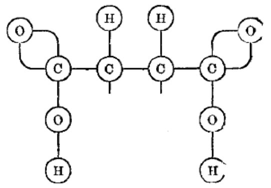
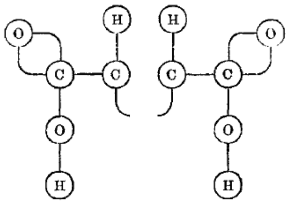
 Graphic formula A  Graphic Formula B	Both the chemical graphs shown here conform to the formula $C_4H_4O_4$. Both formulae A and B, drawn using the conventional valencies for the elements involved, will support the chemical properties of fumaric acid and maleic acid. Formula A is ruled out as one of the carbon atoms has two spare or unused bonds – or 'affinities'. In formula B the spare bond on each carbon atom will unite to result in a carbon to carbon double bond (in modern terms). It is formula B that represents both fumaric acid and maleic acid as explained below.
 This single formula represents both fumaric acid and maleic acid.	Of the two alternatives above, Crum Brown (1865:234) argues that only this one 'is admissible, for the theory of atomicity taken strictly does not admit of free affinities in a molecule.' As both fumaric acid and maleic acid can be represented by a single graphical formula, they are therefore examples of *absolute isomers.*

Figure 29: Isomeric forms of fumaric and maleic acids
Source: Crum Brown's *On the Theory of Isomeric Compounds* (1878) page 234

It is important now to make the connection between observations made on an iconic diagram and the discovery that fumaric and maleic acids are *absolute isomers.* In order to reveal something hidden within these graphical formulae – an 'other truth' hidden within the two molecules – Crum Brown performs an experiment on the two graphical formulae. By drawing out the two graphical formulae Crum Brown (1865:234) is able to reason that of the two alternatives graphic formula A has to be rejected because 'the theory of atomicity taken strictly does not admit of free affinities in a molecule'; an inspection of formula A (figure 29) shows one of the carbon atoms to have two bonds not connected to any other atom. It is for this reason that Crum Brown rejects formula A as a possibility, thereby concluding that as both fumaric and maleic acids can be represented by only formula B they are 'absolute isomers'. In this introduction to Peirce's formulation of iconicity, it is worth noting that the way in which Crum Brown and Frankland use graphic notations – diagrams in chemistry – to disclose knowledge of their chemical objects aligns with Stjernfelt's (2007:90/91) account of an icon as,

> [T]he only kind of sign involving a direct presentation of qualities pertaining to its object…[and]…the only sign by the contemplation of which more can be learnt than lies in the directions for its construction…[whereby]…in order to discover these initially unknown pieces of information about the object hidden in the icon, some deductive experiment on the icon must be performed.

More examples exist in the writings of Frankland (1866) and Crum Brown (1861, 1865) where chemical graphs act as iconic signs and a vehicle for creative thought, leading to the unveiling of new knowledge about the chemists' objects of study.

4.4 Arguments against iconicity

Having offered a brief étude into iconicity I will now take the second point indicated in the introduction to this chapter: the issues around *representation* in science and in particular the arguments against iconicity. Earlier we encountered Hookway accounting for Peirce in terms of the 'resemblance between a sign and what it signifies'. The Peirce scholar Randall Dipert (1996:373) states that it was 'C. S. Peirce's claim that resemblance or similarity, what he termed 'iconicity', is an important part of the general phenomenon of linguistic, artistic, and even mental representation'. The connection between iconicity and resemblance and similarity is supported by Peirce's writings: 'I call a sign which stands for something merely because resembles it, an *icon* (W5:163, 1885; emphasis in the original). Peirce seems to suggest that icons represent by *resembling* their objects. There is however a longstanding problem in the philosophy of science with this approach predicated on *resemblance.* Before developing a claim for the periodic table as an iconic representation, some of the arguments against iconicity on the grounds of resemblance need to be considered.

Some of the recent debate around representation has been concerned with qualifying the relation of ‘resemblance’. One of the strongest critiques of *resemblance* in this context was made nearly fifty years ago by Nelson Goodman (1968) who Daniel Cohnitz and Marcus Rossberg (2016) describe as ‘one of the most influential philosophers of the post-war era of American philosophy [whose] philosophical interests ranged from formal logic and the philosophy of science to the philosophy of art’. Goodman’s objections to resemblance as a necessary condition for representation remain influential and feature in the current literature on *representation.* For example, Michael Newall (2010:91) states, ‘Nelson Goodman is the most famous critic of resemblance theories’. In his *Languages of Art* Goodman argues that resemblance is an insufficient condition for depiction.

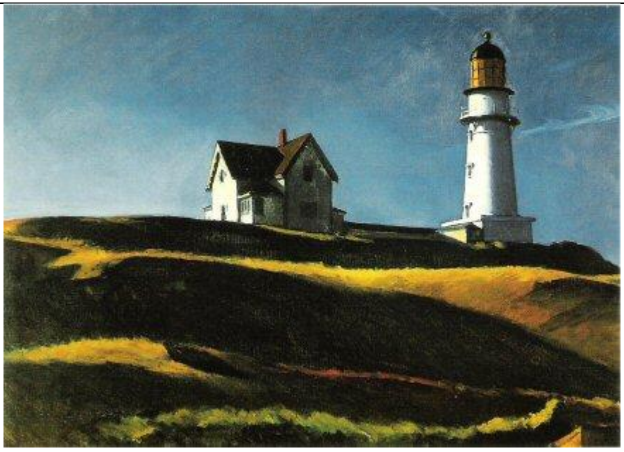


Figure 30: ‘Lighthouse Hill’ by Edward Hopper (1927)
Source: Dallas Museum of Art, USA

In a much quoted example Goodman (1968:5) argues that for any picture - such as Edward Hopper’s painting of a lighthouse – to represent an actual lighthouse, then Hopper’s painting, ‘must be a symbol for it, stand for it, refer to it; and that no degree of resemblance is sufficient to establish the requisite relationship of reference. Nor is resemblance *necessary* for reference; almost anything may stand for almost anything else. A picture that represents—like a passage that describes—refers to and, more particularly, denotes it. Denotation is the core of representation and is independent of resemblance’ (emphasis in the original).

Goodman rejects the significance of ‘resemblance’ as the mandatory relation between a picture and what it represents. This is because for Goodman resemblance is a symmetrical relationship (if A resembles B then B resembles A). This is not the case for one of Hopper’s lighthouse paintings. Hopper’s canvas represents a lighthouse; the lighthouse does not represent Hopper’s canvas: the relationship between the two is asymmetric. Also according to Goodman (1968:4) resemblance unlike representation is reflexive, ‘an object resembles itself to the maximum degree but rarely represents itself’. From Goodman’s (1968:4) perspective, the representational relationship between Hopper’s painting and the lighthouse is one of denotation and not one of resemblance which ‘in any degree is no sufficient condition for representation’.

There have been a number of counter-arguments against Goodman’s position. Randall Dipert argued against Goodman’s position that resemblance is independent of representation on the grounds of the symmetry of the relations involved. In taking the symmetric relation ‘sibling-of’ and the asymmetric relation ‘uncle-of’, Dipert (1996:381) argues:

> We might then conclude, using Goodmanian logic and language, that the uncle-of relation is "independent" of the sibling-of relation; that is, that a useful conceptual analysis of the relation "uncle" does not involve the notion of "sibling".

Resemblance and representation are founded on different symmetry relations. So too are ‘uncle-of’ and ‘sibling-of’. Dipert argues that rejecting resemblance (symmetric) as being wholly independent of representation (asymmetric) is as invalid as claiming that the brother relation (symmetric) is wholly independent of the uncle (asymmetric) relation. Dipert (1996:380) concludes that Goodman’s arguments based around the symmetry of relations ‘would be a useful contribution to the discussion if anyone had ever seriously proposed that the signification relationship is exactly and only the resemblance relationship. So far as I am aware, no one ever has’. From a different perspective Steven French (2003:1478) argues, ‘transporting Goodman’s approach into the scientific context is not unproblematic’. In response to Goodman’s rejection of resemblance as a condition of representation in not being reflexive or symmetric, French (2003:1478) argues that in science ‘we do not simply model a phenomenon, we model it as something’. Part of Goodman’s (1968:5) objection to resemblance as a necessary condition for representation is that, ‘almost anything may stand for almost anything else’. This, argues French (2003:1478), might be agreed ‘when it comes to artistic objects’ but is not the case for scientific representation or model for ‘if the appropriate relationships are not in place between the relevant properties then the ‘‘model’’ will not be deemed scientific’. Returning to Frankland’s graphical formula for aniline (Figure 28), French’s ‘appropriate relationships’ between ‘the relevant properties’ might include the type of each atom present (C, H, and N) and the number of each atom present in the molecule (6, 7 and 1 respectively) as well as their respective valencies. A representation based on a graphical formula with a different set of atoms, or the same set but in different numbers, would not correspond to an empirical analysis for aniline and so, in French’s words, ‘would not be deemed scientific’.

There have been other objections to iconicity around similarity or likeness. For example Arthur Bierman (1962:245) went as far as to say that, ‘there are no iconic signs at all’ for the reason that, ‘[t]here are no signs whose denotation and signification depend solely on their resemblance to that which they denote’. In stressing the connection between iconicity and resemblance Bierman (1962:245) further argues that even if resemblance exists between an object and its sign, it is still not possible to make ‘the further claim that the resemblance is the basis for one of the resembling terms being a sign’. Also, as Ambrosio (2010:153) recalls, ‘Umberto Eco stated that “the category of iconicity is useless”. In his *Theory of Semiotics,* Eco (1976:191) writes of ‘six naïve notions’ around iconicity with one being ‘that the so-called iconic sign is *similar* to its object’ (emphasis in the original). One of the puzzlements around the notion of the icon for Eco (1976:193) is, can ‘one [be] really sure that iconic signs are ‘similar’ to the objects they stand for? Indeed, is one sure they stand for objects at all? By referring to a picture of a glass of cold beer Eco challenges the relation of similarity between the picture and a cold glass of beer by stating, ‘[t]here is neither beer nor glass on the page, nor is there a damp icy film’. The relation between the picture and its object is for Eco is a perceptual mechanism. The picture and the cold beer itself, Eco (1976:193) argues, ‘rely on the ‘same’ perceptual ‘structure’, or on the same system of relations’.

Another response to what Callender and Cohen (2006:68), characterise as ‘‘the constitutional question’: what constitutes the representational relation between a model and the world’, was provided in terms of ‘similarity’ by Ronald Giere (2004:742) when he argues that, ‘scientists use designated *similarities* between models and aspects of the world to form both hypotheses and generalizations’ (emphasis added). In advancing his argument Giere stresses the importance of the scientist’s intention in ‘exploiting *similarities* between a model and that aspect of the world it is being used to represent’ (emphasis in the original). This emphasis on the scientist’s intention is a defence against the objection that similarity is a weak form of correspondence, as any one thing might be similar to any other in a number of respects. In reinforcing the importance of intention Giere (2004:747) lays stress on how the model or representation is used when he states, ‘[i]t is not the model that is doing the representing, it is the scientist using the model who is doing the representing’. From Giere’s perspective when considering the ‘constitutional problem’ on how a model or diagram ‘represents’ we must consider intention: Crum Brown (see above) uses graphical formulae to represent fumaric acid and maleic acid for the purpose of determining whether they are absolute isomers. Taking Giere’s approach here we are connecting Crum Brown’s graphic formulae as representations of their chemical objects with his practice of representing.

A view on how a scientific model or diagram relates to the world founded on partial isomorphism is offered by Steven French and Newton Da Costa (2003:49), where ‘A is partially isomorphic to A^1 when a partial substructure of A is isomorphic to a partial substructure of A^1’. Returning to Crum Brown’s use of graphical formulae to show absolute isomerism, the ‘partial substructures’ present in the target molecules of fumaric and maleic acids - the types of atoms present (C, H and O), the number of these atoms and their bonding relations - are isomorphic to the graphical formula as depicted. Expressed slightly differently and with reference to maleic acid, the number of atoms, the types of atoms and their bonding relations as depicted by the graphical formulae, stand in a one-to-one correspondence to the equivalent partial substructures within the maleic acid molecule – 4C, 4H and 4O atoms with their bonding relations as depicted. Where Giere’s account advances representation as a form of similarity founded on intention and use, French and da Costa offer a view of similarity in terms of partial structural isomorphism.

I would argue that objections to iconicity around resemblance and likeness should not necessarily lead to a rejection of Peirce in this context as he does not always use likeness as a superficial similarity or appearance. He makes this clear in his example of a drunken man demonstrating the virtues of self-restraint,

> It may be questioned whether all icons are likenesses or not. For example, if a drunken man is exhibited in order to show, by contrast, the excellence of temperance, this is certainly an icon, but whether it is a likeness or not may be doubted. The question seems somewhat trivial. (CP 2.282, 1895)

The power of the iconic drunk to present the benefits of sobriety is dependent on the onlooker’s ability to interpret and to project: don’t drink to excess! The drunken man is a metaphor for the benefits of moderation and thus a mediated icon. Peirce would maintain that we never experience pure icons, but only mediated ones; he writes, ‘for a pure icon does not draw any distinction between itself and its object. It represents whatever it may represent, and whatever it is like, it in so far is. It is an affair of suchness only' (CP 5.74, 1903).

Likeness is also a term Peirce uses when dealing with certain mathematical representations,

> The reasoning of mathematicians will be found to turn chiefly upon the use of likenesses, which are the very hinges of the gates of their science. The utility of likenesses to mathematicians consists in their suggesting in a very precise way, new aspects of supposed states of things… (EP2:6, 1894)

In this way a mathematical function is able to operate iconically [likenesses] in facilitating the disclosure of a novel relation. The relationship between mathematical functions and 'likeness' can be seen here when Peirce states,

> Particularly deserving of notice are icons in which the likeness is aided by conventional rules. Thus, an algebraic formula is an icon, rendered such by the rules of commutation, association, and distribution of the symbols. (CP 2.279, c1902)

To illustrate this consider the quadratic expression, $x^2 – 3x – 10 = 0$. In order to solve this equation we need to be familiar with certain conventional rules such as what it meant by 'x-squared', a 'minus' or an 'equals' sign. With the aid of these conventional rules plus the knowledge of how to solve a quadratic equation (not detailed here), a rearrangement of this mathematical relation reveals the previously unknown roots of the equation to be $x = 5$ and $x = -2$. In gaining this new knowledge Peirce stresses the iconicity of the original function – note again the facility of an iconic representation to reveal novel facts,

> This capacity of revealing unexpected truth is precisely that wherein the utility of algebraical formulae consists, so that the iconic character is the prevailing one.
> (CP 2.279, c1902)

I hope in this section to have shown something of the range played by similarity, or 'likeness', in Peirce's account of iconicity. In his account of representation Peirce is not using 'likeness' in a way that sits within the realm of Goodman's objections to the use of resemblance in art theory or Eco's earlier rejection based on the relations between a cold glass of beer and its image.

4.5 Mauricio Suárez's approach to representation

Before approaching the periodic table in the context of iconicity it is worth considering in greater detail arguments around isomorphism, similarity and resemblance in the context of representations. A fuller understanding of these terms, and isomorphism in particular, will be helpful when later arguing the case for iconicity in relation to Ursula Klein's (2001) development of Berzelian formulae as 'paper tools'. These terms form part of Mauricio Suárez's approach to representation. Suárez (2010:91) considers two approaches to representation:

> The interest from analytical philosophy is related to the notion of reference, and the metaphysics of relations; the interest from philosophy of science is related to an attempt to understand modelling practices. These two distinct forms of inquiry into the nature of representation may be distinguished as the 'analytical inquiry' and the 'practical inquiry.

The periodic table appears to offer a bridge between Suárez's two approaches. Firstly Mendeleev was concerned with 'reference and the metaphysics of relations' - how the term element as depicted by the various symbols within the table refers to the substances encountered in the laboratory – for example Hg and the silvery coloured liquid mercury metal. In chapter three I argued that the concept of *relations* was important to Peirce and to Mendeleev. We saw how Mendeleev accounted for compounds such as mercury oxide in terms of the meaning of the term 'element': the *relations* between the free elements mercury and oxygen and the compound mercury oxide. In particular we saw Mendeleev address the puzzle that when silvery coloured liquid mercury and colourless oxygen gas combine, the free elements are not apparent in the red coloured product of mercury oxide. The free elements – here mercury and oxygen – Scerri (2013:30) refers to as 'elements existing as simple substances' and when combined as red mercury oxide as 'the metaphysical element, abstract element, transcendental element…element as a basic substance'. Continuing Scerri's argument, mercury considered as a 'basic substance', is an abstract bearer of properties whilst lacking its phenomenal properties such as its silvery liquid appearance, that is mercury as a simple substance. In concerning himself with the identity of a chemical element Mendeleev is engaging with a metaphysical aspect of chemistry.

In this next example we see Mendeleev (1871:43) keen to distinguish between the terms 'simple substance' and 'element'. A simple substance, Mendeleev (1871:43) argues, 'is something material – metal or metalloid – endowed with physical properties'… [whereas] …the term "element" designates those material particles of simple and compound substances which determine their behaviour from a chemical and physical point of view'. Thus carbon is an element but coal, graphite and diamond are simple substances. Returning again to chapter three we saw how Mendeleev frames the purpose of chemistry in terms of understanding the *relations* between the chemical and physical properties of simple and compound substances – such as mercury, oxygen and mercury oxide – and the intrinsic qualities of the elements contained in them. We see here Mendeleev engaging both with the simple and compound substances encountered in the laboratory and with what Scerri earlier described as 'the metaphysical element' or 'element as a basic substance'. As Gordin (2012:83) explains, '[s]ubstances found in nature were merely instantiations of the abstract notion of an element which was truly the organizing principle of matter' – and subsequently arranged by Mendeleev in order of atomic weight as the periodic table. For, as Scerri (2008:170) states, Mendeleev 'insisted that his periodic classification was primarily concerned with this sense of the term 'element' and not as observable simple substances'.

Secondly, the periodic table would appear to bridge the second of Suárez's two approaches in terms of 'practice' – where the practical inquiry, as Suárez (2010:92) states, is concerned with a particular representation's 'context of application…[with an]…emphasis on *use*' (emphasis in the original). The practical inquiry focusses upon the many different ways representations are used in science with an emphasis on the context of their application. Suárez's approach chimes with the context of Mendeleev's inquiry where he put the periodic table to use in the search for novel knowledge of the chemical elements – to be discussed in greater detail in the following chapters. Also, and in relation to context, one of the main origins of Mendeleev's system, as with Cooke before him, was pedagogic: to provide a scheme that made the assimilation of chemical knowledge more accessible to their students. Mendeleev's first paper on the periodic table was published in February 1869 and shortly before volume two of his *Principles of Chemistry* (Kaji 2002). Thus it might be argued that the initial purpose of the periodic table was linked to that of the *Principles* which Mendeleev (1901:vii) expresses in pedagogical terms as: 'to acquaint the student not only with the methods of observation, the experimental facts, and the laws of chemistry, but also with the insight given by this science into the unchangeable substratum underlying the various forms of matter'.

Whilst Suárez (2010:91) concedes that his categories of analytical and practical inquiry 'are not exclusive' it is interesting that Mendeleev's periodic table appears, initially at least, to draw on them both. Following a brief tour of Suárez's analytical and practical conceptions of inquiry I will re-introduce Peirce's formulation of iconicity which I argue, in support of Ambrosio (2014), offers a way of avoiding Suárez's polarising approach – demonstrating also the virtue of taking scientific representation as being integrated within the whole creative enterprise of inquiry. I hope to show that by using the periodic table as a case study, Peirce's iconicity bridges Suárez's two categories of analytical and practical inquiry; the middle way suggested by Ambrosio (2014) between Suárez's (2010) two approaches.

Analytical and Practical inquiries into representation

There are, Suárez (2010:95) argues, two conceptions of representation within the analytical inquiry and which draw on the concepts of 'similarity' and 'isomorphism' we came across earlier,

> The similarity conception of representation [sim]: A represents B if and only if A and B are similar [and] [t]he isomorphism conception of representation [iso]: A represents B if and only if A and B instantiate isomorphic structures.

We will see later how Suárez rejects attempts to reduce the necessary constituents of scientific representation to similarity and isomorphism. Nevertheless Suárez's 'analytical' approach is useful to this project as it frames an aspect of Mendeleev's own inquiry: his concern with exploring the nature of the mutual relations between the chemical elements framed in terms of their physiochemical properties, and how this was to be best represented.

The analytical approach treats representation as an analysis of the relations between the target or object of investigation and the form of representation, sometimes referred to as the source. In simple form if X is the source and Y its target then it can be said that 'X represents Y'. Representation is then a relation, R, such that the statement 'X represents Y' is equivalent to 'R holds between X and Y'. The nature of R, what Suárez (2010:92) refers to as the 'constitutional question', is comprehended as a detailed conceptual analysis of the relations existing between the source and the target. As part of his analysis Suárez (2010) offers two reductionist accounts. The first reduces representation to similarity and the second to isomorphism. Both accounts are substantive which, explains Suárez (2010:94), 'takes it that representation is a robust property or relation of sources and targets'. This is in contrasts to Suárez's (2010:94) deflationary account where 'representation is not a robust property or relation of sources and targets'. In this case representation focusses on some of the functional relations between source and target within the context of a particular inquiry. Suárez's account deploys the terms similarity and isomorphism which are mathematical concepts. Examining each term within this context offers an insight into their differences of emphasis and meaning.

Two similar triangles have the same shape, but can be different sizes. Their similarity is retained in that their angles are all equal even though one triangle may be larger than the other. By definition two triangles are similar if two sides are in the same proportion and the included angle is equal. One similar triangle may then act as the representation of the other – or vice versa as this is both a reflexive and a symmetrical relation. In abstract algebra, isomorphism is a bijective map f, such that both f and its inverse f^{-1} are structure-preserving mappings. As with similarity, isomorphism is also a reflexive and symmetrical relation. Isomorphism is a mathematical concept and it is difficult to see it as a test of representation outside of this domain. Graphs can be tested for isomorphism using complex algorithms.

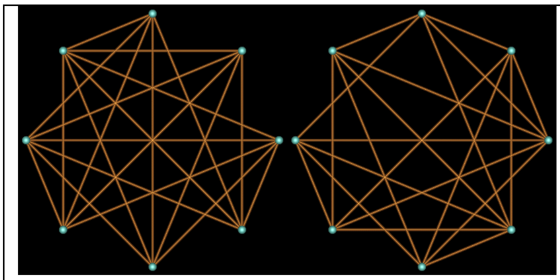
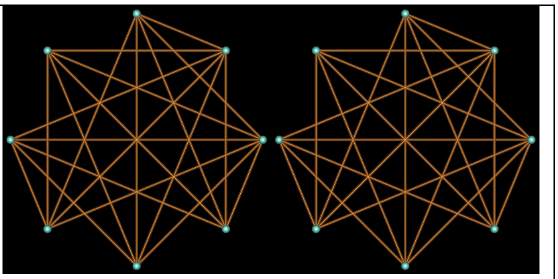
	
Are these two graphs[47] isomorphic?	An algorithm shows the answer to be 'yes'

Figure 31: Isomorphic graphs

The two graphs are said to be *isomorphic* because the relevant algorithm rearranges their vertices so that the corresponding edge structure is exactly the same. As can be seen bijective mapping between these two mathematical structures makes the object identical to the target. Representations in science are often not mathematical entities – and the process of representation is not reflexive or symmetrical. Isomorphism best applies where the source and its target are mathematical objects. In terms of representations in science Suárez (2010:96) argues that, isomorphism 'has a problem with under-determination' in that 'the physical world underdetermines its mathematical structure – which may only be ascribed under a particular description'. Take for example mathematical representations of

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[47] URL: http://www.dharwadker.org/tevet/isomorphism/ last visited 3/10/13

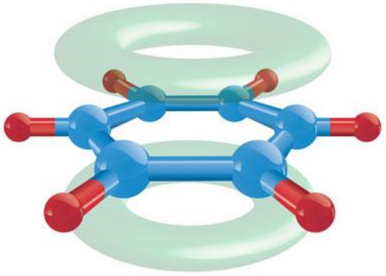
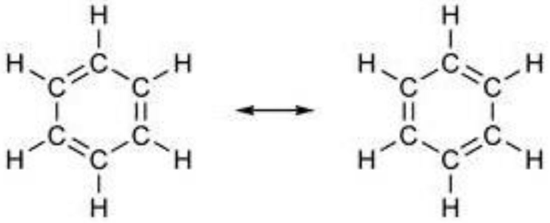
unobservables, such as atoms or electric fields. One of the foundations of quantum mechanics is a model of electron behaviour given by Heisenberg's uncertainty principle:

$\Delta x \, \Delta p_x \geq h/2\pi$	Without delving into the mathematics, this can be interpreted as, the more precisely the position of an electron is known, the less precisely the momentum is known at that instant.

Figure 32: Heisenberg's uncertainty relation

It is hard to see how isomorphism applies here. Bijective mapping of the electron (target) onto the equation (source) is impossible. Isomorphic graphs can be mapped bijectively – but how can the uncertainty relation be mapped? What this particular approach appears to ignore is the context of scientific practice; how a physicist might use this particular representation of an electron. In an earlier paper Suárez (2003:225) is critical of theories of representation 'that attempt to reduce scientific representation to similarity or isomorphism' for the reason that such 'reductive theories aim to radically naturalize the notion of representation, since they treat scientist's purposes and intentions as non-essential to representation'. The analytical approach makes no reference to the context in which a particular representation is used by science. Suárez (2010:99) argues that by including 'intentionality' representation is no longer 'a simple dyadic relation' between an object and its representation, but 'essentially triadic' between the object, its representation and the mind of the scientist.

By way of contrast the practical inquiry forsakes an analysis of representational relations. It takes instead a view on the context within which a particular scientific representation is used – representations, Suárez (2010:92) explains, 'must be properly understood in their context of application'. Examples here might include a three dimensional model for the methane molecule, Kekulé's structural formula for benzene, or one of Newton's equations of motion. The practical inquiry understands these models within the context of how a scientist might *use* them. Take for example these two different representations for the benzene (C_6H_6) molecule.

<table>
<tr><td></td><td></td></tr>
<tr><td>This model[48] depicts the ring structure of benzene with a π-cloud of delocalised electrons above and below the plane of the ring.</td><td>The two equivalent hybrid structures of benzene are depicted as Kekulé structures[49] demonstrating the distribution of the single and double bonds to the resonant structure of the molecule.</td></tr>
<tr><td colspan="2">Figure 33: Diagrammatic representations of the benzene molecule</td></tr>
</table>

These two models have different uses depending on the aspect of benzene that is the focus of study. The first provides some description of electron distribution. The second depicts the type of covalent bonds (single and double) and illustrates the nature of the 'resonant hybrid'. This in turn goes some way to explaining why benzene's chemistry is not typical of other organic molecules with carbon to carbon double bonds such as cyclohexene. From this it is important to recognise, within the context of Suárez's practical inquiry, that there are different ways by which a scientific model is able to represent. The context of use cannot be separated from how the model functions in mediating between ourselves and the world. Questions for example concerned with the distribution of electrons around the benzene nucleus are best considered using the delocalised π-cloud representation, whilst questions focussing on the reaction mechanism of between benzene and chlorine and the seemingly lack of chemical reactivity of benzene as an unsaturated organic molecule are better considered from the perspective of the Kekulé structures.

Having rejected the analytical approach to representation Suárez makes the case for a non-reductive deflationary account. Non-reductive implies that an analytical definition of the representational relation R in terms of something else does not apply; deflationary in that representation highlights some of the dependencies that exist between the target and the object and also that R is assumed rather than spelled out. The robustness or mathematical exactness required of isomorphism does not apply. The deflationary account depicts

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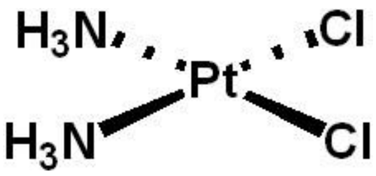
[48] URL: http://www.isis.stfc.ac.uk/science/bioscience/benzene-thumbnail10870.jpg last visited 25/05/2016

[49] URL: https://paulingblog.files.wordpress.com/2010/06/benzene-structures.jpg last visited 25/05/2016

representation as a practice embedded within the context of use. Suárez (2010:97) sets out a number of conditions that his preferred non-reductive and deflationary account must meet. Firstly in terms of the inferential conception, ‘representation is a ‘two vector’ notion, requiring on the one hand representational force and on the other hand inferential capacities’. By using the term ‘vector’ Suárez establishes the non-symmetric and directional character of his preferred method – i.e. Source→Target. His second condition relates to inferential capacity. For example in chemistry, the source must enable an experienced chemist to draw valid inferences about the target – to allow surrogative reasoning[50]. This underlines the important part played by context within the practical inquiry.



This is a representation[51] of the anti-cancer drug cis-platin. The directional assumption Suárez makes is that the image points to the drug molecule. The chemist by reasoning surrogatively is able to determine the number and type of atoms present. By applying the conventions of perspective the molecule is ‘flat’, square-planar with the chlorine atoms described as ‘cis’ to one another. This specific shape is essential to the molecule’s anti-cancer activity and again by surrogative reasoning the drug is thought to act by bonding to the cell DNA in forming cross-links between adjacent purine bases on the same strand of the double helix. This process of representation is non-reflexive and non-symmetric.

Figure 34: Diagrammatic representation of the cis-platin molecule

This representative account for cis-platin and its anti-cancer action seems plausible enough and might be found in any chemistry text book. The problem here, argues Ambrosio (2014:266), is that ‘Suárez considers directionality as a requirement of representation and treats it as a precondition for representation’. Taking the case of cis-platin as an example, directionality need not, in my view, be assumed. How chemists construct a model for the molecule cis-platin, and then go on to infer how it might bond to DNA in order to disrupt

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[50] The original connection between surrogative reasoning and scientific representation is due to Chris Swoyer (1991). The process functions, Swoyer (1991:452) claims, because ‘the arrangements of things in the representation are like shadows cast by the things they portray’. Surrogative reasoning, states Swoyer (1991:453), ‘is reasoning about a structural representation in order to draw inferences about what it represents’.

[51] URL: http://www.chemicalconnection.org.uk/chemistry/topics/images/mm8c.jpg last visited 4/10/13

processes within the mutated cells, is integral to the surrogative reasoning process whereby novel information on its possible anti-cancer mechanism is discovered. The very nature of directionality arises out of how the model of cis-platin is constructed and then used to uncover information about its therapeutic action – how for example it bonds on to DNA. This in turn comes back to an issue of constitution of relations – a part of the previously dismissed analytic approach.

How to resolve this impasse? Ambrosio (2014:226) emphasises the need to move away from a focus on justifying representative relations (analytical inquiry), or the ways in which representations are used (practical inquiry), and recognise that 'what we *do* with representations depends on how we *construct them'* (emphasis in the original). I will show how Mendeleev came to discover the relations pertaining to the chemical elements through the construction of the periodic table; through his process of representing. In addition I will show that this accords with Peirce's account of iconic representations which as Ambrosio (2014:270) states, 'entail the discovery of a common relational structure between representations and the objects they stand for, and this discovery happens through the process of representing'. Importantly I will show that for Mendeleev this begins as a practical pencil and paper exercise of constructing and experimenting on diagrams attempting to depict the physiochemical relations between the chemical elements. We will see that the fruitfulness of the periodic table, for example in predicting the occurrence of the three novel eka-elements, surfaced through Mendeleev's process of representing diagrammatically the physiochemical relations between the chemical elements. It is here that Charles Peirce's formulation of iconicity, and through a study of Mendeleev's inquiry, can offer an account that recognises aspects from both the analytical as well as the practical inquiry. For as we will see Mendeleev, in constructing his table, dealt with the structural relations between the chemical elements as well as using the table to draw inferences.

Before moving on to consider Mendeleev's periodic table in detail I should like to explore Peirce's iconicity further still. In order to do this I will re-examine an earlier case study: Ursula Klein's (2001) investigation of Berzelian formulae as *paper tools* in chemistry. This study is relevant to this chapter as it develops some of the earlier points made on the constitution of *representation*. Klein rejects Peirce's formulation of iconicity as a means of framing the representational relation between Berzelian formulae and their chemical objects. I hope to show how Peirce's formulation of iconicity might have offered a secure analytical framework for Klein's inquiry.

4.6 Iconicity and 'paper tools'

Ursula Klein's (2001) work on Berzelian formulae introduces the term 'paper tool'. Whilst alluding to Peirce's sign system, Klein rejects Peirce's formulation of iconicity as an interpretative framework, preferring instead her own term *iconic symbol.* Klein's study is relevant as it focusses on a study where scientific representations are seen to be generating new knowledge but one which rejects Peirce's formulation iconicity as an interpretive framework. In this section I apply the concept of iconicity to Berzelian formulae and argue that Klein misunderstood Peirce's concept of the iconic sign. Recalling a number of points developed in earlier chapters, a key characteristic of an iconic representation is its epistemic fruitfulness in revealing new information about its object of study. It is this that differentiates iconic from indexical and symbolic representations.

Klein's particular study deals with an inquiry beginning in the early decades of the nineteenth century into organic compounds such as ether, using chemical formulae first published in 1813 by the Swedish chemist Jacob Berzelius (1779 – 1848). European chemists at this time, argues Klein (2001:14), 'applied Berzelian formulas as enormously productive tools on paper or "*paper tools*"' (emphasis added). Klein compares Berzelian 'paper tools' to the usual laboratory tools, such as glassware and the chemical balance, as means of creating new knowledge. These epistemically fruitful paper tools might be considered iconic in the Peircean terms described earlier. However, Klein (2001:16) in a passing reference to Peirce argues that, 'the distinction between icons and symbols does not work for Berzelian formulas' preferring instead the conflated term 'iconic symbols'. The reasons for Klein not deploying Peirce's notion of iconicity will be considered in a moment.

I argue that in rejecting Peirce's sign system as 'not work[ing]' in this case, Klein has lost the opportunity of using the rich interpretative framework offered by Peirce's formulation of signs in her arguments for Berzelian formulae as paper tools. Klein prefers instead her own term *iconic symbol*. Peirce recognised that a particular sign, such as a chemical formula, need not operate solely indexically, iconically or symbolically. For example Peirce acknowledged that 'it would be difficult if not impossible to instance an absolutely pure index or to find any sign absolutely devoid of the indexical quality' (CP 2.306). Furthermore, Peirce held that a representation that is solely iconic makes no distinction between itself and its object of study and in that sense is not a likeness. An icon, explains Peirce, 'can only be a fragment of a completer sign' and a pure icon 'is independent of any purpose [as] it serves as a sign solely and simply by exhibiting the quality it serves to signify' (EP2: 306, 1904). I will show that whilst being symbolic is an aspect of Berzelian formulae, they also function as iconic representations. In short, there was no need for Klein to invent the new category of *iconic signs* whilst rejecting Peirce's formulation.

Why then does Klein not accept Peirce's formulation of iconicity when describing Berzelian formulae as paper tools, preferring to invent the new category, *iconic symbols*, instead? It is I believe Klein's (2001:16) view of iconic signs as 'represent[ing] their objects by virtue of being isomorphic to them' that prompts her not to develop Peirce's formulation of iconicity. I would argue that isomorphism is not necessary for iconicity. I will later argue that iconicity is founded on homomorphism – a partial but structure preserving mapping from source to target – which surfaces through the process of representing.

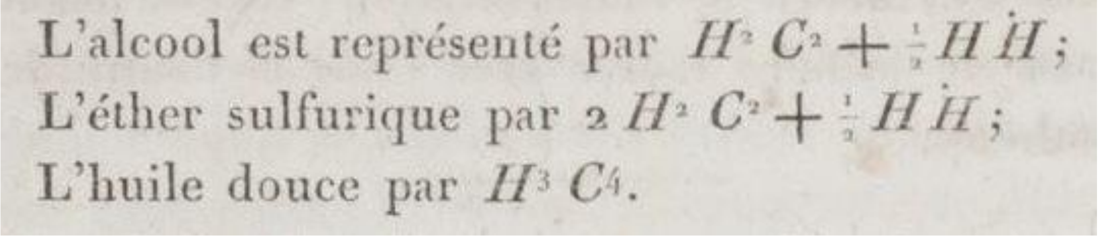
Recalling a couple of the main arguments from earlier in this chapter, the term *isomorphic* describes a relation between mathematical sets; in this case A and B as mathematical structures stand in equivalent relation one to the other. Isomorphism is a controversial notion amongst philosophers of science. However, such a situation, argues Suárez, (2003:228) 'demands that there be a one-to-one function that maps all the elements in the domain of one structure onto the elements in the other structure's domain and vice versa, while preserving the relations defined in each structure'. Returning to Peirce's drunken man as an icon of temperance, it is hard to see how the relational frameworks of the drunk and the sober can be mapped as a one-to-one function; isomorphism is not a necessary condition of the iconicity at work here. Furthermore, consider these two statements by Peirce: firstly that an icon is 'sign which stands for something because it resembles it' (CP 3.362) and secondly that many diagrams – and I would also include Berzelian formulae here – 'resemble their objects not at all in looks; it is only in respect to the relations of their parts that their likeness consists' (CP 2.282). The particularly controversial issue here of how Peirce characterises iconicity as relation of resemblance or likeness was discussed earlier. Conditions of 'resemblance' between the (chemical) object and its sign (Berzelian formulae) in terms of the 'relations of their parts' is as I will argue later iconic, but not an isomorphic relation as Klein claims. Such a relation between the object and its sign is better described as homomorphic. It is worth pursuing the homomorphic character of iconicity a little further in order to challenge Klein's rejection of Peirce's iconicity on the grounds of it being an isomorphic form of representation.

Ambrosio (2014:269) argues that Peirce's theory of iconic representations is better expressed 'as homomorphic representations [which] accounts for structure preservation as a relation which is discovered through the process of representing'. Following Ambrosio's account, homomorphism does not involve an isomorphic one-on-one mapping but the mapping of the larger source domain onto a smaller target domain with the essential structural relations preserved – a weaker form of morphism than isomorphism. For example the famous London Underground map is an iconic diagram that shares spatial relations with the stations it represents and allows the traveller to experiment on different routes of travel between two fixed stations. The relation between the map and the actual underground system is at best homomorphic, not isomorphic. There is not a one-to-one (isomorphic) relation in terms of distances or exact special locations of the many stations represented. In more general terms an icon is a construction of a specific set of relations and properties that are also maintained by its target. Support for this approach is offered by Sun-Joo Shin (2002:31) who also treats iconicity as a case of 'homomorphism between representing and represented facts'. I later hope to show that a Berzelian formula acts as an iconic sign with a homomorphic mapping of relations between it and the chemical object represented.

The Berzelian formula for water is $H^{2}0$. This formula has a symbolic aspect in that a chemist, understanding the conventions around its construction, recognises that it represents a compound of the elements hydrogen and oxygen in a 2:1 ratio such that the combining weights of these two elements is also known. The Berzelian formula preserves the relations of elemental composition and their relative proportions with water as the object. The formula makes no attempt to map or represent other possible relations such as the spatial distribution of atoms within the molecule represented. I would therefore argue for a homomorphic relationship between the Berzelian formula and its chemical object of water. As well as acting as symbols, early nineteenth century chemists, by formulating and writing Berzelian formulae on paper, used these as a basis for thought experiments to propose the structure of organic compounds such as acetal. In this way Berzelian formulae acted as iconic signs having a homomorphic relation to their objects. This can be seen in Klein's own case study drawn from nineteenth century investigations into the character of organic compounds. In modern terms the action of sulphuric acid on ethanol (alcohol) yields ether - of interest as an early anaesthetic - plus a number of by-products. In today's terms,

$2CH_3CH_2OH$ --(concentrated H_2SO_4)→ $CH_3CH_2\text{-}O\text{-}CH_2CH_3$ + H_2O
ethanol diethylether water

In 1827 Jean Dumas and Polydore Boullay[52] investigated this reaction subsequently publishing a paper[53] which Klein (2001:19) claims to be 'one of the first historical documents in which Berzelian formulas were widely used as paper tools for modelling organic reactions and the binary constitution of organic compounds'. For example Dumas and Boullay (1827:309) make the following claims and offered the following Berzelian formulae to represent the binary composition of three of the organic compounds involved in their study, alcohol, ether and the by-product 'sweet wine oil':



L'alcool est représenté par $H^2 C^2 + \frac{1}{2} H\dot{H}$;
L'éther sulfurique par $2 H^2 C^2 + \frac{1}{2} H\dot{H}$;
L'huile douce par $H^3 C^4$.

Figure 35: Berzelian formulae for alcohol, ether and 'sweet wine oil'
Source: Jean Baptiste Andre Dumas and Polydore Boullay, 'Memoire sur la Formation de l'Ether sulfurique', *Annales de Chimie et de Physique* 36 (1827): 294-310.

A year later (1828) these authors published a second paper[54] where, as Klein (2001:21) explains, they 'concluded with formula models of the binary constitution of the organic compounds, which they constructed by manipulating formulas on paper'. For example Dumas and Boullay offered the following Berzelian binary-formulae for alcohol, ether and the by-product 'sulfovinic acid' as, ($4\ H^2C^2 + 2\ H^20$), ($4\ H^2C^2 + H^20$) and ($4\ H^2C^2 + 2\ S0^3$) respectively; another example of the use of Berzelian formulae as paper tools for demonstrating organic reactions and the binary constitution of their reactants and products.

The composition of 'sulfovinic acid', also a by-product of the distillation of alcohol, had long been a subject of interest to chemists. Later and in 1833, Theophile Pelouze investigated the formation of ether by the action of phosphoric acid on alcohol which also produced the by-product 'phosphovinic acid' and believed to be analogous to 'sulfovinic acid'. In Klein's (2001:23) account, Pelouze arrived at the Berzelian formula of phosphovinic acid 'exclusively on the basis of the quantitative analysis of the new compound, without carrying

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[52] Jaime Wisniak (2010:59) describes how Boullay died aged twenty nine from the burns he received when a bottle of ether he was holding broke and was ignited by a nearby flame.

[53] Jean Baptiste Andre Dumas and Polydore Boullay, "Memoire sur la Formation de l'Ether sulfurique," *Annales de Chimie et de Physique* 36 (1827): 294-310 cited in Klein (2001:32)

[54] Jean Baptiste Andre Dumas and Polydore Boullay, "Memoire sur les Ethers composes," *Annales de Chimie et de Physique* 37 (1828): 15-53 as cited in Klein (2001:32)

out the usually customary experiments to study the reactions of ‘phosphovinic acid’. In place of the ‘customary experiments’, Klein (2001:23) argues that ‘the successive transformation of inscriptions [Berzelian formulae] were the decisive steps of Pelouze's model construction’. I would argue that by manipulating the Berzelian formulae in order to determine the formula for ‘phosphovinic acid’ (in the absence of any study of its chemical properties) Pelouze was performing experiments on (Peircean) icons as represented by the Berzelian formulae. This particular case study concludes with Klein (2001:24) claiming,

> Pelouze's rhetoric represented his formula model of the binary constitution of phosphovinic acid from phosphoric acid and alcohol as if it were a necessary consequence of the experimental data. Finally he argued that it could be concluded from this result that the analogous sulfovinic acid must also consist of sulfuric acid and alcohol.

The manipulation of Berzelian formulae was a substitute for the type of supporting evidence usually gathered empirically in the laboratory – these manipulations of Berzelian formulae can also be thought of as experiments on iconic-representations resulting in the creation of new knowledge – the formulation of ‘sulfovinic acid’. Finally Klein (2001:26) deals with Leibig’s investigations into the organic compound acetal, and concluding,

> Liebig did not perform any experiments to study the reactions of acetal in order to support the model. As Pelouze had done in the case of phosphovinic acid, he constructed the model merely by manipulating chemical formulas.

Again a formulation is offered for a novel substance not as the result of laboratory experiments but by experimenting on Berzelian formulae which I argue are iconic representations. By 1833 and by various manipulations of Berzelian formulae, Liebig had proposed formulas for phosphovinic acid, acetal, spirit of wood, and acetic acid ether – new knowledge arrived at through experimenting on iconic Berzelian formulae. I would suggest that in their study of organic chemistry Dumas, Boullay and Liebig used Berzelian formulae to prompt surrogative reasoning from which they inferred the formulation of substances such as sulfovinic and phosphovinic acids. The process here is described by Klein (2001:23) as depending on the ‘manipulation of Berzelian formulas [as] the decisive means’ whereby the formulation of these compounds are discovered; the construction, inspection and manipulation of formulae leading to novel knowledge. I would argue that the process Klein describes here is consistent with the dynamic act of constructing and scrutinizing an iconic representation. Klein (2001:30) indicates the iconic-like fruitfulness of Berzelian formulae when she states that, when in 1834 Dumas introduced into chemistry the concept of a substitution reaction, it was 'the particular epistemic constellation of a controversy over rival models of binary constitution, the manipulations of formulas and their visual display of possible recombination had *suggestive* power for Dumas' (emphasis added). In brief, Dumas was inquiring into the reaction between chlorine and alcohol and proposed a scheme where atoms hydrogen that formed part of the alcohol molecule were replaced or substituted for in a step-wise fashion by chlorine atoms and carried away (in modern terms) as hydrogen chloride (HCl). Dumas, states Klein (1999:165), 'was not looking for a new explanation of organic reactions when he started…it was 'suggested' by the manipulation of [Berzelian] chemical formula': Berzelian formula functioning as iconic representations in revealing novel knowledge.

As has been argued earlier, iconic representations are integral to the creative process of scientific inquiry. They are however not purely iconic but contain symbolic and indexical qualities as well, having homomorphic relations with their objects of study. Berzelius used the conventionally agreed symbols to represent the elements, with numbers acting as indexical signs, drawing attention to the combining ratios. There was in my view no necessity for Klein to reject Berzelian formulae as iconic and to create the new category of *iconic symbol.* I believe *iconic symbol* is a redundant term: from a Peircean position all symbols are partly iconic – just as all icons are partly symbolic. The term *iconic symbol* does not allow us to discriminate what makes Berzelian formulae – described by Klein (2001:29) as 'quasi-algebraic' – and their construction into equations particularly interesting. Earlier we saw how Peirce reasoned that equations as well as diagrams are iconic. I would argue that Berzelian formulae, by the way they support surrogative reasoning, their inferential capacity and epistemic fruitfulness, have much in common with Peirce's iconic diagrams. Berzelian formulae, argues Klein (2001:30) not only conveyed information of 'chemical proportions' but also aided chemists 'with their experimental investigations of organic chemical reactions'. Whilst not disagreeing with Klein here I would add that their value to chemists was also their functioning as iconic representations: disclosing novel features of the chemical reactions they were engaged with.

This section addresses one of the few accounts in the literature to make reference to Peirce's theory of signs as part of a case study in to scientific inquiry. I have also sought to further develop Peirce's notion of iconicity, its connection with surrogative reasoning, and to extend iconicity to a broader range of chemical representations. In the next section I will develop Peirce's formulation of iconicity in greater detail and then to use this as a lens through which to examine Mendeleev's periodic table.

4.7 Three aspects of iconicity and the process of inquiry

Winfried Nöth (2008:83) points out that Peirce has 'given innumerable definitions of the icon', a view shared by Michael Shapiro (2008:817) when he states that, 'Peirce attempted many definitions of *icon* over the entire span of his life' (emphasis in the original). At this point I should like to propose three key aspects of Peirce's formulation of iconicity which would need to map on to the periodic table for it to function as an *icon*. These key aspects, supported by others, will be applied to the very early stages in the development of Mendeleev's table and its first published edition in 1869. Later developments of Mendeleev's inquiry will be the subject of chapters to follow. There now follow three criteria which I believe capture a number of key functions of an iconic representation such as the periodic table and its part in Mendeleev's inquiry:-

a) epistemic fruitfulness

Peirce's formulation of iconicity is associated with epistemic fruitfulness and as described earlier,

> A great distinguishing property of the Icon is that by the direct observation of it other truths concerning its object can be discovered than those which suffice to determine its construction. (CP 2.279, 1895)

The epistemic fruitfulness of this formulation of is emphasised by Stjernfelt (2007 and 2011) when taking it as part of the basis for his *operational* account of iconicity. Stjernfelt (2011:397) argues that here Peirce captures an 'epistemologically crucial property of the icon: it is an operational specification of the concept of similarity'. Following Stjernfelt, an iconic sign, whilst representing a number of qualities of its object, is also capable of engaging our thought processes so that more can be learned than was necessary for the sign's construction. Later I will show how Mendeleev's earliest attempts at a systematic arrangement of the chemical elements enabled him to propose knowledge that went beyond what was known at the start of the process. Such an *operational* approach to iconicity argues Stjernfelt (2011:397), 'separates the icon from any psychologism: it does not matter whether sign and object for a first (or second) glance seem or are experienced as similar; the decisive test for iconicity lies in whether it is possible to manipulate or develop the sign so that new information as to its object appears'. From his *operational* perspective, Stjernfelt (2011:398) states that icons are epistemically fruitful being ‘signs with implicit information that may be made explicit’, describing this as a ‘non-trivial [definition of an icon] because it avoids the circularity threat in most definitions of similarity’ – something we encountered earlier in the chapter. Later in the chapter we will see how Mendeleev and others made explicit information that was implicit within the form of the periodic table.

As was stated at the start of the chapter, Peirce positions iconic representations as a dynamic constituent of scientific inquiry. For as Ambrosio (2014:256) argues, ‘the very process of constructing and inspecting an iconic representation (a process that for Peirce involves a dynamic act of interpretation) discloses novel features of the objects or states of affairs being investigated through the representation’. We will later see how Mendeleev arrived at his first published table by a process of ‘construction’ which involved working with a number of preliminary sketches. Furthermore, for the periodic table to act as an iconic sign we will need to show that a similarity of relations was discovered between the elements of its construction and the chemical elements themselves that enabled Mendeleev to perform successful thought experiments in order to reveal knowledge previously hidden. The capacity to generate new knowledge, claims Hookway (2003:102), is ‘the key to iconicity [which] is not perceived resemblance between the sign and what it signifies but rather the possibility of making new discoveries about the object of a sign through observing features of the sign itself’. It is by observing the antics of the (iconic) drunk that we might discover the benefits of not binge-drinking.

b) surrogative reasoning

Peirce stated,

> Remember it is by icons only that we really reason, and abstract statements are valueless in reasoning except so far as they aid us to construct diagrams. (CP 4.127, 1893)

I would argue that one of the most useful features of an iconic representation is its capacity for enabling surrogative reasoning (Swoyer 1991), to facilitate what Gabriele Contessa (2007:48) describes as drawing ‘surrogative inferences from the model to the system’. By examining the process of construction I hope to show that the periodic table was iconic in enabling Mendeleev to use his diagrammatic representation to infer something of the relations between the chemical objects it represents. Furthermore I will show that this was very much a practical activity as Mendeleev engaged in ‘pencil and paper’ experiments on two sketched proto-forms of his first periodic table published in 1869.

The importance of visual representations to both the generation and communication of new knowledge was emphasised by David Gooding. As we will see Mendeleev's arrangement of the chemical elements as the periodic table served both to promote his creative thought processes and as a means of communicating his periodic law. Gooding (2004b:10) names, 'interpretative images whose cognitive (generative) and social (communicative) functions are inextricably linked [as]…*construals*' (emphasis in the original). In the coming section I will show how Mendeleev experimented by sketching out a number of arrangements of the chemical elements in order to explore the pattern of their physiochemical relations which led on to the first published arrangement in February 1869. These early proto-forms of Mendeleev's arrangements might be thought of as construals by fulfilling the function the Gooding (1990:115) describes as 'enabl[ing] the earliest stages of the interpretation of a new phenomenon'. This connection with Gooding's work will be taken up again later in the chapter.

c) a system of relations

The third criterion relates to diagrams such as the periodic table,

> A Diagram is a representamen which is predominantly an *icon of relations* and is aided to be so by conventions. Indices are also more or less used. It should be carried out upon a perfectly consistent system of representation, one founded upon a simple and easily intelligible basic idea. (CP 4.418, 1903, emphasis added)

For the periodic table to be considered as an iconic diagram I will need to show that is constructed as a system of relations. Furthermore the periodic table is not a purely iconic sign. I will show that it depends upon 'conventions' [symbols] and indices as part of its construction. All three of Peirce's triad of signs operating as the periodic table – symbol, index and icon – will need to be shown as founded on well-defined and easily comprehended principles. Indexical and symbolic signs differ from iconic signs are necessary to the periodic table functioning as an icon by providing a form and structure to work within. For example, elements such as the alkali metals lithium, sodium and potassium, which Mendeleev placed at different positions in his proto-scheme are represented in conventionally symbolic form – Li, Na and K. The positioning of the alkali metals as a common row or group of elements is indexical as this is understood to bring together a set or family of elements with similar chemical properties. Atomic weight values are indexical in drawing attention to the organising principle underlying the arrangement.

Interestingly I will show how Mendeleev occasionally used only the atomic weight (indexically) without the accompanying symbol to draw attention to the position of an element within the scheme.

4.8 Iconicity and the early periodic table

As with many discoveries, the periodic system had a number of antecedents such as Alexandre-Émile Béguyer de Chancourtois (1820-1886), John Newlands (1837-1898), William Odling (1829-1921) and Josiah Cooke. The debt he owed to these earlier researchers is acknowledged by Mendeleev whose own success is described by Heinz Cassebaum and George Kauffman (1971:326) as repeatedly demonstrating 'the use of the system in solving the chemical problems of the time' so that 'the scientific world first learned of this discovery, so pregnant with future possibilities, from Mendeleev and Meyer, whereas Odling underrated his own efforts'. The mention of future generative power is here again a tilt towards the periodic table's iconic status.

The periodic law developed in early 1869 as a part of Mendeleev's two volume book *The Principles of Chemistry*. The book's purpose was an attempt to systemise the extensive corpus of inorganic chemistry so as to make it more accessible to his students. Mendeleev began with valency as his organisational framework. Volume one ended with the halogens with the alkali metals forming the first chapter of volume two. It is here that Mendeleev is thought to have paused in search of an alternative organising scheme – volume one had covered only eight elements leaving the remaining fifty five to the second volume. Mendeleev then adopted atomic weight as his new organisational criterion. In a single day, February 17th, 1869, Eric Scerri (2007:106) records 'Mendeleev not only began to make horizontal comparisons but also produced the first version of a full periodic table that included most of the known elements'.

I would argue that it is only by considering the creative endeavour – the inquiry – that Mendeleev was engaged in that the full representational impact of his first table can be appreciated. Only four useful documents are thought to survive from Mendeleev's earlier work leading up to this publication – appropriately held by the Mendeleev Library in St Petersburg. The Russian scholar Bonifatii Mikhailovich Kedrov's (1903-1985) highly authoritative *Day of a Great Discovery*[55](1958), is a detailed account of Mendeleev's work based on an analysis of primary sources. These include a number of early working drafts of

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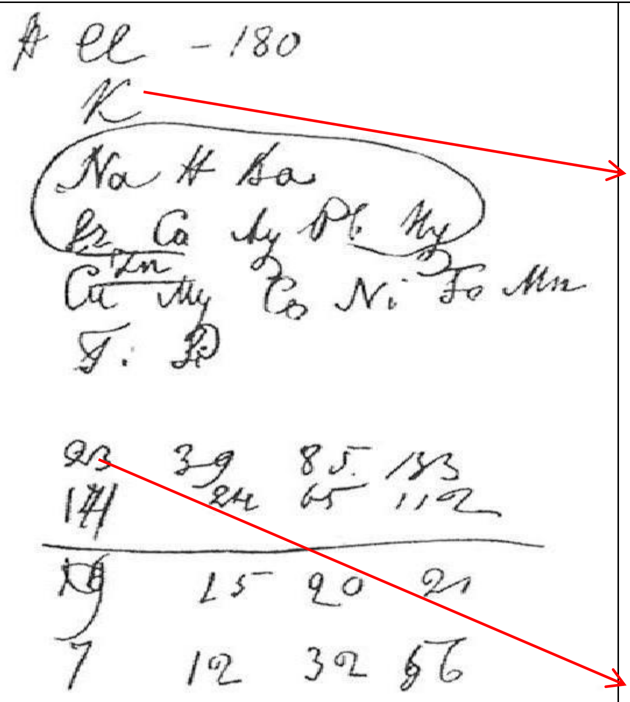
[55] Bonifatii Mikhailovich Kedrov, *Den' odnogo velikogo otkrytia* (Moscow, 1958).

Mendeleev’s table. Some of these primary sources are reproduced as facsimiles in Cassebaum and Kauffman (1971) and are used in what follows. The earliest known attempt by Mendeleev to build a scheme based on atomic weight rather than on valencies was identified by Kedrov as having been written on the back of a letter sent to Mendeleev on February 17, 1869, by Aleksei Ivanovich Chodnev, Secretary of Russia’s Imperial Free Economic Society. These early sketches are a practical pen and paper exercises which reveal something of Mendeleev’s surrogative reasoning:



The organisation and analysis of the information shown here has the feel of a pencil and paper experiment. Notice that Mendeleev has positioned potassium (K) under chlorine (Cl) – both elements have very different chemistries but similar atomic weights and valency.

Mendeleev has also brought together the atomic weights of the alkali metals and as well as the elements related to Zn – two sets of elements with similar properties. He calculates the difference in atomic weights between pairs of elements in the same column.

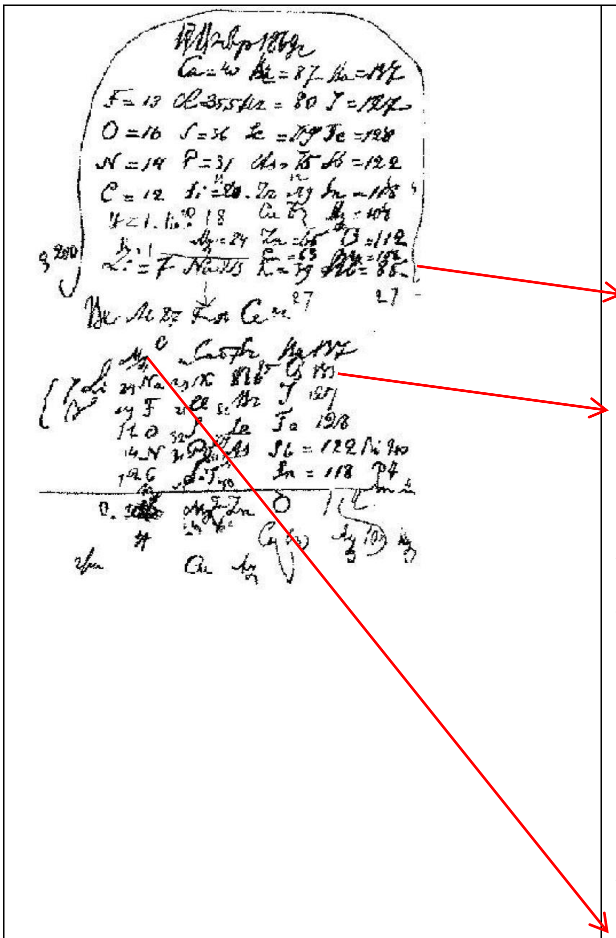
23(Na)	39(K)	85(Rb)	133(Cs)
14 (?)	24(Mg)	65(Zn)	112 (Cd)
9	15	20	21

Notice too that Mendeleev's is using both chemical properties and atomic weights as organising principles.

Figure 36*:* The first of Mendeleev's two incomplete tables of February 17th, 1869
Source: B. M. Kedrov and D. N. Trifonov, 'Zakon periodichnosti…, Moscow: Izdatel'stvo "Nauka",1969' (via Heinz Cassebaum and George B. Kauffman,1971, 'The Periodic System of the Chemical Elements: The Search for Its Discoverer', *Isis* **62**(3)

Notice in figure 36 how on occasion Mendeleev used atomic weight as an indexical sign to draw attention to the position of a particular element. For example 23 and 39 stand as placeholders for the elements sodium and potassium.

A second incomplete table of February 17, 1869 is recorded by Cassebaum and Kauffman (1971:322) and again from Kedrov's primary sources.



Here again Mendeleev appears to be engaged in a pen and paper practical experiment - reasoning surrogatively - on how to best position the elements. The alkali metals (Li, Na, K, Rb, Cs) which are first near the bottom of the upper table have been placed between the alkali earth metals and the halogens in the lower table. In the top table the atomic weights run left to right. In the lower table from top to bottom. In the bottom table chemically similar elements are brought together in rows and there is a more ordered arrangement of atomic weights. There is also the suggestion of an unknown element (?3) at the start of the halogen sequence.

From the bottom table, for example,

	Mg (24)	Ca(40)	Ba(137)	
Li(7)	Na(23)	K(39)	Rb(85)	Cs(133)
?(3)	F(9)	Cl(35.5)	Br(80)	J(127)

Figure 37: The second of Mendeleev's two incomplete tables of February 17th, 1869 Source: B. M. Kedrov and D. N. Trifonov, 'Zakon periodichnosti…, Moscow: Izdatel'stvo "Nauka",1969' (via Heinz Cassebaum and George B. Kauffman,1971, 'The Periodic System of the Chemical Elements: The Search for Its Discoverer', *Isis* **62**(3)

I would argue that these two drafts served as iconic representations enabling Mendeleev to engage in surrogative reasoning. I believe what we are witnessing here is Mendeleev's practical process of representing as a pencil and paper exercise involving both constructing and experimenting on his diagrams. Through these practical experiments Mendeleev seeks out the representative relations which he will infer also hold for the chemical elements. Importantly it is iconicity that characterises the perspicuousness of these diagrammatic proto-forms of the periodic table and makes surrogative reasoning possible. With respect to the second criterion of iconicity given earlier, these iconic diagrams are at the heart of Mendeleev's surrogative reasoning as he decides how to arrange the elements. For example in figure 36 Mendeleev experiments by placing the gas chlorine above the reactive metal potassium. A line seemingly separates the chemically similar elements potassium and sodium. In figure 37 Mendeleev brings together the chemically similar metals sodium and potassium as horizontal row of elements along with lithium, rubidium and caesium. Other chemically similar elements such as the halogens fluorine, chlorine, bromine and iodine are also grouped together in rows.

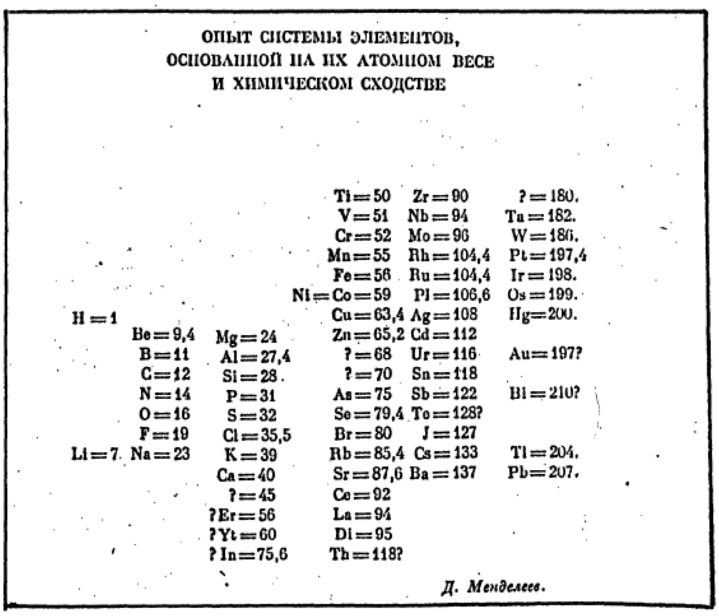
These, the very earliest results of Mendeleev's pen and paper experiments, might be thought of in Gooding's (1990:115) term as a 'construals', being a representation 'articulating interpretative possibilities'. Such representations or *construals* Gooding continues, 'enter discourse as the practical basis for realizing and communicating novel experience…[u]ntil the wider significance of novel information has been sketched out'. I believe that these very early sketches capture and contextualise the results of Mendeleev's exploratory surrogative reasoning on the relation between the physiochemical properties of the chemical elements. Furthermore that these earliest 'construals' – signifying Mendeleev's embryonic communication of his thought processes – later gave rise to more complete representations of the periodic relations between the chemical elements such as his first published scheme of 1869.

With regards to the third criterion of iconicity, these proto-forms of Mendeleev's system are based upon a system of relations founded on atomic weights which Scerri (2006:116) describes as Mendeleev's 'key to classifying the elements'. The diagrams are, in Peirce's earlier words, 'aided…by conventions' in that the elements are identified by an agreed convention of symbols. The atomic weight values included are indexical in drawing attention to the intelligible system of relations upon which the table is based. Finally looking at figure 37 there is also the suggestion of new knowledge – epistemic fruitfulness – in Mendeleev's suggestion of an additional halogen preceding fluorine and shown with an atomic weight of three and as the indexical sign '?3'.

In his essay 'Prolegomena to an Apology for Pragmaticism' (1906) Peirce writes in relation to iconic diagrams, 'chemists have ere now, I need not say, described experimentation as The putting of questions to Nature. Just so, experiments upon diagrams are questions put to The Nature of The relations concerned' (CP, 4.530). The two tables above enabled Mendeleev to 'ask of nature' what are the most effective organising criteria for the elements. By experimenting on his (iconic) diagram Mendeleev seems to be working towards an answer in terms of a system of relations founded on atomic weight and aided by what Scerri (2006:120) describes as an 'understanding of the individual chemical natures of the elements, and their compounds..[which]…gave him an intuitive sense of how the elements should be grouped'.

4.9 The first published form of Mendeleev's system of elements (1869)

The first form of Mendeleev's periodic system was published on 17th February 1869. Copies were printed in both Russian and French under the title of *An Attempt at a System of Elements, Based on their Atomic Weights and Chemical Affinities* – hereafter referred to as the *Attempt*.



ОПЫТ СИСТЕМЫ ЭЛЕМЕНТОВ,
ОСНОВАННОЙ НА ИХ АТОМНОМ ВЕСЕ
И ХИМИЧЕСКОМ СХОДСТВЕ

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28.	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	J=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

Д. Менделеев.

Mendeleev's use of 'system' underlines his belief that his arrangement was founded upon a set of principles – established by inquiry and using the preliminary iconic diagrams discussed earlier.

Figure 38*:* Mendeleev's first table as a single sheet handout, 17th February 1869
Source: *Persistence and Periodicity: a study of Mendeleev's contribution to the Foundations of Chemistry* by John Russel Smith, PhD thesis Chelsea College, University of London 1976, page 217

This single sheet hand-out of Mendeleev's appeared shortly afterwards in the Russian journal *Zhurnal Russkago Fiziko-Khimicheskago Obshchestva.* Soon after this Mendeleev's system was published the German journal *Zeitschrift für Chemie*[56] where the table is also accompanied by a brief introduction and eight short notes. To begin Mendeleev (1869b:25) makes the following claim,

> If one arranges the elements in vertical columns according to increasing atomic weight, such that the horizontal rows contain analogous elements, also arranged

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[56] Mendelejeff, D. 1869. 'On the Relationship of the Properties of the Elements to their Atomic Weights'. *Zeitschrift für Chemie* **12**:405-406

> according to increasing atomic weight, one obtains the following table, from which it is possible to derive a number of general deductions.

Not surprisingly given the earlier discussion around Mendeleev's earlier hand-drawn proto-tables, this opening statement establishes atomic weight as providing the framework of relations upon which his iconic table is based. Firstly note that Mendeleev sets out the founding rationale for the periodic table – elements arranged as 'vertical columns according to increasing atomic weight' - as the 'simple and easily intelligible basic idea (CP 4.418)' that also forms a part of the third criterion of iconicity. Furthermore Mendeleev sets out the two-fold *relations* between the chemical elements and his diagrammatic representation: increasing atomic weight with elements of similar chemical properties collected in sets as horizontal rows. Again as with the earlier discussion, in line with the third criterion of iconicity, Mendeleev's diagrammatic table is 'aided by conventions' or chemical symbols. The meaning of each chemical symbol is understood by chemists across national frontiers as a matter of convention. For example the original table is printed in Russian which includes symbols such as Be, B and C which his international readers would understand by convention to indicate the elements beryllium, boron and carbon. Indexical aspects of the table include: horizontal rows of individual symbols for the chemical elements which draw attention to the various families of elements such as the alkali metals (Li, Na, K, Rb, Cs) and the halogens (F, Cl, Br, I). Also and as mentioned earlier, atomic weight values are indexical in pointing to the table's underlying feature of organisation. Other indexical signs will be considered below.

His opening remarks completed, Mendeleev (1869b:26) then sets out eight 'general deductions' that follow from his periodic arrangement of the elements. The final three point towards the possibility of new discoveries thereby indicating the likelihood of the periodic table to be epistemically fruitful, a critically important characteristic of an icon and the first criterion of iconicity given earlier:

> 6. It [the periodic table] allows one to foresee the discovery of many new elements, e.g analogs of Si and Al with atomic weights between 65 and 75
> 7. It is to be expected that some atomic weights will require correction, e.g., Te cannot have an atomic weight of 128, but rather one between 123 and 126.
> 8. The above table suggests new analogies between elements. Thus Bo(?) [Ur] appears as an analog of Bo and Al, which is well-known, has long been firmly established by experiment.

In point (6) Mendeleev suggests that the periodic table points to the discovery of new elements, recorded in the table as the indexical signs ?68 and ?70. These elements were later discovered to be gallium (69.2) and germanium (72) respectively. Mendeleev includes a third prediction recorded in the table as '?45' – also an indexical sign - which was later to be shown to be scandium (Sc=44.6). These are Mendeleev's three now famous predictions and sometimes known as the eka-elements: eka-boron (scandium), eka-aluminum (gallium) and eka-silicon (germanium). There is also the lesser known prediction '?180' which was later shown to be hafnium. In point (8) Mendeleev emphasises the iconic fruitfulness of his scheme in suggesting the likelihood of new chemical similarities between the elements.

In order that the elements tellurium (Te) and iodine (I) are placed with their chemical analogs it was necessary for Mendeleev to reverse their order of appearance as determined by their atomic weights. This explains point (7) where Mendeleev predicts that tellurium's atomic weight will need correcting from 128 to a value somewhere between 123 and 126. This would place tellurium in correct numerical sequence between antimony (Sb=122) and iodine (I=127). Time was to prove Mendeleev incorrect although he held that the atomic weight of tellurium to be incorrect at 128 for the whole of his life.

In time the three eka-elements were discovered: eka-aluminium (gallium) 1875, eka-boron (scandium) 1879 and eka-silicon (germanium) 1886. After these discoveries Mendeleev continued to point out the continuing fruitfulness (iconicity) of his system. For an example in his Faraday Lecture of 1889 Mendeleev refers to the problematic case of beryllium. Discovered in 1798 beryllium resembled the trivalent metal aluminium in its properties. As the formula of aluminium oxide was Al_2O_3, the formula of beryllium oxide was thought to be analogous to this as Be_2O_3. As Mendeleev (1889:650) states there was some support for this in terms of 'the specific heats of the metals and the isomorphism of the two oxides'. Nevertheless during the construction of his first periodic table (1869) Mendeleev placed beryllium with the divalent metal magnesium. On this basis the formula for beryllium oxide would be analogous to magnesium oxide (MgO) as BeO. Deciding which particular formula to support, Be_2O_3 or BeO, gave rise to what Mendeleev (1889:651) describes as 'a divergence of opinion [that] lasted for years'. The success of the iconic periodic table in correctly projecting beryllium as a divalent metal with an oxide BeO was confirmed, as Mendeleev (1889:650) describes, by 'Nilson and Petterson [who showed] the density of the vapour of beryllium chloride [to be] $BeCl_2$ [which] obliges us to regard beryllium as a bivalent metal'. With the resolution of this dispute, Mendeleev (1889:650) claims that, 'the mutual relations of the elements became more apparent than ever before' – note again Mendeleev's reliance on the concept of *relations* as described in chapter three. Finally Mendeleev (1889:650) claims that the confirmation of beryllium being divalent was as significant to the periodic table 'as the discovery of scandium'.

4.10 Conclusion

Writing in the New Scientist (12 February 1994) Dennis Rouvray states, 'chemistry without the periodic table is as hard to imagine as sailing without a compass'. This description is apt since sailing and chemistry are both practical activities engaged in voyages of discovery. This chapter has, I would argue, demonstrated the value of considering scientific representations as described by Charles Peirce's account of iconicity, being wholly integrated into the creative process of inquiry. I would argue that 'likeness' as qualified by Peirce, does not exhaust the relations of representation but helps to highlight some distinctive features of particularly fruitful kinds of representations – such as the periodic table. I would agree with Stjernfelt (2015:37) when he states that, 'Peircean iconicity is not restricted to visual nor perceptual similarity, nor to easily recognizable resemblance'. Furthermore I would argue that iconicity is about process rather than completed products. This study of Mendeleev shows that we can reformulate even constitutional questions through iconicity by focussing on relations as dynamic and dependent on particular representative purposes, rather than being all consumed with 'the' relation of representation. Through his constructions of the periodic table, Mendeleev engaged in a process of enunciating and interpreting the physiochemical relations between the chemical elements, subsequently positing undiscovered elements and revised atomic weights. Mendeleev presented his novel findings as published forms of the iconic periodic table.

Chapter Five

The Periodic Table and Iconic Robustness:

Novel questions and new predictions in the light of nature's resistance

5.1 Introduction

A precise summary of Peircean iconicity is given by Peter Skagestad (2004:254) who states, 'the value of the iconic representation, [as] Peirce repeatedly insisted, lay in the possibility it afforded of performing experiments on our thoughts, by changing some elements in the diagram and literally seeing new relations appear'. In this chapter I will introduce the term *iconic robustness* to describe how, as an iconic sign, the periodic table retains its fruitful capacity to promote thought experiments and predictions whilst also undergoing a number of reconfigurations in response to what will later be described as 'nature's resistance'. As we shall see Mendeleev's original table of 1869 underwent a number of changes, both in response to the need to better accommodate existing elements such as the rare earths, as well as to the discovery of new elements such as the noble gases. In the previous chapter a case was made for the periodic table being an iconic diagram. My hypothesis here is that the periodic table can be shown to have demonstrated iconic robustness through these various restructurings. I define iconic robustness as: the continuing capacity to generate knowledge of novel relations between the chemical elements without being thwarted by nature's resistance and within the context of a fallible inquiry. Before this, however, I will examine more closely two aspects of Mendeleev's inquiry that are relevant to my claim for iconic robustness. Firstly, how are the factors that necessitated a change in the format of Mendeleev's table characterised? Secondly, how might we describe the epistemic approach of inquirers such as Mendeleev as they encountered these factors? Encounters that changed the way the relations between the chemical elements were depicted diagrammatically, whilst not impeding the epistemic fruitfulness – the iconicity – of the periodic table.

5.2 The periodic table – nature strikes back

When an increasing force is applied to a metal or plastic it will often change shape or deform – a thin sheet of aluminium can be deformed into a useful food container – before eventually failing entirely. This section considers the 'forces' of nature at play in the form of novel knowledge that resulted in a number of 'deformations' – or changes of format – to the periodic table and the effect this had on its iconicity. Before proceeding further it is worth sketching out something on Chang's (2012a and 2012b) formulation of *active* *scientific realism* as I shall be drawing on some of the concepts he develops later in this section.

In his book *Is Water H_2O?: Evidence, Realism and Pluralism*, Chang (2012:205), having first reviewed the basis for the claim that water is H_2O states: ‘I will propose a doctrine called *active scientific realism* , which maintains that science should strive to maximize our contact with reality and our learning about it’. Where Chang (2012:205) appeals to *active realism* to ‘help make better philosophical sense of the seemingly haphazard and untidy development of the sciences of water’, my hope is that aspects of his approach will work in similar way for the development of Mendeleev’s periodic table in terms of its iconic robustness. Chang (2015a:203) formulates an operational definition of *reality* as ‘whatever is not subject to one’s will’, and of *knowledge* as ‘an ability to act without being frustrated by resistance from reality’. The metaphorical use of ‘resistance’ is further extended when Chang (2015:215) states that ‘[o]ur epistemic activities can be successful only if nature, or reality, does not prevent what we are trying to achieve’; what Chang describes as ‘nature’s *resistance*’ (emphasis in the original). As an example Chang (2012:216) argues that if an attempt to synthesise pure water by reacting exact stoichiometric quantities of hydrogen (1g) and oxygen (16g) fails, ‘this is because nature did not cooperate with our plans’ - nature has resisted or kicked back against our attempt.

It is now possible to take elements of Chang’s arguments and to apply these to the periodic table: if an attempt to accommodate a novel element or family of elements into the periodic table seemingly fails, I take this also to be a case of ‘nature’s resistance’ or kickback. Nature has refused to cooperate with our attempt to position the novel elements. Part of my argument for the iconic robustness of the periodic table is to do with the effect of nature’s refusal to cooperate, kicking back at attempts to better accommodate existing elements or to assimilate novel ones. Chang (2012:216) argues ‘knowledge can be seen as a state of ability to do things without being foiled by significant resistance from reality’. I will argue that novel knowledge is gained when this initial resistance seemingly fades as a result of our intervening in some way. In the case of Mendeleev’s inquiry, such interventions will be shown to take the form of a reconfiguration of the periodic table, but with no loss in its epistemic fruitfulness and capacity to promote further thought experiments. It is through such interventions that Mendeleev and others sought to engage in an intelligent way with nature’s resistance.

Examples of the resistance nature offered at various times include: the taxing problem of accommodating the rare earths element and the discovery of novel elements such as the noble gases. Notwithstanding Mendeleev's success in first accommodating the sixty or so known elements as well as his subsequent successful predictions of the three eka-elements, nature was later to 'kick back' at his system. Nature resisted Mendeleev by presenting a number of elements he was at first unable to place. I will show that the periodic table demonstrated iconic robustness in that whilst it required reconfiguration in order to meet nature's resistance, it remained productive in its capacity to suggest new lines of inquiry and to pose new questions. The periodic table demonstrated a capacity to push back against nature's resistance as atomic weights were recalibrated and new elements accommodated; all might be described as the effects of nature's kickback. To take a metaphor from the study of materials, the periodic table demonstrates a capacity for 'plastic deformation'. For example, nature kicks back in the form the newly discovered element argon. The subsequent new inquiry into the discovery of the noble gases involves a new set of experiments performed on the iconic periodic table which reveals novel relations between the chemical elements. The periodic table undergoes a deformation or change in format as a result but without fracturing completely or loss of iconicity.

In an unpublished MS 693 (1904) Peirce states: 'knowledge is a plastic, applicable stuff, - a putty whose solid part, the barytes or the lead, is the percepts[57], of which more and more is worked up in the oil of reflection'. The persistence of percepts is here likened by Peirce to the great power of lead and the mineral barytes in resisting corrosive chemical reagents such as the mineral acids. With the periodic table, 'percepts' might be likened to those elements which, unable to be accommodated within the scheme, force their way into Mendeleev's consciousness. The periodic table responds as 'plastic applicable stuff' to Mendeleev's as he analyses and makes judgements on the problem of elements such as the rare earths; an effect of the 'oil of reflection'. In the next section I should like to examine the second aspect linked to the periodic table's iconic robustness: the epistemic approach adopted by Mendeleev and others as they reflected on nature's resistance. A definition of iconic robustness will be offered towards the end of the chapter once the case studies have been explored.

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[57] The term *percept* is one Peirce uses as part of his account of perception. Sandra Rosenthal (2004:193) explains that for Peirce 'all knowledge begins with perception'. Thus perception is essential for any scientific inquiry such as Mendeleev's. A percept, Rosenthal (2004:194) continues 'is that sensory element which is presented in perceptual awareness' which in turn 'instigates the formation of perceptual judgement'. As a sensory element, a percept, Catherine Legg (2014:100) argues, 'compels my thinking insofar as I cannot pretend that it is not present in my consciousness'.

5.3 An epistemic approach to facing nature's resistance

My term iconic robustness also works off Peirce's conception of fallibilism. I will argue that, during the development of the early periodic table, Mendeleev demonstrates a generally fallibilist approach. Such an approach was also taken by William Ramsay (1852 – 1916) in his positioning of the noble gases into Mendeleev's scheme. Later in the chapter and through the case studies I will argue that a fallibilist approach is significant to formulating a definition for iconic robustness. Firstly I should like to set out the concept of *fallibilism* as established by Peirce.

The purpose of science, Peirce argues, is 'to learn the lesson that the universe has to teach'. He likens the process to journeying across the landscape of knowledge where on occasion,

> [T]he solid ground of fact fails… [and]…from that moment [our] position is only provisional…[we] must then find confirmations or else shift [our] footing. Even if [we do] find confirmations, they are only partial. [We are] still not standing upon the bedrock of fact. [We are] walking upon a bog, and can only say, this ground seems to hold for the present. Here I will stay till it begins to give way. (EP2:55, 1898)

Taking up Peirce's analogy, during the course of an inquiry we are never in a position to claim to have reached the epistemic equivalent of *terra firma* – the absolute end of inquiry. We must be open to new discoveries which may unsettle our position and prompt further inquiry. Fallibilism, claims Houser (2006:13), 'is the understanding that no matter where we are in our journey and no matter how solid the ground may feel beneath our feet, at any time it may begin to give way'. Thus from a fallibilist position, our beliefs about the world are provisional in the likelihood that new facts will come to light and challenge our beliefs. New facts are likely to initiate a new inquiry and a subsequent revision of our beliefs.

Such a fallibilist understanding can be detected in Mendeleev's early writings on the periodic table. For example, Mendeleev notes that similar elements such as iron, cerium, palladium and platinum have very similar atomic weights, while this is not the case for other similar elements such as lithium, sodium and potassium which present marked differences in atomic weights. This caused Mendeleev (1869a:37) to question the 'solidity of the ground beneath his feet' and to recognise a need to shift his footing, for he states: '[p]erhaps, as a consequence of the closer study of these groups, the system of elements arranged in groups will have to be changed'. Mendeleev recognises the possibility of adjusting the arrangement of groups within his scheme.

There are echoes here of Peirce's view that a commitment to fallibilism 'requires a man to be at all times ready to dump his whole cart-load of beliefs, the moment experience is against them' (CP 1.55, 1896). The early periodic table of 1869 demonstrates the provisional state of Mendeleev's knowledge. The rare earth elements were not fully positioned within the scheme. Later the discovery of argon and the other noble gases would present their own challenge to Mendeleev's table. Peirce justifies a fallibilist approach when he states that 'knowledge is never absolute but always swims, as it were, in a continuum of uncertainty and of indeterminacy' (CP 1.171, 1879). Knowledge of the chemical elements, with the possibility of new members being discovered and adding to those already known, might be said to present such a case of uncertainty and indeterminacy. We saw in chapter four an example of Mendeleev's fallibilist approach: he accepted the first attempt of 1869 was not final implying the possibility of future change. We shall see how as Mendeleev's enquiry unfolds, each revised configuration of the periodic table is taken as provisional, a fallible representation of the relations between the chemical elements.

During this chapter and via a series of case studies I will seek to develop the term iconic robustness in relation to the periodic table with respect of two factors. Firstly in relation to the way it pushed back against 'uncertainty and indeterminacy' – the effect of 'nature's resistance' – whilst continuing to function as an iconic representation by disclosing new relations. Secondly in relation to the nature of the inquiry: I will argue that iconic robustness is dependent upon a representation being part of a fallibilist inquiry. Christopher Hookway (2003:119) argues that 'the Peircean [fallibilist] model hopes to account for false belief and reference by placing an individual judgement within an indefinitely large inclusive context of thoughts within which other (actual or possible) thinkers can correct and revise our current fallible opinions'. I will show how Mendeleev and Ramsay adopted such an approach in being prepared to correct and adapt their opinions on how the relations between the chemical elements are depicted diagrammatically. What follows are two case studies. Firstly, Mendeleev's attempt to accommodate the rare earth elements. Secondly, the issues surrounding the correct positioning of the noble gases within Mendeleev's scheme will be examined. These are contrasting studies in that the rare earths were known at the time of Mendeleev's first published attempt of 1869 where the noble gases were discovered later. Through these cases and in the light of Peirce's fallibilism and supported by aspects of Chang's (2012a) *active (scientific) realism* I will attempt to demonstrate iconic robustness as it applies the periodic table. Here I am referring to Chang's (2012) operational definition of reality, which is his response to the debate around scientific realism[58]. Chang (2012:217) proposes an active doctrine, 'which affirms that science should strive to maximize our contact with reality in order to learn as much as we can'. As we will see Chang takes reality – the world in which we live – as being whatever is not subject to our own will and capable of offering resistance to our plans and to our beliefs. I will conclude the chapter with definition of iconic robustness constructed via these sources.

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[58] An exhaustive account of the issues around scientific realism lies beyond the scope of this thesis. Anjan Chakravartty (2017) states: 'Scientific realism is a positive epistemic attitude toward the content of our best theories and models, recommending belief in both observable and unobservable aspects of the world described by the sciences.'

5.4 The rare earth elements[59]

As a part of the acknowledgements to his book, *Episodes from the History of the Rare Earth Elements* (1996), Christopher Evans notes that, 'relatively few scholars [are] working in the subject area covered'. Perhaps the most detailed scholarship of recent times is that of Pieter Thyssen and Koen Binnemans (2013 and 2015). The rare earth elements were known at the time of Mendeleev's first attempt (1869) at systemising the elements and presented a particular challenge in that they did not fit easily in to Mendeleev's scheme. What will later be described as the 'rare earth crisis' might be taken as an example of nature's resistance to Mendeleev's scheme. By way of response Mendeleev was prepared and willing to adjust his scheme in an attempt to maintain the rare earths as intelligible and coherent elements within his system. I will argue that the periodic table remained an iconic representation notwithstanding the reconfiguring required to adapt to these troublesome elements. Furthermore I will argue that in effecting these changes Mendeleev adopted a fallibilist approach.

5.4.1 The rare earth elements and Mendeleev's *Attempt* of 1869

The rare earths were included in Mendeleev's first *Attempt* which we met in the previous chapter and shown again below. One of the problems Mendeleev faced was that the rare earth elements were difficult to extract in a pure form which made an accurate determination of their atomic weights problematic. Atomic weights were determined in part by knowing an element's valency. The values used by Mendeleev assumed the rare earths to be divalent; this later proved to be incorrect. This was not a problem peculiar to the rare earth elements; the atomic weights of other elements such as thallium, lead and uranium had also been wrongly determined.

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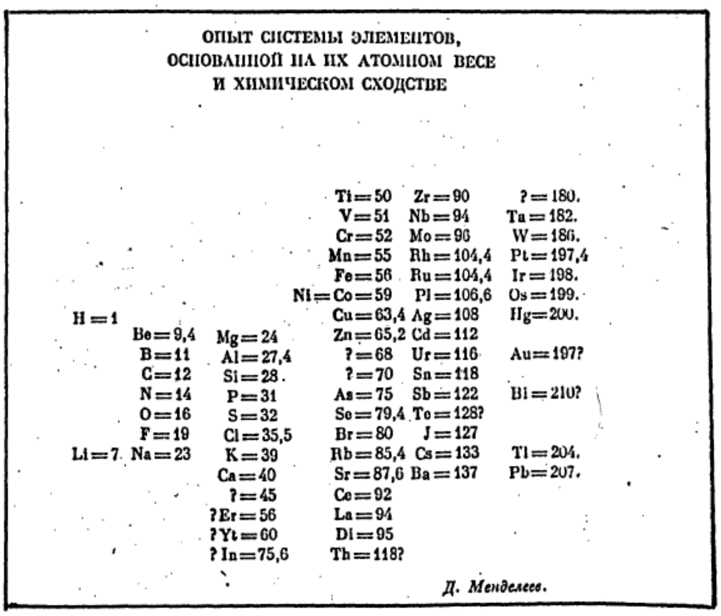
[59] There is an irony in the part played by the rare earths in the history of the periodic table. The prediction of eka-boron, and its subsequent discovery as scandium by Nilson in 1879, is often considered as one of the events that gave support to Mendeleev's scheme. Today's chemists often find it convenient to classify scandium as a rare earth – the very set of elements Mendeleev found so difficult to position.



ОПЫТ СИСТЕМЫ ЭЛЕМЕНТОВ,
ОСНОВАННОЙ НА ИХ АТОМНОМ ВЕСЕ
И ХИМИЧЕСКОМ СХОДСТВЕ

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28.	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	J=127	
Li=7.	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

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The elements are arranged as six vertical columns in order of increasing atomic weight. This gives nineteen horizontal rows of elements of relatively similar physiochemical properties.

At the bottom of the table are seven elements: indium (?In=75.6), and thorium (Th=118?) plus the five rare earths, erbium (?Er=56), yttrium (?Yt=60), cerium (Ce=92), lanthanum (La=94) and didymium (Di=95).

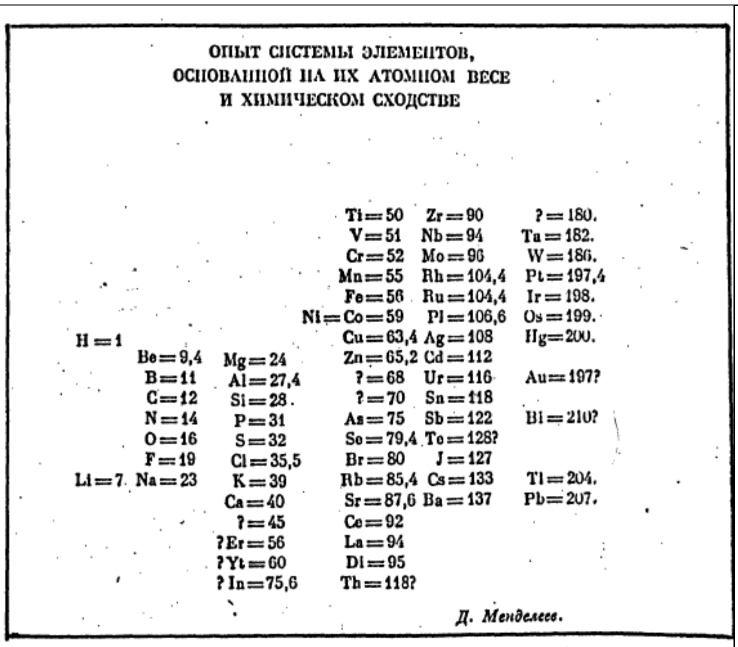
The element shown as ?45 is Mendeleev's prediction of eka-boron later to be identified as scandium

Figure 39: Mendeleev's first table as a single sheet handout, 17th February 1869
Source: *Persistence and Periodicity: a study of Mendeleev's contribution to the Foundations of Chemistry* by John Russel Smith, PhD thesis Chelsea College, University of London 1976, page 217

Two months after the circulation of his *Attempt,* Mendeleev's paper 'On the Correlation of the Elements' and their Atomic Weights was read to the Russian Chemical Society, and subsequently published in the society's *Zhurnal Russkoe Fiziko-Khimicheskoe Obshchestvo* (1869). It is here that Mendeleev argues for atomic weight being an element's defining characteristic regardless of whether that element exists in its free state (such as elemental magnesium) or as one of its compounds (magnesium combined with oxygen in the form of magnesium oxide). One piece of empirical evidence in support of Mendeleev's first *Attempt* is that ordering the elements by atomic weight produces groups that accord with known sets or families of elements with similar chemical properties, such as the alkali metals (Li, Na, K, Rb, Cs) and the halogens (F, Cl, Br, J [I]). Mendeleev's (1869a:35) fallibilist approach is evident in stating himself to be 'quite conscious of the fact that this attempt is not final' adding that 'in many cases there still exist strong doubts regarding the place of such element as have not been sufficiently investigated'. In general, whilst elements of low and stable atomic weights had been relatively well studied, this was not so for elements of higher atomic weight. Unsurprisingly therefore Mendeleev (1869a:37) adds that for elements of less stable atomic weights, 'there exists quite understandably, complete uncertainty' as to their position within the scheme – adding that 'among these are, for example, yttrium, thorium and indium' – all three elements forming part of what will later be described as the *rare earth crisis* (Thyssen and Binnemans, 2015). Mendeleev (1869a:30) demonstrates a fallibilist approach when he states that although there 'does not exist a single universal principle, capable of withstanding criticism' whereby the elements might be ordered, there are nonetheless some groups of elements that 'form a whole and represent a natural order' – that is, sets of element long known to have similar chemical properties. As examples of these natural groups Mendeleev (1869a:30) cites the 'halogens, the alkaline earth metals' adding also the rare earths which he describes as 'the companions of cerium'. Whilst recognising the rare earth elements as a natural group, Mendeleev is unsure where to place them. He eventually settles in his first *Attempt* for a block at the bottom of what is sometimes known as the 'long form' of the table.

Looking at the arrangement above, the positioning of these seven elements is not ideal for they interrupt the general increase in atomic weights on which the table is founded. The disruption caused by the rare earths is explained by Thyssen and Binnemans (2011:10) in that, if omitted completely, the sequence of atomic weights 'would have passed from the unknown element with an atomic weight of 45 to titanium with an atomic weight of 50, and from strontium with an atomic weight of 87.6 to zirconium with an atomic weight of 90, completely in accordance with the gradual increase in atomic weight'. Whilst natural groups such as the halogens fitted Mendeleev's scheme he found the rare earths more problematic to position. Throughout this early paper, and in addition to the uncertainties noted above, Mendeleev describes a number of possible changes that might be made to improve the arrangement of the elements as tabulated in his original *Attempt*. Notice too in the following discussion how Mendeleev's table functions iconically and in accord with the third key aspect of iconicity from chapter four: Mendeleev's processes of reasoning being predicated on the iconicity of the periodic table in proposing different arrangements of the elements.

In the coming section I will argue that Mendeleev's earliest periodic table (1869, figure 39) demonstrated iconic robustness by undergoing change - analogous to plastic deformation - in order to absorb and accommodate the impact of nature's resistance in the form of the rare earth elements. In response to the challenge offered by these elements we see Mendeleev engaging with his iconic representation and adjusting the structure of his table to establish new relations between the chemical elements. As Thyssen and Binnemans (2015:166) argue 'both the transition metal groups (iron, palladium and platinum group) and the rare-earth groups (cerium and erbium group) exhibited a transitional function'. On this basis Mendeleev suggests the following restructuring of his table as a possibility. The table is reproduced again (figure 40) to make the argument easier to follow.



ОПЫТ СИСТЕМЫ ЭЛЕМЕНТОВ,
ОСНОВАННОЙ НА ИХ АТОМНОМ ВЕСЕ
И ХИМИЧЕСКОМ СХОДСТВЕ

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	J=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

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Mendeleev notes that the early elements of the fourth column (Mn, Fe, Co, Ni, Zn) form a 'transition' to later members of the third column (Cl, K, Ca). Thus the atomic weights of Co, Ni, Cr, Mn and Fe represent a 'transition' from Cu and Zn to Ca and K. Having made this connection Mendeleev (1869a:37) states that 'perhaps for this reason *their positions will have to be changed'* (emphasis added). These elements might be better placed, 'in the lower rows instead of the upper rows, then one would obtain three columns here which would, in many respects, exhibit similarities'. This *change* he explains would give three columns of elements with similar properties: Co, Ni, Cr, Mn, Fe, also Ce, La, Di, Pl, Ru, Rh and thirdly Pt, Ir, Os

Figure 40: Mendeleev's first table as a single sheet handout, 17th February 1869
Source: *Persistence and Periodicity: a study of Mendeleev's contribution to the Foundations of Chemistry* by John Russel Smith, PhD thesis Chelsea College, University of London 1976, page 217

Here Mendeleev – reasoning by engaging with his iconic representation – is setting out changes that would, if carried out, result in a significant restructuring of his table. There are a number of other similar and far-reaching changes described in some detail by Mendeleev. On each of these occasions the periodic table demonstrates its iconic capacity in being integral to Mendeleev's thought processes and reasoning as he attempts to assign the chemical relations between the rare earth elements and the wider elements in general. Throughout the course of these changes, brought about by the resistance offered by the rare earth elements to Mendeleev's scheme, the periodic table demonstrates its iconic robustness: it 'flexes' to accommodate Mendeleev's proposals whilst making both the new relations visible and inferring the possibility of new relations.

In commenting on the possible changes to reposition the rare earth elements Mendeleev adopts a fallibilist position. He also retains a belief in his iconic table's capacity to respond to the changes he is proposing whilst retaining its ability to reveal new knowledge; its iconic robustness. Take for example this statement made by Mendeleev (1869a:37) at the time of presenting his first *Attempt* to the Russian Chemical Society in March 1869,

> The system of elements proposed here is, of course, *not to be considered as completely closed*, but it appears to me to be based upon such data and such natural approximations, that its existence can hardly be regarded as doubtful; for the numbers confirm the similarities which result from the study of the compounds of the elements. (emphasis added)

A fallibilist approach is suggested in Mendeleev recognising the scheme not to be 'completely closed'. To draw again from Chang's (2012a:221) active realism: '[b]ut what reality does, or what it allows us to do, is not governed by how we explain or predict what happens'. Through the periodic table Mendeleev tests an aspect of reality: the relations between the chemical elements. Reality on the other hand is 'not governed by how we explain or predict what happens' – our descriptions are likely to be an incomplete representation of the world; Mendeleev accepts for his part that his table is not 'completely closed'. Notice too that Mendeleev's mention of 'natural approximations' and 'similarities' captures Peirce's fallibilist approach discussed earlier in that our knowledge is never absolute for a degree of uncertainty and of indeterminacy always exists. Notwithstanding the 'incompleteness' of the periodic table at this stage Mendeleev continues to demonstrates its iconic robustness by emphasising its ability to point towards new relations. Put another way, by 'the direct observation' of his periodic table, Mendeleev is able to demonstrate that 'other truths concerning its object can be discovered than those which suffice to determine its construction' (CP 2.279, 1895) – the second criterion of iconicity developed in the previous chapter.

Returning to figure 40, in the light of a number of elements with properties similar to the metals iron, cerium, palladium and platinum, Mendeleev (1869a:37) argues that as a result, 'the system of elements arranged in groups will have to be changed such that in certain parts of the system the similarity between members of the horizontal rows will have to be considered, but in other parts, the similarity between members of the vertical columns'. The periodic table flexes again – but Mendeleev continues to emphasise its continuing iconic robustness as able to reveal new truths concerning the relations between the chemical elements. Mendeleev (1869a:37) proposes ‘three [new] columns which… in many respects, exhibit similarities’ – new (iconic) relations revealed as – ‘one column containing cobalt, nickel, chromium, manganese and iron; a second column containing cerium, lanthanum and didymium, palladium, rhodium, ruthenium and, lastly a third column containing platinum, iridium and osmium’. New configurations open up the possibility of new relations between the periodic table’s chemical objects whilst simultaneously demonstrating its iconic robustness, its epistemic fecundity.

The critical interplay between Peirce, inquiry, the fruitful nature of scientific representations and iconicity is captured precisely by Chiara Ambrosio (2014:256) when she writes,

> In emphasizing the iconic nature of scientific representations, Peirce seemed to suggest that a key characteristic of the representative tools and practices constructed and used by scientists is their fundamental fruitfulness, and indeed it is this fruitfulness that distinguishes iconic representations from indexical and symbolic ones.

In experimenting on his representation Mendeleev is generating new knowledge – the table is proving to be *fruitful.* By this measure Mendeleev’s periodic table is an iconic representation. The periodic table’s iconic robustness is evidenced by its capacity to respond to nature’s resistance whilst pointing towards new relations between the elements of its construction.

5.4.2 Mendeleev’s table of 1871 - another attempt to solve the rare earth problem

The British chemist, historian of chemistry and later head of the Caius Laboratory at Cambridge, Matthew Pattison Muir (1848–1931), was an undergraduate at the time of Mendeleev’s early publications. In the year Mendeleev died Pattison Muir described his paper ‘The Periodic Regularity of the Chemical Elements’ (1872) as ‘one of the most important contributions ever made in the advancement of accurate knowledge of natural phenomena’[60]. This particular paper was published in Liebig’s journal *Annalen der Chemie und Pharmacie*[61] and it is this paper which William Jensen (2002:21) claims, ‘defined the periodic law and table for the rest of the 19th century and which served as a primary

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[60] Cited Kaji, M. Kragh, H. and Pallo G. (2015:87)

[61] D. Mendeleejeff, ‘Die periodische Gesetzmässigkeit der chemischen Elemente’ (The Law of Periodic Regularity of the Chemical Elements), *Ann. Chem. Pharm.*, 1872, Suppl. 8, 133-229.

reference for western chemists'. Also by way of recognition, in 2012 the Division of the History of Chemistry of the American Chemical Society's Citation for Chemical Breakthrough was given to St. Petersburg State University for this particular paper of Mendeleev's. This paper, explains the American chemist and historian of chemistry David Lewis (2014:4), 'was a German translation… of the paper that had already appeared in the [Russian journal] *Zhurnal*[62]' the year before (1871). The German journal *Annalen* had a much wider readership than its Russian counterpart. It is the English translation of Mendeleev's *Annalen* paper that will be referred to here, as published in Jensen (2002). The historian of chemistry Ferenc Szabadváry (1988:71) explains Mendeleev's new attempt at dealing with the problem of the rare earth elements as follows:

> The table which appeared in 1871 is already in the usual form. In this year Mendeleev performed an important change - arbitrarily - with rare earth elements: he assumed that they were trivalent, and correspondingly recalculated their atomic weights, that is, instead of YO and LaO he calculated with Y_20_3 and La_20_3. He then listed yttrium with an atomic weight of 88, lanthanum with 137 and cerium with 138.

As will become apparent Mendeleev alters the way the table is set out with the chemical groups appearing as vertical columns and the periods as horizontal rows – as is the case today. Importantly he assigns new values to the atomic weights of the rare earths which results in a re-positioning of these elements within the table. Having set out the rationale for his system Mendeleev (1872:56) states:

> No natural law acquires any scientific importance unless it introduces, so to speak, some practical consequences – in other words, unless it admits of logical conclusions which explain the unexplained, point to previously unknown phenomena, and especially if the law produces predictions which can be confirmed by experiment.

The periodic table is the diagrammatic representation of the 'natural law' Mendeleev is referring to here. By assigning to the table such characteristics as the capacity to 'explain the unexplained', to 'point to previously unknown phenomena' and in 'making predictions

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[62] D. Mendeleev, *Estestvennaya sistema elementov iprimenenie ee k ukazaniyu svoistv nekotorykh elementov*. (The natural system of the elements and it application in the prediction of the properties of certain elements), *Zh.Russ. Fiz.-Khim. O-va.*, 1871(3): 25-56.

which can be confirmed by experiment', Mendeleev is making a claim for the new table's continuing ability to reveal unexpected truths, for its iconic nature. The periodic table will, states Mendeleev (1872:56), 'stimulate the completion of the newer areas of science', and lists the following four applications,

> To the determination of the atomic weights of insufficiently studied elements;
> To the determination of the properties of presently unknown elements;
> To the correction of the magnitude of atomic weights;
> To the completion of our knowledge of the forms of chemical combination;

As Mendeleev's table develops and reconfigures it retains its fruitful capacity to promote thought experiments in these four areas. This I claim is evidence for the periodic table's continuing iconicity – the capacity to indicate new research questions. Some insights into Mendeleev's (1875:47) thought experiments are given by his 'determination of the atomic weight' of cerium as an 'insufficiently studied element', which I discuss in the next section.

5.4.3 Recalibrating cerium's atomic weight – Mendeleev's thought experiment

The element cerium was earlier believed to have an equivalent weight of approximately 45 – in common with lanthanum and didymium. With identical valencies this resulted in these rare earth elements having near identical atomic weights[63]. Each element is obtained from the same source (cerite), and difficult to extract in a pure form. As a result their atomic weights are difficult to assign with precision. In seeking to recalibrate cerium's atomic weight Mendeleev (1872:71) offers the following thought experiment: 'if CeO is accepted as the formula of the ordinary suboxide, then Ce = 92 [the value in the first table of 1869]', but, 'if one accepts the formula Ce_2O_3 for the suboxide, then Ce = 138 [the value in the new table]'. The valency of cerium changes as a result from two to three. This is an example of a form of change Szabadváry earlier in this chapter was seen to judge as 'arbitrary'. As Mendeleev (1872:72) concedes, 'in attributing this composition of the highest oxide one is still *assuming* an oxide of the formula Ce_2O_3, though this has not yet been obtained and none of its independent salts are known' (emphasis added). In the case of the changes made to the atomic weights of ytterbium and erbium Mendeleev (1872:76) states, 'there are at present no available facts to confirm the correctness of these modifications'. Nevertheless, by changing the valencies of the rare earth elements from two (CeO) to three (Ce_2O_3), Mendeleev's thought experiments offered revised values for their atomic weights.

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[63] Atomic weight = equivalent weight x valence

These elements were then each placed within a reconfigured table – but now no longer as a common group as was the case in the first Attempt of 1869 but distributed between groups III and IV. Three of the five rare earths are positioned in Group III (Yt, 88; Di, 138, Er, 178) and the other two in Group IV (Ce, 140; La, 180) although the question marks against each of these elements indicates that uncertainty remains – as can be seen in figure 41:

Mendeleev's thought experiments on atomic weights – Group IV revised to include the rare earths cerium and lanthanum (indicated below)

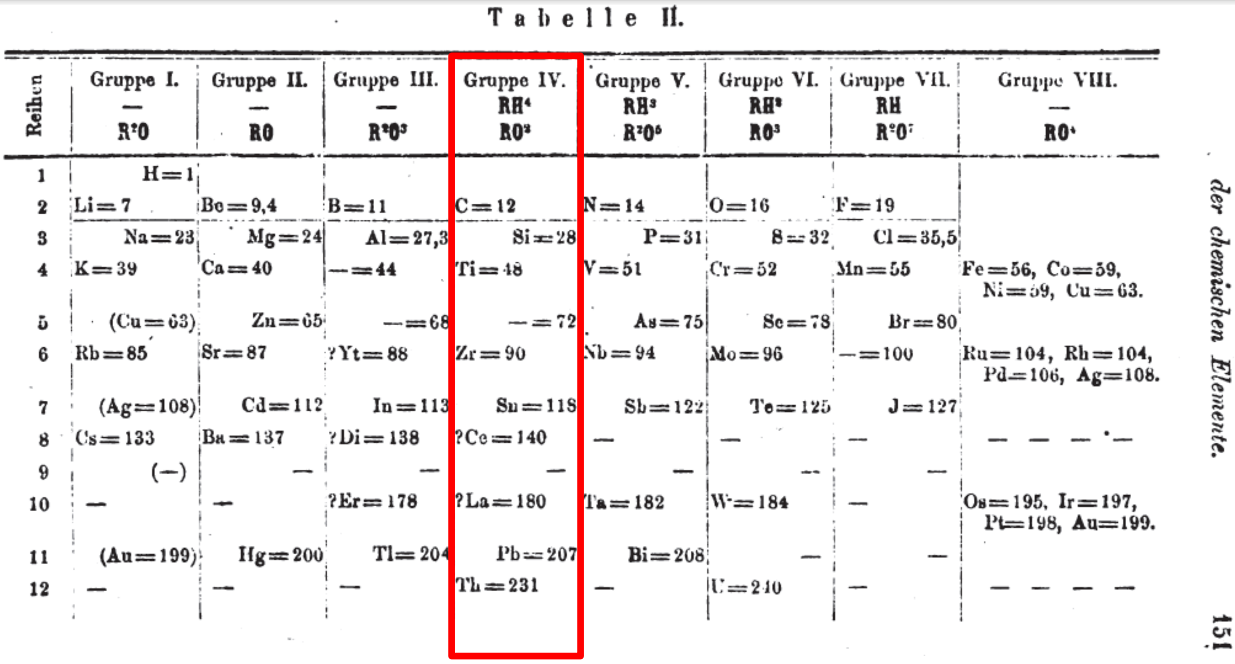

Tabelle II.

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

der chemischen Elemente. 151

Figure 41: Mendeleev's Table II from 1872
Source: page 151 of D. Mendeleejeff, *Die periodische Gesetzmässigkeit der chemischen Elemente*. Ann. Chem. Pharm., 1872, Suppl. 8, 133-229.

By assuming cerium's higher oxide to be CeO_2, with a corresponding valency of four and atomic weight of 138, Mendeleev then justifies placing cerium in Group IV as indicated in figure 41: Ti, Zr, Ce, La, Th. These new changes in the table's overall configuration do not impair its iconic capacity to reveal novel knowledge. This can be seen in Mendeleev's further thought experiments upon the new relations established by the re-positioning of the elements – for example the likely effectiveness of CeO_2 as a chemical base. The Group IV dioxides – the cerium analogues – are: TiO_2, ZrO_2, CeO_2, LaO_2 and ThO_2. Mendeleev argues (1872:72) that CeO_2 is likely to be 'weakly basic' on the grounds that 'it is placed in the fourth group after TiO_2, with very indistinct basic properties, and after ZrO_2, whose basic character is more pronounced'. Here again, notwithstanding this new arrangement of the elements, the revised table of 1871 demonstrates its iconic robustness: retaining its iconic power of pointing towards new knowledge – in this case the likely basicity of CeO_2.

Mendeleev did not solve the *rare earth crisis* and after 1872 his attention turned to researching the properties of gases and the nature of the luminiferous ether. It is Thyssen's and Binnemans's (2015:156/170) somewhat triumphalist view that Mendeleev, 'definitely grasped the essence of the subject-matter better than any other chemist at the time' and that during this period he 'loved to give his thoughts free rein and he had all faith in the successful future development of his system'. A system which Gordin (2004:50) summarises as follows: 'In 1871 Mendeleev thought of the periodic system as a tool that not only formulated all of current chemistry, *but also generated research questions to ground a research school'* (emphasis added). It is partially this *generative* capacity that demonstrates the continuing iconicity of the periodic table during this time of development and readjustment. It is this capacity for generating new questions within the context Mendeleev's fallibilist inquiry that demonstrates the periodic table's iconic robustness. Whilst Thyssen and Binnemans's claim for Mendeleev appreciating the problem of the rare earth elements 'better than any other chemist' is perhaps rather overstated, he did develop a diagrammatic representation capable of prompting a number of conceptual possibilities as to how the *rare earth problem* might be solved.

There are other strong Peircean connections to Mendeleev's inquiry that are worth mentioning at this point. In addition to induction and deduction, Peirce argues that scientific inquiry also involves 'abduction' and characterised as 'the process of forming an explanatory hypothesis' and as 'the only logical operation which introduces any new idea; for induction does nothing but determine a value, and deduction merely evolves the necessary consequences of a pure hypothesis' (CP 5.171, 1903). In the seventh of his *Harvard Lectures on Pragmatism* (1903) Peirce comments on Mendeleev recognising both the need to alter atomic weights in order to fit some elements into his scheme, as well as his successful predictions of the eka-elements. By applying methods such as these to arrive at the periodic law, Peirce states, 'the anticipation that such [the periodic law] might be the truth, not amounting to a positive assertion yet by no means sinking to a recognition of bare possibility, was the Abductive conclusion' (PPM:283). There are two points here that relate to Mendeleev's form of reasoning and to his overarching approach to inquiry. Firstly by abductive reasoning Mendeleev was able to discover his particular view of chemical relations: the periodic law. By abductive logic and diagrammatic reasoning – Peircean methods of gaining knowledge – Mendeleev sought to give a sense of meaning to his hypothesis through his table. Whilst his hypothesis of the periodic law continued to align with the empirical data, the table remained secure. Secondly Mendeleev demonstrates

Peirce’s fallibilist methodology in that he positions the periodic table between the twin outliers of ‘positive assertion’ and ‘bare possibility’. The iconic robustness of Mendeleev’s table is grounded in its continuing fruitfulness in pointing out new relations between the chemical elements within the context of his fallibilist inquiry, reconfiguring in response to nature’s resistance.

5.5 The noble gases

Around twenty-five years later, with the discovery of argon, Mendeleev appeared to depart from his fallibilist approach believing his table to be unable to accommodate this new element. In their essay ‘Epistemological and Ontological Status of Chemical Relations’ (2010), Andrés Bernal and Edgar E. Daza (2010:97) argue that Mendeleev denied argon as an element ‘in an attempt to protect his oeuvre’ with the main issue being ‘not whether noble gases could exist in absolute terms, but if they existed within the scope of chemistry’. By this stage the periodic table appears to have ossified, at least for Mendeleev, who takes a stand of protective entrenchment. Argon and the other noble gases represent a further instance of nature’s resistance to Mendeleev’s system. Whilst Mendeleev initially stepped aside from accommodating these novel elements into his scheme, William Ramsay and Lord Rayleigh took a different approach. Their attitude to nature’s kickback falls within Chang’s (2012a:216) account of how, ‘we go on learning, doing humble inductions, but also expecting that something can always go wrong and eventually will; when it does, that will be the start of another episode of inquiry’. This new episode of inquiry forms the next section.

5.5.1 Argon: a new element makes its first appearance

An early indication of nature’s resistance to the periodic table in the form of the noble gases is given in Rayleigh’s letter published in the journal *Nature* (1892). Here Rayleigh reports his work on the density of nitrogen. In particular he comments on the discrepancy he discovered in the density of nitrogen when produced by two different methods. In the first nitrogen is extracted from the atmosphere by removing first the oxygen with heated copper and then the carbon dioxide by reacting it with potash (potassium carbonate). The remaining gas, thought to be impure nitrogen, was then dried, passed through the cycle again and finally dried in turn by sulphuric acid, potash and phosphoric anhydride. Great care was taken to ensure the final volume of gas collected was considered to be pure nitrogen and free from oxygen, carbon dioxide and water vapour.

The second method, which Rayleigh attributes to Ramsay, is similarly exact but in place of the heated copper the air is mixed with ammonia which in turn reacts with atmospheric oxygen to yield nitrogen and water. The resulting product is dried and is a sample of nitrogen gas from two sources: the atmosphere and the product of the reaction between oxygen and ammonia. The samples of nitrogen from each method should have the same density. In his letter Rayleigh (1892:512) notes two different values, 'the relative difference, amounting to about 1/1000 part' which he comments, 'is small in itself; but it lies entirely outside the errors of the experiment, and can only be attributed to a variation in the character of the gas'. The density of the nitrogen prepared by the second method was found to be 1/1000 less than the value for the first, where the sole source of the nitrogen is atmospheric air. It is in such surprising results – in clashes with reality - that Chang (2012:xix) offers the pragmatist's standpoint whereby 'reality offers resistance to our ill-conceived schemes' and that this sometimes led to the creation of knowledge, in this case the discovery of a new chemical element.

We see here too Peirce's continuing interest in chemistry and in argon in particular. In an unpublished paper on the noble gases Peirce, in admiration of Rayleigh's achievements, asks the following rhetorical question: '[w]hat, please dear reader, would any but a very superior man have done about that minute discrepancy? He would have pooh-poohed it, minimising it, tried to ague it away'. After describing Rayleigh's approach – the very reverse of trying to argue away discrepancy - Peirce concludes that 'it follows that the atomic weight of argon is 40 or thereabouts; or very nearly the same as potassium. It is, thus, very unlikely that it is nitrogen' (MS1037 c1890). This surprising if small discrepancy in the density of nitrogen discovered by Rayleigh also connects to two other Peircean themes. Firstly in his essay 'The Fixation of Belief' (1877) Peirce explains how inquiry is prompted by such a surprise result which in turn fosters a sense of doubt. For, as Peirce states, 'the irritation of doubt causes a struggle to attain a state of belief' adding, 'I shall term this struggle inquiry' (EP1:114). The purpose of inquiry is, Peirce continues, to overcome such doubts as a means of 'settling belief' (EP1:116). The further inquiry into the noble gases by Ramsay, Rayleigh and others might be interpreted being in search of 'settling' their belief in the composition of the atmosphere and eventually in a new group of chemical elements. Secondly in his classification of signs, Peirce argues that one way indexical signs function is by compelling our attention:

> A rap on the door is an index. Anything which focusses the attention is an index. Anything which startles us is an index, in so far as it marks the junction between two portions of experience. (CP 2.286, 1897)

The 'surprising' discovery of the differences in density of nitrogen, according to how it had been generated, acted as an indexical sign by drawing Ramsay's attention to the possibility of a new and undiscovered gas. With hindsight it is possible to explain Rayleigh's two different results in terms of the existence of argon in the atmosphere. In the second method 'nitrogen' is prepared as from the atmosphere contaminated with argon to which nitrogen from the chemical reaction of ammonia and oxygen has been added. This sample contains proportionately more nitrogen than that produced by the first method and so has a lower density given that the density of argon is approximately 1.4 times that of nitrogen.

Some two years after Rayleigh's letter appeared in *Nature*, Ramsay and Rayleigh made a public announcement of their discovery of argon in August 1894 at the British Association meeting in Oxford. On hearing of their discovery, Michael Gordin (2004:210) records Mendeleev telegramming Ramsay, '[d]elighted at the discovery of argon. Think molecules contain three nitrogen bound together by heat'. It is Gordin's view that Mendeleev had 'resisted a novel discovery in chemistry that could be interpreted as violating his periodic law'. Mendeleev's table was at that time unable to accommodate an element with an atomic weight of 40. If the atomic weight proved correct argon would need to be placed between chlorine and potassium. Such a position didn't exist, for unlike the famous three successful eka-elements, Mendeleev had made no prediction for an element of atomic weight 40.

Mendeleev's response, if Gordin's view is accepted, is an attempt to face down nature's *resistance* to his scheme in the form of this newly discovered element. To be fair to Mendeleev, his suggestion of 'three nitrogen' or N_3 (an analogue to ozone, O_3) was not a unique position to hold with respect to argon. The chemist and historian John Wolfenden (1969:570) has pointed out that the suggestion that argon was an allotropic form of nitrogen (N_3) had also been made by the Scottish chemist and physicist James Dewar (1842 – 1923) in a letter to the *Times* published on 16th August, 1894. In fact Dewar wrote two letters dated 15th and 16th August 1894 which were subsequently reprinted in *Chemical*

News (1894) where he makes the case for 'argon' as triatomic nitrogen. In the second letter[64] Dewar concludes,

> It is not for the first time that chemists and physicists have been tempted to believe in the production of an allotropic form of nitrogen, and to accept it as explaining certain curious phenomena, but hitherto the assumption has always broken down on more careful investigation. This time we may be permitted to hope that the elusive allotropic form has been fairly captured.

Unlike Mendeleev, Dewar was probably less concerned with the problem the discovery of argon might present for the periodic table but with his own experiments on the liquefaction of air. In a presentation to the Chemical Society later that same year, Dewar (1894:300) in a paper on this same topic claims that when recording the temperature at which two samples of liquid nitrogen evaporated, '[n]itrogen obtained from atmospheric air has been compared in this manner with nitrogen prepared from nitric oxide without any differences between them being detected'. Thus unlike the density differences Rayleigh first observed between 'atmospheric' and 'chemical nitrogen', Dewar finds their comparative boiling points to be the same. We might conclude that Dewar was not working to the same degree of accuracy as Rayleigh or perhaps, in Peirce's words, had 'pooh-pooed' seemingly anomalous results away.

News of the discovery of argon travelled to America. In a brief article titled 'A New Atmospheric Element', in the *American Journal of Chemistry* (October 1894), E.H Quinam (1894:719) cites William Crooke's spectral analysis of argon as indicating 'the lines differ in position from those of nitrogen'. Nevertheless Quinam (1894:780) also includes Dewar's view, 'that the new element may be an allotropic form of nitrogen [N_3] analogous to red phosphorus [P_4]'. These brief details on the possibility of argon being a form of nitrogen are given simply to demonstrate that Mendeleev's telegrammed response to Ramsay offered a suggestion that sat within the context of chemical opinion at that time.

Accounts of the discovery of argon are well documented in the literature (see for example Wolfenden 1969 and Giunta 2001) and will not be detailed any further here. What is worth noting however is Rayleigh's 'puzzlement' and surprise in his discovery that the densities of the two nitrogen samples had defied his expectations. It might also be said that in this

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[64] Reported in *Chemical News* 1894, volume 70 page 88 – and reprinted from *The Times* 16th August 1894

surprise result Rayleigh had experienced a clash with reality - a reality independent of his expectations; an aspect of scientific inquiry described by Chang (2012:257) as ‘not everything will go to plan…that is how reality surprises us’. As we will see, Mendeleev did not respond initially as Chang (2012:257) would recommend, by having ‘contingencies’ and thereby ‘a kind of science that has the capacity for handling surprises’. For Mendeleev did not believe his table was able to accommodate the surprise discovery of argon. Fortunately Ramsay and Rayleigh were able to show that the failure of Mendeleev’s table as it was then constructed, to receive argon, did not herald the failure of his whole scheme as a result.

5.5.2 The discovery of argon – Nature’s clash with Mendeleev’s iconic periodic table

Again this is not the place to detail the discovery of argon, or later in the account the other noble gases. Details will be given on how argon lends support to the iconic robustness of Mendeleev’s table in confronting the resistance of Nature presented by these novel elements.

In January 1895 Rayleigh and Ramsay presented their joint paper, ‘Argon, a New Constituent of the Atmosphere’, to the Royal Society. This paper set out the findings of their research prompted initially by Rayleigh’s surprise results concerning the density of nitrogen and described earlier. A measure of Ramsay and Rayleigh’s (1895:208) determination to settle the question of argon as a new element can be seen in their statement that they ‘thought it undesirable to shrink from any labour that would tend to complete [this] verification’. In formulating their conclusions Ramsay and Rayleigh (1895:235) refer again to the surprising result – the discrepancies in the densities of nitrogen referred to in Rayleigh’s letter to *Nature* – when they state, ‘if the newly discovered gas [argon] were not in the atmosphere, the discrepancies in the density of "chemical " and "atmospheric" nitrogen would remain unexplained’. The clash with reality instanced by Rayleigh’s original ‘discrepancies’ has prompted a new inquiry in order to settle belief. Nature’s initial resistance has generated new knowledge in the existence of argon. At the beginning of the chapter we referred to Chang’s (2012a:216) account of *active realism* where he accounts for knowledge as being, ‘a state of ability to do things without being foiled by significant resistance from reality’. In the work of Rayleigh and Ramsay new knowledge is produced by confronting nature’s initial resistance to a particular state of affairs and through the process of inquiry.

The copy of Mendeleev’s table in figure 42 is dated February 1895, the year of Ramsay and Rayleigh’s publication on the isolation of argon as presented to The Royal Society in January.

Table54(P27)

[X] РАСПОЛОЖЕНИЕ ЭЛЕМЕНТОВ ПО ГРУППАМ И РЯДАМ

ГРУППЫ:	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ряд 1.	. H							
» 2.	Li .	Be .	B .	C .	N .	O .	F .	
» 3.	. Na	. Mg	. Al	. Si	. P	. S	. Cl	
» 4.	K .	Ca .	Sc .	Ti .	V .	Cr .	Mn .	Fe. Co. Ni. Cu.
» 5.	. (Cu)	. Zn	. Ga	. Ge	. As	. Se	. Br	
» 6.	Rb .	Sr .	Y .	Zr .	Nb .	Mo .	— .	Ru. Rh. Pd. Ag.
» 7.	. (Ag)	. Cd	. In	. Sn	. Sb	. Te	. J	
» 8.	Cs .	Ba .	La .	Ce .	Di? .	— .	— .	— — — —
» 9.	. —	. —	. —	. —	. —	. —	. —	
» 10.	— .	— .	Yb .	— .	Ta .	W .	— .	Os. Ir. Pt. Au.
» 11.	. (Au)	. Hg	. Tl	. Pb	. Bi	. —	. —	
» 12.	— .	— .	— .	Th .	— .	U .	— .	
	R^2O	R^2O^2 . RO	R^2O^3	R^2O^4 RO^2	R^2O^5	R^2O^6 RO^3	R^2O^7	Высшие окислы. RO^4
	—	—	—	. RH^4	. RH^3	. RH^2	. RH	Водородные соед.

This table Smith (1974:202) states as being published in an 1895 Russian edition of Mendeleev’s *Principles of Chemistry* and headed ‘arrangement of the elements by groups and series’. Mendeleev makes no provision for an unknown element with an atomic weight of 40 – argon’s value according to Ramsay and Rayleigh (1895)

Figure 42: Mendeleev’s periodic table from 1895
Source: *Persistence and Periodicity: a study of Mendeleev’s contribution to the Foundations of Chemistry* by John Russel Smith, PhD thesis Chelsea College, University of London 1976, page 275

Argon’s atomic weight remained a matter of speculation when Ramsay and Rayleigh (1895:236) published their paper,

> Argon is approximately 20 times as heavy as hydrogen, that is, its molecular weight is 20 times as great as that of hydrogen, or 40. But its molecule is monatomic, hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of

> the elements in that mixture, taken for the proportion in which they are present, must be 40.

On balance argon was thought to be a monatomic gas with an atomic weight of 40. Furthermore Ramsay and Rayleigh's (1895:234) investigations had shown that argon would not combine with any other element finding it to be 'a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very opposite character, ranging from sodium and magnesium on the one hand, to oxygen, chlorine, and sulphur on the other'. In forming no compounds argon must be considered to have a valency of zero. This presented an additional problem for Mendeleev who had not conceived of zero-valency elements when constructing his system. The impact of nature on the periodic table by the existence of an element with an atomic weight of 40 was expressed by Arthur Rucker, President of the Physical Society, in the discussion immediately following Ramsay and Rayleigh's paper[65],

> I can only, in conclusion, say that, whatever the effect may be upon the great chemical generalization of Mendelejeff, that is, after all, an empirical law which is based, at present, upon no dynamical foundation. If it holds its own in this case, it will, of course, strengthen our belief in it, but, on the other hand, I do not think that it stands on the footing of those great mechanical generalizations which could not be upset without upsetting the whole of our fundamental notions of science.

The periodic table has encountered Nature's *resistance* in the discovery of argon. If sufficiently stable and able to accommodate and to sustain the existence of this new element, then the standing of Mendeleev's scheme will be enhanced. If not, then it will fall – but as the physicist Rucker explains – without shattering the edifice of science – as might be the case if Newton's dynamical laws were to suffer a similar fate. Both Ramsay and Rayleigh are far more optimistic about the capacity for Mendeleev's iconic scheme to withstand the discovery of argon and to assimilate it within a new structure yet to be determined. Elements with an atomic weight of around 40 are: chlorine (35.5), potassium (39.4), calcium (40.0) and scandium (44.0). But to position argon anywhere within this set of elements would be to displace them away from the family or group of elements they each share some chemical similarity with. However unlike Rucker, Ramsay and Rayleigh (1895:236) appear to assume that Mendeleev's scheme would in time cope.

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[65] Reprinted in the *Journal of the American Chemical Society* 1895, **3**(3):239-240

> If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed.

Both Ramsay and Rayleigh accepted the possibility that the periodic table as it then stood might be incomplete; there is no suggestion here that the discovery of argon marks its demise. This was not the case for all commentators at the time who foresaw Mendeleev's scheme as being unable to push back successfully against Nature's *resistance*.

In an article in *Chemical News* (1895) the Prague chemist Bohuslav Brauner writes in support of argon being tri-nitrogen (N_3). This was motivated in part by his view of the fixedness of Mendeleev's table as it was then constructed, being unable to accommodate argon in some newly reconstructed form. As part of their investigations into argon, Ramsay and Rayleigh claimed that specific heat data indicated argon to be a monatomic gas, thereby ruling out the possibility of triatomic nitrogen N_3. This Brauner (1895:79) attempts to overcome by suggesting that the three nitrogen atoms in lie 'very close to each other in the molecule' and that this would explain 'its [N_3] great inertia' and so 'might be assumed to behave *physically* like a single atom' (emphasis in the original). Interestingly Brauner (1895:79) suggests that microorganisms, then known to convert the nitrogen compound ammonia into nitric acid, might offer a successful method to separate the three nitrogen atoms in 'argon' as N_3 - for he asks, 'is it not possible that such a source might have some action on 'argon''. As with other chemists at the time Brauner accepted Mendeleev's system but felt it to be a fixed structure, by implication lacking the necessary flexibility required to survive the readjustment needed to accommodate a novel element. This attitude is apparent when Brauner (1895:79) states that 'as an orthodox Mendeleeffian, I find great difficulty in assuming the existence of a new elementary gas having the atomic weight 29 or 40 or 80, its boiling point being -187^0'. Such a boiling point, argues Brauner (1895:79), 'would better correspond to a gas similar in its nature to nitrogen'. In his Mendeleevian 'orthodoxy' Brauner is unable to conceive of Mendeleev's system readjusting to accommodate argon – but Mendeleev's iconic form was to prove to be more adaptable than Brauner and similarly *orthodox Mendeleeffians* supposed. Brauner's self-confessed orthodoxy indicates him to be no fallibilist in this context.

Just three months after Ramsay and Rayleigh presented their paper to The Royal Society Mendeleev addressed a meeting of the Russian Chemical Society (March 14, 1895) where he rejected the existence of argon as a monatomic gas with an atomic weight of 40. Instead

Mendeleev argues for a polyatomic molecule of some sort – such as Ar_2 or Ar_3 (using today's symbol for argon). Where Ramsay and Rayleigh had used specific heat data to argue against the possibility of a polyatomic entity, Mendeleev claimed that polyatomic argon's great chemical inertness might result in the same specific heat characteristics as a monatomic gas. Of particular interest is the statement Mendeleev (1895:543) makes in defence of the existing structure of his periodic table as being inviolate: 'if we admit that the molecule of argon contains but one atom, there is no room for it in the periodic system'. By not slotting into the periodic table as it was then constructed Mendeleev (1895:543) claims that is seems therefore 'very unlikely that the atomic weight of argon might be about 40'. Here Mendeleev is sufficiently sure of the format of the table as it was then constructed to use it as a framework to judge the likelihood of argon having an atomic weight of 40. The table comes first and argon must fit within it. There is no sense that his table might be sufficiently adaptable to accommodate argon within a revised format without violating the general principles upon which it is founded: an arrangement of the chemical elements in order of increasing atomic mass where elements of similar physiochemical properties recur periodically. This is in stark contrast to the way Mendeleev experimented with different formats of his scheme in order to accommodate the rare earth elements. In the case of the noble gases Mendeleev's earlier fallibilist approach seems to have deserted him. We will see later however, that Ramsay adopts a fallibilist approach into how argon fits into Mendeleev's scheme.

The possible threat argon presented to Mendeleev's table in an unreconstructed form was expressed by the American chemist from Johns Hopkins University Ira Remsen[66]. In a review of Ramsey and Rayleigh's 1895 paper, Remsen (1895:310), whilst conceding that more research was necessary to confirm the nature of argon adds, 'if the time should ever come when Mendeleeff's table has to be given up, something better will take its place'. In refusing to concede argon to be a monatomic gas with an atomic weight of 40 Mendeleev was in part defending his table against the possibility of being 'given up'. The possible fall of the periodic table as a result of the discovery of argon was also alluded to in an editorial in *Nature* (February 1895), and soon after Ramsay and Rayleigh's presentation to The Royal Society. In a lengthy review the author comments (*Nature* 1895, volume 51 page 337) 'the periodic classification of the elements cannot, and ought not, to be abandoned at the first challenge'. Whilst the writer encourages further inquiry into the experimental evidence

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[66] Remsen is recorded as attending Charles Peirce's *Metaphysical Club* at Johns Hopkins; see for example W4:xxxix

around Ramsay and Rayleigh's work on argon the point is made: possible abandonment of the periodic table should argon have the properties they had suggested.

Taking Chang's (2012a:203) position on reality 'as whatever is not subject to one's will', and knowledge as 'an ability to act without being frustrated by resistance from reality', then Mendeleev is demonstrating here some frustration at nature's resistance to his periodic system by attempting to subject the atomic weight of argon to the 'will' of his periodic system. He does not accept, at this time at least, that his iconic table is sufficiently compliant to accommodate a novel and unexpected element. There is instead, Mendeleev (1895:543) argues, much to favour the hypothesis that 'the molecule of argon contains three atoms, its atomic weight would be about 14, and in such a case we might consider argon as condensed nitrogen, N_3' – which of course would fit neatly into the framework of the periodic table as it then was.

5.5.3 The discovery of terrestrial helium[67]

Approximately two months after Ramsay and Rayleigh's paper on argon, Ramsay then discovered helium in the mineral cleveite. In a short statement in *Nature* (March 1895) Ramsay describes how in his search for possible compounds of argon his attention had been drawn to the mineral cleveite which, earlier studies had noted, evolved a small amount of nitrogen when warmed with sulphuric acid. His idea, Ramsay (1895:512) explains is, 'if the so-called nitrogen turned out to be argon, to try if uranium could be induced to combine with argon'. After further purification, an excited Ramsay (1895:512) reports that the gas 'consists of a mixture of Argon and Helium!' In a paper to The Royal Society on helium in April 1895 Ramsay (1895a:88) offers what he describes as a remark 'of a speculative nature', that 'the general similarity of helium…to argon, in not being affected either by red-hot magnesium or by sparking with oxygen in presence of potash, makes the inference probable that they belong to the same natural group'. The problem is of course that Mendeleev's table as then constructed has no suitable group for these two new elements. Nature's *resistance* to the periodic table appears to have increased with the discovery of helium.

Approximately a quarter of a century had passed since between Mendeleev's first periodic system in 1869 and the discovery of argon and helium. In that time Mendeleev's table had become for many chemists an established part of their discipline. The Canadian chemist

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[67] Helium had been previously discovered in 1868 and before Mendeleev first periodic table in 1869, by Pierre Janssen during a spectral analysis of a solar eclipse.

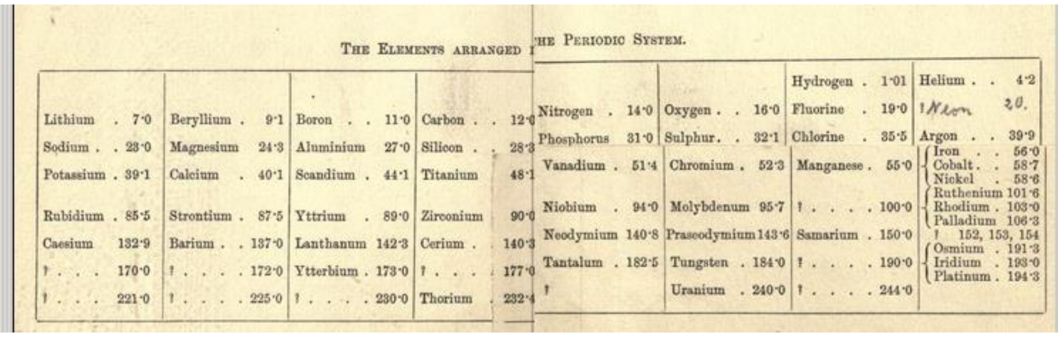
W.W Andrews perhaps spoke for those who believed Mendeleev's table to be sufficiently secure to survive these two elements. In commenting on the dilemma posed by argon and helium Andrews (1895:235) offers the following plea to fellow chemists,

> Let us imitate the sublime faith of Mendeleeff, and we may rest assured that the order and multiplied analogies revealed by the Periodic Classification form a basis of fact which is not to be shaken. Argon and helium will drop into their places and open up new vistas of analogy and suggestion.

Firstly Andrews's comment is not in the spirit of fallibilism when he speaks of 'sublime faith' in Mendeleev and his scheme as a 'fact which is not to be shaken'. Nevertheless, note the iconic and epistemically fruitful claims for the periodic table in Andrew's claim of 'analogies revealed'. In particular the final sentence is highly reminiscent of the case made for the iconic nature of the periodic table in an earlier chapter. In two more years we will see Ramsay relying on the iconic nature of the periodic table to reveal just such 'new vistas of analogy' in the suggestion of the undiscovered noble gas neon.

Not all chemists however were as hopeful, being more of the opinion expressed by RM Deeley (1895:279) in an article in *Chemical News* (1895) where he states that the discovery of argon and neon 'has undoubtedly had the effect of shaking the confidence of chemists in the periodic classification of the elements'. The atomic weights of argon and helium had been calculated on the basis of their densities and also on their specific heat ratios which gives an indication of atomicity. Whilst in their original paper Ramsay and Rayleigh accepted that the value they had calculated was perhaps inconclusive; nonetheless on balance they considered both helium and argon to be monatomic. As has been described earlier, other chemists speculated that given the chemical inertness of both gases, a different state of molecular dynamics might exist supporting other possible atomicities. On this point Deeley's (1895:279) belief in the iconic robustness of Mendeleev's system is expressed in his concluding sentence when he writes that given this uncertainty 'would it not be well to follow the indications of the Periodic Law…rather than a doubtful theory concerning the dynamics of the molecule?'

In place of such speculations and in a rather more practical way Ramsay too shows his belief in Mendeleev's iconic system. In his text *The Gases of the Atmosphere*, published in 1896 and a year after the discovery of helium Ramsay (1896:218/9) makes a speculative 'drop' of argon and helium into their places within the table,



THE ELEMENTS ARRANGED I HE PERIODIC SYSTEM.

						Hydrogen . 1·01	Helium . . 4·2
Lithium . 7·0	Beryllium . 9·1	Boron . . 11·0	Carbon . . 12·0	Nitrogen . 14·0	Oxygen . . 16·0	Fluorine . 19·0	? Neon 20.
Sodium . . 23·0	Magnesium 24·3	Aluminium 27·0	Silicon . . 28·3	Phosphorus 31·0	Sulphur . . 32·1	Chlorine . 35·5	Argon . . 39·9
Potassium . 39·1	Calcium . 40·1	Scandium . 44·1	Titanium 48·1	Vanadium . 51·4	Chromium . 52·3	Manganese . 55·0	Iron . . 56·0 Cobalt . . 58·7 Nickel . 58·6
Rubidium . 85·5	Strontium . 87·5	Yttrium . 89·0	Zirconium 90·0	Niobium . 94·0	Molybdenum 95·7	? . . . . 100·0	Ruthenium 101·6 Rhodium . 103·0 Palladium 106·3
Caesium 132·9	Barium . . 137·0	Lanthanum 142·3	Cerium . 140·3	Neodymium 140·8	Praseodymium 143·6	Samarium . 150·0	? 152, 153, 154
? . . . 170·0	? . . . . 172·0	Ytterbium . 173·0	? . . . 177·0	Tantalum . 182·5	Tungsten . 184·0	? . . . . 190·0	Osmium . 191·3 Iridium . 193·0 Platinum . 194·3
? . . . 221·0	? . . . . 225·0	? . . . . 230·0	Thorium . 232·4	?	Uranium . 240·0	? . . . . 244·0	

Figure 43: Ramsay's arrangement of the elements as a periodic system
Source: Ramsay's *The Gases of the Atmosphere* (1896) page 218/9
* Note that neon has been pencilled in by a later reader of the book: 'Neon 20'

Here Ramsay presents argon and helium as monatomic, inert gases with atomic weights of 39.9 and 4.2 respectively and as a new group on the far right of the table. By positioning argon (39.9) between chlorine (35.5) and potassium (39.1) Ramsay adds another irregularity in the atomic weight sequence to that shown by the reversal of tellurium and iodine[68] in Mendeleev's original table of 1869. What is important is Ramsay's (1896:240) inherent belief in the iconic robustness of Mendeleev's scheme to accommodate these two new elements and to suggest new research questions, whilst at the same time being aware 'that these suggestions are of a wholly speculative nature' adding also his 'firm conviction that no true progress in knowledge has ever been made without such speculations'.

5.5.4 Ramsay's prediction of neon and the nature of the periodic table's iconicity

Now in possession of new evidence - the chemical similarity of helium and argon - Ramsay is prompted to add an entirely new group of elements to his table: helium followed by a gap and then argon. In a way similar to Mendeleev's earlier predictions of the eka-elements Ramsay (1897:380) states his predictions for the missing element between helium and argon as,

> There should, therefore, be an undiscovered element between helium and argon, with an atomic weight of 16 units higher than that of helium, and 20 units lower than argon, namely 20.

Susan Haack (1971:41) characterises Peirce's fallibilist position as follows: 'we should always be willing to revise our beliefs in the light of new evidence'. This statement I believe captures Ramsay's approach to the noble gases in relation to the periodic table. We also see Andrews's earlier hope that the (iconic) periodic table would 'open up new vistas of

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[68] Tellurium and iodine are covered over in the above table by the folded section of the page indicated

analogy' being fulfilled in Ramsay's speculations. By assuming the continuing iconic nature of a reconfigured periodic table Ramsay (1897:379) takes the opportunity of 'indulging in the dangerous luxury of prophesy,' in predicting the atomic weight of a yet undiscovered member of the group.

5.5.6 The discovery of neon, krypton and xenon

By September 1898 Ramsay had discovered neon, krypton and xenon. In a later paper to The Royal Society (1901) Ramsay, with Morris Travers, set out in detail the physiochemical properties of the first four members of the group we know today as the noble gases. If these four noble gases are monatomic, claim Ramsay and Travers (1901:83), 'they would form a group by themselves, Helium (4), Neon (20), Argon (40), Krypton (82), Xenon (128)'. At the end of their paper and to illustrate how the noble gases fit into the periodic arrangement Ramsay and Travers (1901:89) offer the following graph of atomic volume[69] (vertical axis) plotted against atomic weight (horizontal axis):

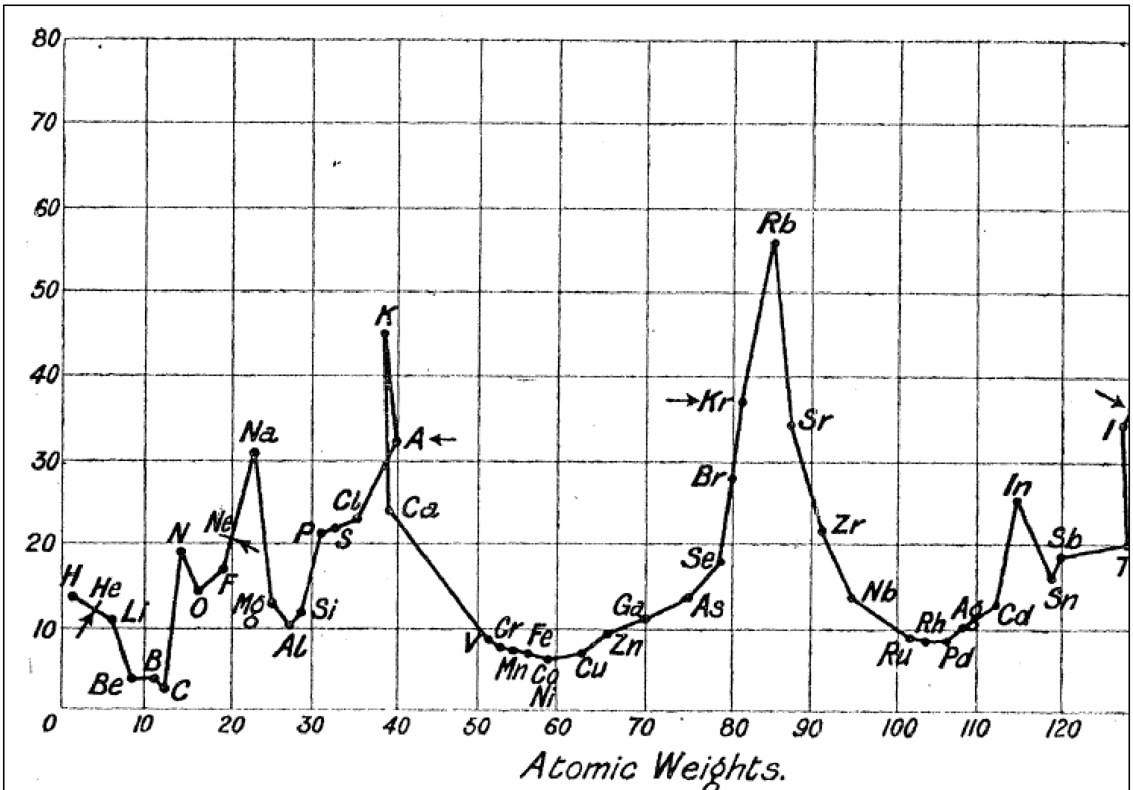

Figure 44: Graph of atomic volume against atomic weight for the elements hydrogen to caesium
Source: Ramsay, W and Travers, M. 1901. 'Argon and Its Companions'. *Philosophical Transactions of the Royal Society of London*. **197** pages 47 and 47

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[69] Atomic volume is the volume in cm^3 occupied by the atomic weight of an element expressed in grams – for example the volume occupied by 12g of carbon (3.4 cm^3 for the allotropic form of diamond)

Looking at the graph small arrows indicate the noble gases He, Ne, Ar, Kr and Xe. There is a general periodic trend: a general increase in atomic volume across a period[70] with the alkali metals (Li, Na, K, Rb, Cs) occupying the maximum values for their respective periods. Ramsay and Travers (1901:88) note that '[t]he periodicity of the inactive [noble gas] elements is obvious'. It is worth quoting at length Ramsay and Travers's (1901:89) position on the periodic scheme, now enlarged by the noble gases,

> [A] study of this arrangement, it must be allowed, is a somewhat tantalising pleasure; for, although the properties of elements do undoubtedly vary qualitatively, and, indeed, show approximate quantitative relations to their position in the periodic table, yet there are inexplicable deviations from regularity, which hold forth hopes of the discovery of a still more far-reaching generalization. What that generalization may be is yet to be divined; but that it must underlie what is known, and must furnish a clue to the explanation of irregularities cannot be disputed.

Firstly notice the description of their inquiry into the chemical elements as 'a somewhat tantalizing pleasure' and how this echoes Peirce's own judgement of 'I need not point out the *tantalising* appearance of relations among the atomic weights which are wanting in exactitude for this speaks for itself; and the more it is studied the more perplexed it shows itself to be' (MS 693:440, c1900, emphasis added). Also Peirce's own unsuccessful search for an exact mathematical framework to the periodic table, seen in chapter three and again later in chapter six, is echoed by Ramsay and Travers above in their observation of the approximate relations between the elements and their atomic weights and 'yet there are inexplicable deviations from regularity'. Importantly for this chapter however, is Ramsay and Travers's hope that some 'still more far-reaching generalization' – a re-emerged form of Mendeleev's table - 'must furnish a clue to the explanation of irregularities'; a belief in the periodic table's continuing epistemic fruitfulness – a belief in its continuing iconicity. Finally throughout the course of their inquiry into the noble gases and their relation to Mendeleev's periodic table, Ramsay and Travers demonstrate Peirce's fallibilist methodology as captured by Hookway (2003:48): '[a]lthough responsible inquirers are destined to reach a point at which their opinions will not be disturbed by further inquiry, there is never any absolute guarantee that this position has been reached. No matter how confident we are that we have the truth, further experience could surprise us'.

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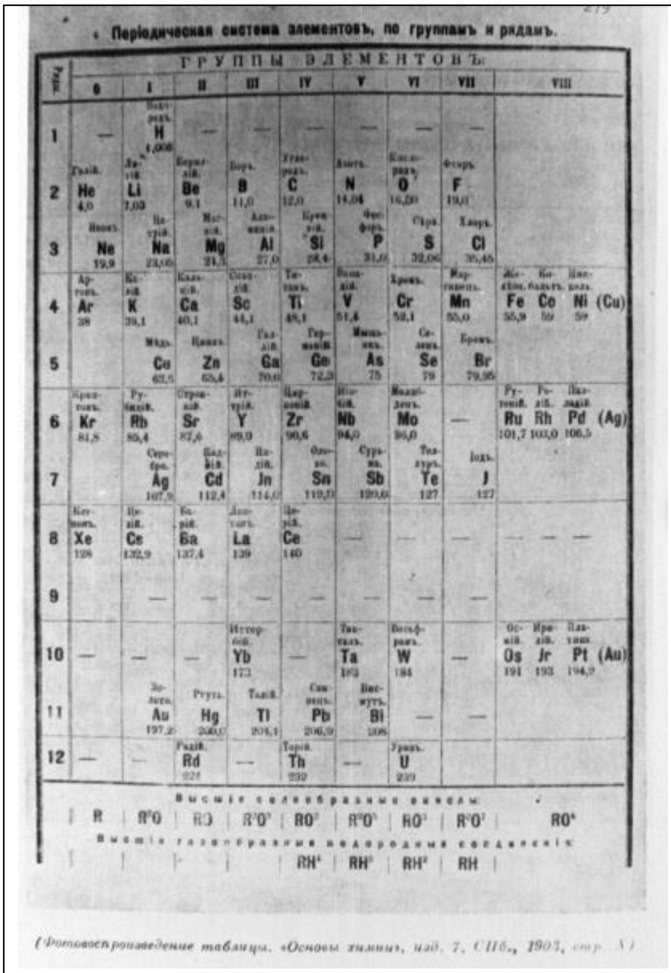
[70] A period is a horizontal row of elements within the periodic table

5.5.7 Mendeleev accepts the noble gases in to his scheme

It was, as Bernadette Bensaude-Vincent (1986:16) describes, ‘thanks to their sound belief in the regular periodic function’ that in 1900 Ramsay and Rayleigh proposed that a new group be added to the periodic table – to the left of the first group of alkali metals. During 1900 Mendeleev and Ramsay met in Berlin where, states Scerri (2007:156), Mendeleev received the noble gases as a new group within the periodic table ‘favourably’. Two years later Mendeleev (1902:30) writes that ‘a zero group of chemically inactive elements must now be recognised’ which he attributes to ‘Ramsay’s exemplary researches’. The 1901 English edition of *Principles of Chemistry* omitted the noble gases but as Masanori Kaji (2002:12) states, by the seventh edition of 1902-1903 Mendeleev had abandoned N_3 and fully accepted the noble gases’. Thus by the beginning of the twentieth century Mendeleev had accepted the noble gases as part of his periodic scheme, as shown below:



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Періодическая система элементовъ, по группамъ и рядамъ.

Ряды	0	I	II	III	IV	V	VI	VII	VIII
1	—	H 1,008	—	—	—	—	—	—	
2	He 4,0	Li 7,03	Be 9,1	B 11,0	C 12,0	N 14,04	O 16,00	F 19,0	
3	Ne 19,9	Na 23,05	Mg 24,3	Al 27,0	Si 28,4	P 31,0	S 32,06	Cl 35,45	
4	Ar 38	K 39,1	Ca 40,1	Sc 44,1	Ti 48,1	V 51,4	Cr 52,1	Mn 55,0	Fe Co Ni (Cu) 55,9 59 59
5		Cu 63,5	Zn 65,4	Ga 70,0	Ge 72,3	As 75	Se 79	Br 79,95	
6	Kr 81,8	Rb 85,4	Sr 87,6	Y 89,0	Zr 90,6	Nb 94,0	Mo 96,0	—	Ru Rh Pd (Ag) 101,7 103,0 106,5
7		Ag 107,9	Cd 112,4	Jn 114,0	Sn 119,0	Sb 120,0	Te 127	J 127	
8	Xe 128	Cs 132,9	Ba 137,4	La 139	Ce 140	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Yb 173	—	Ta 183	W 184	—	Os Jr Pt (Au) 191 193 194,9
11		Au 197,2	Hg 200,0	Tl 204,1	Pb 206,9	Bi 208	—	—	
12	—	—	Rd 224	—	Th 232	—	U 239		
Высшіе солеобразные окислы:	R	R^2O	RO	R^2O^3	RO^2	R^2O^5	RO^3	R^2O^7	RO^4
Высшія газообразныя водородныя соединенія:					RH^4	RH^3	RH^2	RH	

(Фотовоспроизведение таблицы. «Основы химии», изд. 7, СПб., 1903, стр. [illegible])

This short form of the table is from Mendeleev's Russian 1903 edition *Principles of Chemistry* and is headed *Periodic system of the elements by groups and series*.

The five noble gases have been added as 'Group 0' to the extreme left-hand side of the table. Mendeleev has now dropped his objection to argon as being tri-nitrogen.

Interestingly though to avoid further atomic weight inversions Mendeleev states argon – positioned between chlorine (35.45) and potassium (39.1) – to have an atomic weight of 38. For Mendeleev believed that further inquiries into atomic weights would remove all inversions.

Figure 45: Mendeleev's periodic table of 1903
Source: *Persistence and Periodicity: a study of Mendeleev's contribution to the Foundations of Chemistry* by John Russel Smith, PhD thesis Chelsea College, University of London 1976, page 279

Writing in *An Attempt Towards a Chemical Composition of the Ether* (1904) Mendeleev (1904:19) explains that, 'many reasons that induced me to accept firstly argon as an element…[chiefly]…the density of argon is certainly much below 21, namely about 19…while the density of N_3 would be about 21'. The further discovery of more chemically inactive noble gases supported by spectral evidence, as well as their gradation in physical properties with atomic weight, also helped to convinced Mendeleev of this new group of elements. Having finally accepted the noble gases Mendeleev (1904:22) states their accommodation within his scheme to be ‘a critical test for the periodic law’ claiming that it ‘stood the test with perfect success’, a view also endorsed by Peirce in stating, ‘the classification of the elements has been laid bare [for all to see], the group of helium-argon elements has been added’ (CP 8.196, 1905). Taking up these words, in passing this ‘critical test’ nature’s resistance was overcome whereby ‘the group of helium-argon elements has been added’ to Mendeleev’s scheme; the periodic table again has demonstrated its iconic robustness.

5.6 Conclusion

Using the two case studies of the rare earth and the noble gas elements, I have attempted to argue a case for the iconic robustness of the periodic table. This in conjunction with Peirce’s fallibilism and Chang’s account of *r*esistance to nature as featured in his account of active realism. I would claim that the periodic table demonstrated iconic robustness by retaining its capacity to promote thought experiments and to generate new knowledge whilst undergoing structural changes in response to nature’s resistance in the form of new and existing sets of elements.

Mendeleev recognises the rare earths as a natural group of elements but is initially unsure where to place them within his scheme. These elements might be thought of as nature or reality resisting or pushing back against Mendeleev’s scheme. He settles initially for a block at the bottom of his ‘long form’ table of 1869. By adopting a fallibilist approach Mendeleev accepts his scheme is not completely fixed. Through a process of reasoning, integrated with and dependent on the iconicity of the periodic table, Mendeleev conducts a number of thought experiments which entail significant changes in the structure of his table. Nevertheless, new knowledge continues to be generated such as the revised atomic weight for cerium. Thus the periodic table continues to prove fruitful, demonstrating its iconic robustness by pushing back against nature’s resistance - the rare earth elements. The scheme was able to accommodate these novel substances whilst also indicating new relations between the chemical elements.

In Chang’s (2012a:215) terms Ramsay and Travers were successful in revealing the family of noble gases because ultimately, ‘nature or reality [did] not prevent what [they] were trying to achieve’. I have argued that Mendeleev did not adopt a fallibilist approach to the noble gases in relation to their eventual placement in his scheme. By contrast Ramsay and Travers took a more fallibilist line. Whilst unable to formulate a mathematical expression, one based on the order of the elements within the periodic table, to predict the atomic weights of the noble gases Ramsay and Travers (1901:89) state that whilst, '[i]t is possible that such expressions exist…[we]...hope that others, more mathematically gifted than we are, may succeed where we have failed'. In this expression of their hope Ramsay and Travers capture an aspect of Peirce's fallibilism in that there is never any absolute guarantee of the end of an inquiry, for further experience could surprise us. During this particular inquiry the periodic table as an iconic representation showed itself, in Peirce's words, to be 'plastic [and] applicable' (MS 693) and able to overcome nature's resistance as presented in the discovery of the noble gases. In arguing for the noble gases as monatomic elements from which their individual atomic weights might be assigned, Ramsay and Travers (1901:83) generated this knowledge through a process of reasoning with the periodic table and arguing that 'they form a group in themselves'. By embracing this novel group of elements into its structure the periodic table again demonstrates its iconic robustness: the continuing capacity to generate knowledge of novel relations between the chemical elements without being thwarted by nature's resistance and within the context of a fallible inquiry.

Chapter Six

The Periodic Table: iconicity as an alternative view from *practice* to the debate around accommodation and prediction.

6.1 Introduction

In this chapter I will argue that taking the periodic table as an iconic sign, with a focus on Mendeleev's practice of representing, offers a new insight into its epistemology: one that moves beyond the debate around whether the prediction of new elements had a greater impact on the chemical community than the accommodation of exiting elements (Brush 1996, Maher 1988, Scerri and Worrall 2001). This project has already brought together aspects from the 'accommodation' and 'prediction' sides of this debate. In chapter four I presented Mendeleev's periodic table as an iconic sign which might be broadly characterised within the terms 'accommodation' and 'prediction'. Firstly Mendeleev's table represented the physiochemical relations of the existing elements accommodated within the scheme. Secondly the periodic table proved to be epistemically fruitful in pointing towards predicting new relations – new knowledge - such as revised atomic weights and novel elements. In addition chapter five introduced iconic robustness, an attempt to capture the periodic table's continuing iconic fruitfulness – its ability to predict – against nature's resistance to the pattern of relations between elements accommodated within the scheme.

The philosopher David Harker (2008:429) surveys the landscape of this long-running debate in the philosophy of science as follows:

> Scientific theories are developed in response to a certain set of phenomena and subsequently evaluated, at least partially, in terms of the quality of fit between those same theories and appropriately distinctive phenomena. To differentiate between these two stages it is popular to describe the former as involving the accommodation of data and the latter as involving the prediction of data.

The debate centres on whether a particular scientific theory is better supported by the successful prediction of previously unknown facts or by accommodating data available at the time. This is a long-standing (Musgrave 1974) and somewhat polarised debate where, as Harker (2008:444) states, 'examples and counterexamples fuel, but don't settle, the debates'. The periodic table has featured often in these conversations (Scerri and Worrall

2001). Nevertheless the attendant claims and counter-claims fail to capture a coherent view of Mendeleev's practice – the heuristic aspects of his creative inquiry. Rather than use this project to enter one or other side of the debate I should like to take together some of the arguments used by the various protagonists to gain an insight into Mendeleev's representational practice and in that respect to go beyond the current debate. In support of this approach I will draw on some of the ideas developed around *representational practice* by the philosopher of science Andrea Woody (2004 and 2014) and set within the framework of Peirce's iconicity.

In her analysis of representational practice Woody (2004:782) claims that, 'the ultimate aim of most representational practices is to achieve an *articulated awareness* of the nature of the objects and relations constituting that particular domain' (emphasis in the original). Marion Vorms (2010:551) elucidates Woody's point as follows,

> [B]ecoming an expert consists in acquiring an "articulated awareness" of the representations used in [a particular] field'. The more expert you are, the more easily you draw inferences with these representations. Moreover, in addition to solving problems more quickly, the expert has a deeper understanding of the very content of theories, namely of the deductive relationships between the various hypotheses this theory consists in.

Following Vorms's sequence, Mendeleev's *articulated awareness* of the physiochemical relations between the chemical elements is manifested in two ways. Firstly he was able to use the periodic table to draw inferences, such as projecting the properties of novel elements; the periodic table's predictive capacity. Secondly, Mendeleev by devising his scheme demonstrates a deep understanding of the physiochemical relations between the chemical elements and the possibilities this offers for inferential thought. I will show that Mendeleev achieved an *articulated awareness* of the relations between the chemical elements through his practice of representation, engaging via the iconic periodic table with aspects sometimes listed separately under the headings of 'accommodation' and 'prediction'.

By representing the physiochemical relations between the chemical elements in the form of a table, Mendeleev was providing what Woody (204:782) describes as, 'structure to the inferential landscape, enabling the otherwise daunting task of mapping some domain of knowledge'. Mendeleev's representational practice mapped the relations between the chemical elements – the 'inferential landscape' - as the periodic table. I will argue that approaching Mendeleev's practice through the lens of Peirce's theory of iconicity sets out how he developed an *articulated awareness* of the relations between the chemical elements. Such an approach cuts across the two categories of 'accommodation' and 'prediction' by bringing them together within a single approach and offers a novel insight into the periodic table's epistemology. In her re-examination of the periodic law Woody (2014:126) stresses the value of, 'highlighting an aspect of practice that has been curiously neglected: namely, the explicit representational choices made in expressing the periodic law'. Our approach here focusses on Mendeleev's representational choice in depicting the periodic law in diagrammatic form as the periodic table. Other inquirers made different choices – Lothar Meyer for example displayed the relations between the chemical elements in one form as a graph of atomic volume plotted against atomic weight. In her study of representation Vorms (2011:287) argues that, 'if one takes seriously the idea that a study of theorising has to concentrate on the concrete practices of scientists…one has to focus on the cognitive interactions between agents and the representational devices they reason with and manipulate'. In this chapter I focus on Mendeleev's practice of representing as the means by which he engaged with his 'representational device – the periodic table - in order to understand the relations between the chemical elements. To begin with, however, it would be useful to set out aspects of the discussion around 'accommodation' and 'prediction' to be found in the literature.

6.2 Prediction and accommodation

The epistemic value placed on predictive power has featured in the philosophy of science since early times. For example Alan Musgrave (1974:1) notes that the early seventeenth century Jesuit mathematician and astronomer Christopher Clavius argued in favour of Ptolemaic astronomy on the grounds that, 'not only are all the appearances already known accounted for, but also future phenomena are predicted'. As part of his historical survey of what he terms the *Logical versus Historical Theories of Confirmation,* Musgrave (1974:2) records the nineteenth century debate between William Whewell and John Stuart Mill,

> Mill [was]amazed at Whewell's view that 'an hypothesis [...] is entitled to a more favourable reception, if besides accounting for all the facts previously known, it has led to the anticipation and prediction of others which experience afterwards verified. Such predictions and their fulfilment are, indeed, well calculated to

> impress the uninformed [...] But it is strange that any considerable stress should be laid upon such a coincidence by persons of scientific attainments.

In his *Philosophy of the Inductive Sciences*, Whewell (1840:62) argues that a successful hypothesis whilst explaining known phenomena should go beyond this and, '*foretell* phenomena which have not yet been observed' (emphasis in the original). In Whewell's (1840:63) account, a successful hypothesis will both correctly explain current phenomena and 'predict the results of new combinations'; both being necessary as the means by which the hypothesis is 'verified as right and proper'. In support of his argument Whewell (1840:64) offers Lavoisier's 'Oxygen Theory', which whilst able to accommodate the results from known reactions such as hydrogen with oxygen or steam with iron, also 'enabled chemists to *foresee* such facts in untried cases' (emphasis in the original). It was to Whewell's emphasis on the importance of such predictions that Mill objects in the earlier quotation. In the *Logic of Science*, Mill (1882:356) argues against Whewell's position whereby, 'the coincidence of results predicted from an hypothesis with facts afterward observed, amounts to conclusive proof of the truth of the theory'. In chapter 2 we saw how Peirce opposed Mill's argument for inductive reasoning. Peirce's preference for Whewell's approach is clear when he states, 'Whewell's views of scientific method seem to me truer than Mill's' (CP 1.404). Writing after all three eka-elements became known, Peirce uses the success of their predictions as an endorsement of Mendeleev's scheme when he states, [t]he discoveries of Gallium, Germanium, and Scandium have proved that there is some truth in one part of Mendeléef's theory' (EP2:111, 1901).

The philosopher of science Carl Hempel (2013:428) argues, 'it is highly desirable for a scientific hypothesis to be confirmed also by "new" evidence – by facts that were not known or taken into account when the hypothesis was formulated'. To demonstrate a theory justified by the discovery of new phenomena Hempel chooses the Balmer formula for the line emission spectra of hydrogen. In 1885 the Swiss school teacher J. J. Balmer (1825-1898) calculated that the wavelengths (λ) of the four lines in the hydrogen spectra – named alpha, beta, gamma and delta – corresponded closely to the following formula, where n has values of 3, 4, 5 and 6 and b is a constant.

$$\lambda = b\frac{n^2}{n^2 - 2^2}$$

As Hempel explains, Balmer derived his formula from the four lines in the hydrogen spectra of which he had prior knowledge of. Further investigations revealed a total of thirty-five lines in the spectra, all of which agreed well with Balmer's formula. Whilst the additional thirty-one lines might be said to offer confirmatory evidence for Balmer's formula, Hempel (2013:429) asks 'a puzzling question': what if 'Balmer's formula had been constructed only after all the 35 lines now recorded in the series had been fully measured'? In this fictitious case would the Balmer formula be less well confirmed being derived from thirty-five data points compared to being formulated on the basis of four known lines and subsequently confirmed by thirty-one subsequent findings? The difference between the two cases rests on the historical order in which the findings were made – four before Balmer's formulation of his formula and thirty-one after. But if confirmation is considered in terms of how the evidence 'fits' with the theory then why should the historical sequence by which the evidence is accumulated matter? On what basis if any should later successful predictions be counted as offering greater confirmatory weight than the successful accommodation of the data points a particular hypothesis was founded on?

There is a parallel here with Mendeleev's periodic table. The original table of 1869 was constructed using the atomic weights and chemical properties of sixty two known elements. The three eka-elements once discovered conformed to Mendeleev's arrangement. So too the thirty-four spectral lines in hydrogen emission spectra later conformed to the Balmer formula. In the case of Mendeleev's periodic table, to what extent if any, should the successful prediction of the three eka-element lend greater confirmatory weight compared to the accommodation of the original sixty-two (later sixty-five) elements? The confirming advantage of data discovered after the hypothesis argues Hempel (2013:429) is that whilst for '*any* set of quantitative data, it is possible to construct a hypothesis that covers them… [w]hat *is* remarkable, and does lend weight to a hypothesis, is its fitting "new" cases' (emphasis in the original). From this perspective data unknown at the time, but subsequently found to agree with a particular hypothesis, might be taken as successful tests of the original hypothesis. The thirty-four spectral lines discovered after Balmer proposed his formula as well as Mendeleev's three successful eka-predictions can from this perspective be seen as successful confirmatory tests of their respective hypothesis.

A case against the predictive thesis is offered by Laura Snyder (1998:460) when she argues that whilst our ''intuition' that 'predictions of new phenomena are extremely impressive and seem to endow scientists with a kind of mystical power to foretell the future', this is not the way scientists use evidence. Scientists, argues Snyder (1998:467), use evidence 'in the impersonal sense'…

> ‘When a scientist publishes experimental results, claiming that these constitute evidence for a certain theory, she is not claiming merely that these results constitute her personal (factual or normative) reason for believing the theory. Rather, the scientist is claiming that the results constitute a reason—a reason for anyone—to believe the theory'.

Snyder (1998:469) associates this impersonal use of evidence with what she describes as the ‘Objective Concept of Evidence: whether e is evidence for h [hypothesis] does not depend upon anyone’s beliefs or knowledge about e, h, or anything else. Hence if some e is evidence for h, it is so regardless of what any person knows or believes’. By way of illustration Snyder considers the case of a person suffering an outbreak of spots of a particular kind. This is evidence for a case of measles – even if no one has seen the spots. That is to say no one knows that the evidence is true. On the basis of Snyder’s objective concept of evidence, even if no one ever gets to know of the spots, they remain as evidence for a case of measles. Thus if the evidence need not be known in order to confirm the hypothesis – ‘a case of measles’ – then, as Snyder (1998:470) argues, [c]learly if e [evidence] does not need to be known in order to confirm h [hypothesis], then it makes no sense to require that it must be known either before or after h is invented, in order to confirm it’. Balmer based his formula on the known wavelengths of four lines in the hydrogen spectrum. A further thirty-one lines were subsequently found with wavelengths that agreed with his formula. From Snyder’s perspective, whether the spectral data was known before or after Balmer proposed his formula, is irrelevant to whether the data is evidence for his hypothesis. For as Snyder (1998:477) concludes in ‘paraphrasing Gertrude Stein: “evidence is evidence is evidence”. The time at which some information is known relative to the forming of a theory is as relevant to its evidential value as is the time of day a rose is smelled to its status of being a rose’. The economist John Maynard Keynes (1921:349) captures this point when he states[71],

> The particular virtue of prediction or predesignation is altogether imaginary. The number of instances examined and the analogy between them are the essential points, and the question as to whether a particular hypothesis happens to be propounded before or after their examination is quite irrelevant.

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[71] Cited in Achinstein (1998:491)

Applying both Keynes and Snyder's objective stance on evidence to the periodic table, it is the combination of Mendeleev's prior knowledge of sixty or so existing elements, taken together with the three eka-elements, that lends weight to his scheme. That is to say evidence taken as a whole and independent of before or after the scheme was proposed. Chang (2016:89) concedes that 'it is quite difficult to argue against the general point voiced by Snyder, Mill and Keynes', citing sciences such as geology and cosmology which offer little in the way of testable novel predictions. Nevertheless, whilst agreeing that novelty is valuable because of its independence from the evidence used in formulating the original hypothesis, Chang (2016:91) concludes: 'Novel prediction is not the only way to achieve variety of evidence; it is merely a very striking way'.

6.3 The accommodation-prediction debate and the periodic table

This section focusses on how the periodic table appears in this debate. A number of scholars have used Mendeleev's periodic table to argue the relative epistemic merits of prediction of unknown facts versus accommodation of known facts, (Maher, 1988; Lipton, 1991; Scerri & Worrall,2001; Akeroyd, 2003; Brush, 2007; Scerri, 2007). One of the main purposes of this chapter is to argue that taking the periodic table as an iconic sign offers an alternative epistemological perspective by bringing together arguments often separated by the polarising nature of the accommodation-prediction debates. This further develops the case made in chapter six where the iconic robustness of the periodic table was argued in terms of its fruitful capacity to promote thought experiments whilst also undergoing reconfigurations in response to new elements as well as to various false predictions – that is against Nature's resistance or kickback. The iconic robustness of the periodic table combines the table's capacity to accommodate in terms of novel elements – nature's resistance – as well as its capacity to generate new knowledge. It will be helpful to begin by summarising some of the detail of the recent contributions to the 'accommodation-prediction' debate as it applies to the periodic table.

6.3.1 Mendeleev's periodic table: the case for novel predictions.

A novel prediction relates to phenomena unknown at the time of the prediction – such as Mendeleev's three eka-elements. The significance of novel predictions was expressed by Imre Lakatos (1978:114) in stating that it is, 'the successful predictions of novel facts which constitute serious evidence for a research programme'. The reaction of nineteenth century chemists to Mendeleev's periodic table in the light of his novel predictions can be gauged by looking at its treatment in chemistry texts of that period. The first of Mendeleev's three eka-elements to be discovered was gallium (eka-aluminium) in 1871 by Paul Emile Lecoq de

Boisbaudran. The chemist Adolphe Wurtz (1880:155) in his influential text *The Atomic Theory* (1880), published before the remaining eka-elements were known[72], comments on de Boisbaudran's discovery as 'a remarkable fact that one of these gaps [the eka-elements] has since been filled up'. Although Wurtz (1880:155) describes Mendeleev's periodic table as a 'synthesis' and 'a powerful one' he nevertheless remains cautious. In pointing out that there is a generally periodic relationship between physiochemical properties and atomic weight, he notes that the change in atomic weight across a period is irregular and variation in property is not related to this difference – something that also frustrated Peirce. It is Wurtz's (1880:162) view that both these factors present 'real difficulties' for Mendeleev's system. Other difficulties include elements such as copper and nickel, with near identical atomic weights, which suggest the impossibility of providing gaps for unknown elements with atomic weights close to known elements. Finally returning to the discovery of Mendeleev's eka-element gallium, Wurtz (1880:163) notes the atomic weight as determined by de Boisbaudran 'is sensibly different to that which was predicted by Mendelejeff'. What Wurtz does not comment on is that de Boisbaudran noted Mendeleev's predicted density for what was now known to be gallium at 5.9 or 6.0, but as the historian Stephen Brush (1996:604) notes, on redetermination corrected his original density from 4.7 to 5.935 thereby confirming Mendeleev's predicted value. Towards the end of the nineteenth century and after the successful discovery of the two remaining eka-elements, the historian of chemistry F.P. Venable (1896:107) claims that whilst the periodic law attracted the attention of chemists at the time, 'it was only the lucky discovery of some new elements, thus fulfilling certain predictions of Mendeleeff, that brought it prominently before the chemical world'.

The importance of Mendeleev's successful predictions in bringing the periodic table 'prominently before the chemical world' is supported by Stephen Brush's (1996:617) extensive research into the reception of Mendeleev's periodic table by 'spending considerable time perusing the crumbling pages of late nineteenth-century chemistry journals and textbooks' and having confirmed , 'Mendeleev's periodic law attracted little attention (at least in America and Britain) until chemists started to discover some of the elements needed to fill gaps in his table and found that their properties were remarkably similar to those he had predicted'. Writing more recently Brush (2015:167) concludes that there were three reasons for the acceptance of Mendeleev's periodic law and in order of importance,

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[72] Scandium (eka-boron) 1879 and germanium (eka-silicon) 1886

1. it accurately describes the correlation between physicochemical properties and atomic weights of nearly all known elements;
2. it has led to useful corrections in the atomic weights of several elements and has helped to resolve controversies such as those about beryllium;
3. it has yielded successful predictions of the existence and properties of new elements.

Brush's conclusion here is that whilst Mendeleev's successful predictions were important – particularly in bringing the periodic law to the attention of chemists at the time – the successful accommodation of existing data was of greater importance in establishing the law's acceptance.

In his book *Inference to the Best Explanation*, Peter Lipton describes how the case for accommodation rests on a hypothesis being formulated to fit pre-existing evidence. A successful prediction is deduced and verified by observation after the theory has been constructed. Whilst Lipton (2004:165) argues that most people are 'more impressed by predictions than accommodations', he offers no evidence for what might be described as the psychological attraction of predictive effects. Lipton (2004:165) cites Mendeleev to support his predictive thesis: 'when Mendeleev produced a theory of the periodic table that accounted for all sixty[73] known elements, the scientific community was only mildly impressed. When he went on to use his theory to predict the existence of two unknown elements that were then independently detected, the Royal Society awarded him its Davy Medal'. The two unknown elements were gallium in 1875 (eka-aluminium) and scandium in 1879 (eka-boron). The Davy Medal (1882) was shared between Mendeleev and Julius Lothar Meyer. Lipton (2004:165) considers the decider for the award as being 'sixty accommodations paled next to two predictions' – although he offers no historical evidence to support why these two successful predictions were so significant to chemists at the time. It could also be argued that the correct placing of gallium and scandium into the periodic table gave an additional two accommodations thereby further securing the validity of Mendeleev's claims.

The predictivist argument is also advanced by Patrick Maher who uses Mendeleev to support his case. Here Maher (1988:275) argues that, 'if scientists accord no special

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[73] There were in fact sixty two known elements at this time

confirmatory value to predictions, then it is quite inexplicable why their confidence in Mendeleyev's predictions should have increased substantially after one or two of those predictions had been verified’. Both Lipton and Maher stress that the acceptance of the periodic table was due to chemists being convinced by the verification of Mendeleev’s predictions and not the accommodation of new and previously existing elements.

From his extensive research of nineteenth century chemistry books Brush (1996:609) rejects Lipton and Maher’s emphasis on prediction in that ‘unfortunately, [they] give no documentation for their proposition’. Nonetheless Brush (1996:609) does not dismiss the value of the predictive support offered by the discovery of new elements, as ‘many chemists did give some credit for novelty’ but ‘not thirty-one times as much!’ There is no attempt to deny that Mendeleev’s successful predictions played an important role – what Eric Scerri and John Worrall (2001:410) in their extensive paper ‘Prediction and the Periodic Table’ describe as the ‘special psychological effect’ on chemists at the time. Such an effect would have raised the profile of Mendeleev and his periodic table.

The case of the Davy Medal is a point of contention for scholars. The citation to the award reads[74], ‘for their discovery of the periodic relations of the atomic elements’ – with no mention of successful predictions. Lothar Meyer’s work focussed not on predictions but on Avogadro’s hypothesis, atomic weights and atomic volumes; he made no predictions. Both Mendeleev and Lothar Meyer produced very similar versions of the periodic table with only Mendeleev leaving gaps for future discoveries. If predictive success was important to the Society, then why include Lothar Meyer? These inconsistencies, in the opinion of Scerri and Worrall (2001:416), ‘pose a problem for the predictivists’. They point out that the citation emphasises the value of Mendeleev and Lothar Meyer’s classification of the elements ‘in the empirical order of their atomic weights’ and for the ‘marvellous regularity’ their arranging of the elements gave. The only tilt towards prediction might be taken from the closing lines: ‘this periodic series not only enables us to see clearly much that we could not see before; it also raises new difficulties, and points to many problems which need investigation’. It is the view of Scerri and Worrall (2001:417) that the wording of the citation is an embarrassment ‘for those defending the story about the crucial role of the new elements’.

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[74] cited by Michael Gordin (2015:75)

A number of scholars responded to Scerri and Worrall's paper. The absence of any reference to prediction, replied Michael Akeroyd (2003), was due to the Society's sensitivity towards a priority dispute that existed between Mendeleev and Lothar Meyer. In addition Mendeleev was thought to be critical of Meyer for, as Akeroyd (2003:341) describes, not fully comprehending 'the deeper meaning of the periodic system'. The absence of any mention of 'predictive success' is presented as the Society's desire to ameliorate any ill feeling existing between Mendeleev and Meyer – what Akeroyd (2003:341) describes as the 'social factors' at work. Also in response to Scerri and Worrall (2001), Eric Barnes (2005:808) claimed that 'the historical facts demonstrate the truth of predictivism' and that 'the success of a comparatively small number of predictions' culminated 'in Mendeleev's receipt of the Davy Medal by the Royal Society in 1882'. Again no evidence is offered - Barnes appears to assume the Society's motives in privileging predictive success. It is difficult to reconcile Akeroyd and Barne's position to the Society's celebration of 'marvellous regularity' as stated in the citation. If we are to take the wording at face value then, as Brush (1996:609) makes clear, 'the Davy Medal was awarded for accommodation, not for prediction.'

The periodic table was the subject of a long-running priority dispute between Lothar Meyer and Mendeleev. In his account of this conflict, the Mendeleev scholar Michael Gordin (2015:76) argues that the Royal Society by awarding the Davy Medal jointly was seeking to bring the dispute to an end by acting as a 'nonpartisan national organization opting for a middle path' thereby seeming 'to codify a consensus developing even among nationally committed observers', the consensus being that the credit for the periodic table was due to both Lothar Meyer and Mendeleev. It is Gordin's (2015:76) view that the royal Society's decision 'seemed to have calmed matters considerably' and quotes Lothar Meyer's associate, Karl Seubert, describing this as 'a most just and beautiful decision'.

6.3.2 The case for accommodation

The focus of this section is on the accommodation of elements known at the time of Mendeleev's first periodic table (1869). This account will also include the accommodation of the noble gases. As set out earlier in chapter five, the unreactive gases argon and helium[75] were isolated by Sir William Ramsay in 1895 - the first members of a family of elements later to be known as the inert gases. The lack of chemical reactivity made these gases difficult to characterise. Furthermore there were no gaps for them in the periodic

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[75] Helium had been previously discovered in 1868 and before Mendeleev first periodic table in 1869, by Pierre Janssen during a spectral analysis of a solar eclipse. (Nath (2013:257))

table – they were not one of Mendeleev’s predictions – and so needed to be accommodated within his scheme. The atomic weights of helium (4) and argon (40) were later assigned by Ramsay and Lord Rayleigh. Positioning argon into Mendeleev’s scheme proved to be particularly difficult. With an atomic weight of forty, argon should have been placed between potassium in the first group and calcium in the second – but there was no position available. Mendeleev, much distressed as the whole edifice of his scheme became threatened, suggested that argon was not a new element but a triatomic form of nitrogen, N_3. It was, as Bernadette Bensaude-Vincent (1986:16) describes, ‘thanks to their sound belief in the regular periodic function’ that in 1900 Ramsay and Rayleigh proposed that a new group be added to the periodic table – to the left of the first group of alkali metals. They left a gap below helium and above argon for an element yet to be discovered (later neon) and were obliged to accept the irregularity of atomic weight sequence: Ar (40), K (39.1), Ca (40). This has all the hallmarks of Peter Lipton’s (2004) criticism of accommodation - ‘fudging’ - where new information is made to fit in with a particular hypothesis. This new family of elements was named group 0. Ramsay and Rayleigh’s boldness (their ‘fudging’) was repaid as other inert gas elements such neon and xenon[76] were later isolated and took up their allocated positions within the new group. Mendeleev’s scheme was shown to accommodate this new group of elements successfully.

It is worth mentioning at this point that Mendeleev accepted the noble gases into his periodic scheme as group 0, as can be seen from this copy of the periodic table printed in the third edition (1902) of his *Principles of Chemistry*:

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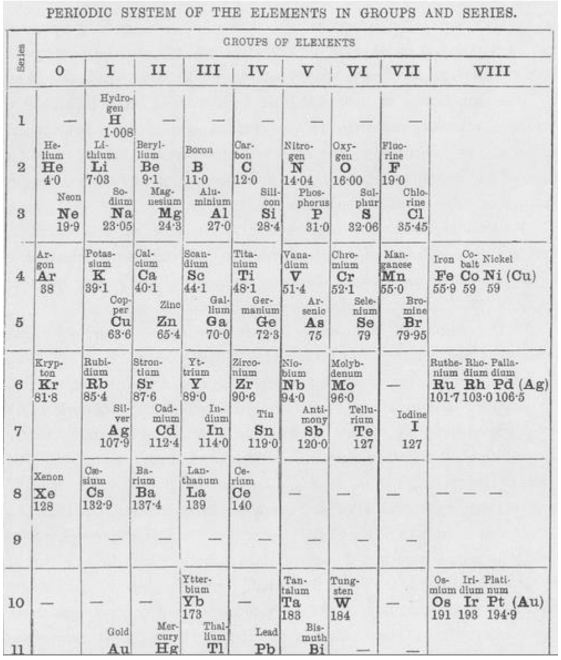
[76] Neon was discovered in 1898 by Sir William Ramsay and Morris Travers, shortly after their discovery krypton (Wolfenden (1969:572))



PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES.

Series	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Hydrogen H 1·008	—	—	—	—	—	—	
2	Helium He 4·0	Lithium Li 7·03	Beryllium Be 9·1	Boron B 11·0	Carbon C 12·0	Nitrogen N 14·04	Oxygen O 16·00	Fluorine F 19·0	
3	Neon Ne 19·9	Sodium Na 23·05	Magnesium Mg 24·3	Aluminium Al 27·0	Silicon Si 28·4	Phosphorus P 31·0	Sulphur S 32·06	Chlorine Cl 35·45	
4	Argon Ar 38	Potassium K 39·1	Calcium Ca 40·1	Scandium Sc 44·1	Titanium Ti 48·1	Vanadium V 51·4	Chromium Cr 52·1	Manganese Mn 55·0	Iron Cobalt Nickel Fe Co Ni (Cu) 55·9 59 59
5		Copper Cu 63·6	Zinc Zn 65·4	Gallium Ga 70·0	Germanium Ge 72·3	Arsenic As 75	Selenium Se 79	Bromine Br 79·95	
6	Krypton Kr 81·8	Rubidium Rb 85·4	Strontium Sr 87·6	Yttrium Y 89·0	Zirconium Zr 90·6	Niobium Nb 94·0	Molybdenum Mo 96·0	—	Ruthenium Rhodium Palladium Ru Rh Pd (Ag) 101·7 103·0 106·5
7		Silver Ag 107·9	Cadmium Cd 112·4	Indium In 114·0	Tin Sn 119·0	Antimony Sb 120·0	Tellurium Te 127	Iodine I 127	
8	Xenon Xe 128	Cæsium Cs 132·9	Barium Ba 137·4	Lanthanum La 139	Cerium Ce 140	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Ytterbium Yb 173	—	Tantalum Ta 183	Tungsten W 184	—	Osmium Iridium Platinum Os Ir Pt (Au) 191 193 194·9
11		Gold Au	Mercury Hg	Thallium Tl	Lead Pb	Bismuth Bi	—	—	

Figure 46: Mendeleev's periodic table of 1902
Source: Jensen, W. 2002. *Mendeleev on the Periodic Law: Selected Writings, 1869–1905*. Dover Publications, Mineola, NY. page 248

Whilst Mendeleev accepted this arrangement, he resisted for some time the addition of the new group of noble gases. One reason for this resistance, Bensaude-Vincent (1986:16) argues, is that the earlier and more symmetrical arrangement of reactive alkali metals and halogens at either side of the system was 'disturbed by the group of inert gases'.

Note that Mendeleev sets the atomic weight of argon at 38 and not 40 as determined by Lord Rayleigh and Ramsey (1895). With an atomic weight of 38, argon does not disrupt the numerical sequence passing from chlorine (35.45) to potassium (39.1).

In placing the inert gases, Ramsay and Rayleigh had both accommodated the new elements and predicted the existence of one yet to be discovered – neon. The practice of these two scientists – their method of practical inquiry – encompassed both the predictive and accommodation processes and was driven in part by their belief in and commitment to Mendeleev's system. By its part in Ramsay and Rayleigh's project the periodic table demonstrated its iconicity in pointing towards a novel element (neon). We see too the periodic table's iconic robustness as it flexes and pushes back against nature's resistance in the form of this newly discovered element, an element without a prearranged place in Mendeleev's table. I believe this particular episode in the history of Mendeleev's scheme illustrates the shortcomings of arguments that attempt to polarise methods of theory construction along one or other approach, a point emphasised by Scerri and Worrall (2001:447) when they write that there is 'again no support in the historical record for the idea that the prediction of neon played any particularly 'crucial' role here or that it counted for any more than the 'accommodation' of argon—if anything, the contrary'. In their view the accommodation of the noble gases casts great doubt on any serious distinction between accommodation and prediction. As we will see later, taking the periodic table as an iconic sign draws together the detail offered by these two positions as a single account, without the need for drawing a distinction in their epistemic value.

One final point on the case of the noble gases: Mendeleev's resistance to accepting these particular novel elements into his scheme shows how the format of his representation of the relations between the chemical elements affected his thought processes. For example the very nature of what it meant to Mendeleev to accept argon as an element into his scheme was directed by his conception of how the table should be constructed. As Andrea Woody (2014:137) argues, for Mendeleev '[c]ertain possibilities seem almost preordained, while to recognize others, even as possibilities, strains tremendously against intuitions cultivated by the representational tools we habitually employ'.

The accommodation of all new elements did not always follow this successful path. For example the rare earth ytterbium was first isolated in 1878 and positioned into the table in 1881 and some four years before the addition of germanium. Mendeleev could accommodate ytterbium (atomic weight 178) only by removing erbium and its place allocated to ytterbium. Mendeleev attempted to reclassify the atomic weight of erbium at 178 in order that it might fit his table one space to the right of ytterbium. This value was contested by some of his contemporaries. Also erbium sat uneasily in this new position in relation to zirconium. Copies of the periodic table dated 1871 include erbium but it has disappeared ten years later in 1881 - a 'Lipton fudge'! Between 1878 and 1882 Mendeleev was successful in predicting the existence of gallium and scandium which both fitted neatly into his scheme as well as positioning ytterbium. At the same time during these five years it proved impossible to accommodate five rare earth elements: erbium, gadolinium, holmium, thulium and samarium. That is to say three successes and five failures in the space of five years. It is Akeroyd's (2003:349) opinion that, 'the detailed successful predictions of the properties of gallium and scandium were essential to counterbalance the discovery of the rare earths'. These failures in accommodation were outweighed by the earlier predictive successes to such a degree that, Akeroyd (2003:349) argues, had Mendeleev proposed his original table as late as 1878 then 'it would never have achieved any theoretical respectability'. The rare earths presented this problem due to the very slight differences in their atomic weights and similar chemical properties.

The philosophical debate around the relative significance of prediction over accommodation will no doubt continue both for the case of Mendeleev's periodic table and for scientific laws in general. Scerri and Worrall (2001:410) conclude that,

> There is no real sign of a 'dramatically altered attitude' towards Mendeleev's table and its underpinnings between, say, 1871 and 1874; there seems instead to have been a gradual process of diffusion and 'acceptance' (though this term too hides important complexities)—a process in which certain 'corrections' of previously accepted 'data' (about atomic weights of known elements) and certain 'accommodations' of already known evidence played equally significant roles alongside the predictive successes.

The accommodation of a number of elements into Mendeleev's scheme was only made possible by him 'correcting' the values for their atomic weights. This was not particularly unusual as values were occasionally subject to revision at that time. One such 'correction' was made to beryllium which up to that time had an atomic weight of either 9 or 14. Mendeleev assigned its value at 9 in order that it would fit into the second group of his table with a valency of two.

An interesting point arises here in how Mendeleev projected new knowledge on the basis of the periodic table. In what sense is correcting the atomic weight of a known element different from predicting the atomic weight of an element yet to be discovered? It is Brush's (1996:599) view that Mendeleev's predictions of the properties of previously unknown elements as well as his corrections to existing atomic weights should both be considered as 'novel predictions'. To differentiate between correcting incorrect data such as atomic weight from giving a property of a previously unknown element Brush (1996:600) introduces the term 'contraprediction'. Mendeleev made a number of successful contrapredictions, including the atomic weights of yttrium, cerium and uranium, which ensured that these elements were accommodated within his scheme. These values were later corroborated independently.

Brush (1996:600) notes the position of a number of philosophers of science that, 'a prediction based on a new hypothesis should disagree with what one would expect on the basis of the knowledge available before the hypothesis was proposed'. On this basis, in the discussion of contrapredictions – such as correcting the atomic weight of uranium from 120 to 240 – Brush (1996:600) takes this further in arguing, 'that if successful novel predictions are better evidence than retrodictions, successful contrapredictions are better yet'. Quite why correcting the atomic weight of say beryllium from 14 to 9 is better evidence for the acceptance of the periodic table than predicting the atomic weight of eka-boron (later scandium) at 44 Brush does not say. Nonetheless Brush (1996:600) is clear in his view that contrapredictions, 'cast doubt on the orthodox view that theories are tested by observations'. This is because such earlier observations as the atomic weight of beryllium as 14, 'themselves are subject to test by contrapredictions'. Although first written some years ago, Brush affirms his commitment to these claims by effectively reprinting the 1996 paper in a more recent book – Brush (2015:156 – 169). As the values of Mendeleev's atomic weights assigned to his 'contrapredictions' were later corroborated by independent experiment, Scerri and Worrall (2001:430) argue that Brush's view on contrapredictions as being 'better yet' is 'un-contestable in view of the just emphasised fact that the corrections of atomic weights were independently supported rather than made simply so as to fit the table'.

This account gives some flavour of the disagreements around the periodic table that continue to exist about the epistemic value of accommodation of compared to novel predictions. Such disagreements are likely to continue for, as the historian of science Mansoor Niaz (2009:62) argues, 'historians and philosophers of science [will] continue to debate as to what was crucial for the acceptance of the periodic law by the scientific community: accommodation of the existing elements or the prediction of new ones'. As we have seen, in terms of the periodic table these claims and counter-claims focus on the relative epistemic merits of the accommodation of existing phenomena – elements known at the time – set against successful predictions of new phenomena – the three eka-elements. Such a polarised view is rejected by Lipton (2004:165) who argues, 'successful theories typically both accommodate and predict'. The purpose of the coming section is not to argue for one particular side of this debate but to view the substance of the arguments from a different perspective: I will argue that the iconic nature of the periodic table provides an opportunity to go beyond the debate around accommodation and prediction outlined in this chapter. The hope is to offer a new perspective on Mendeleev's epistemic endeavour. That is one from the perspective of Mendeleev's representational practice and from the viewpoint of Peirce's iconicity.

6.4. Accommodation and prediction: re-characterising the arguments in terms of practice

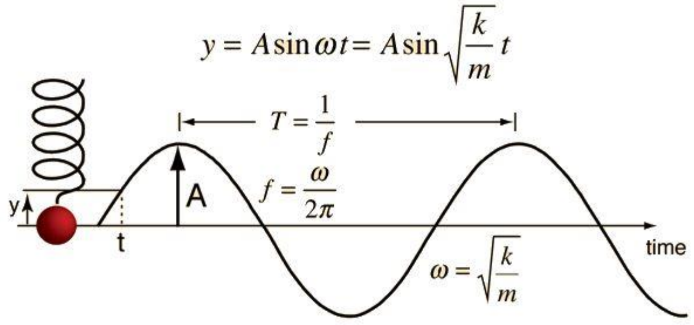
Some encouragement in seeking to look beyond the accommodation-prediction debate is offered in recent scholarship, which casts doubt on whether the periodic table sits easily within the 'accommodation-prediction' framework. For example Andrea Woody (2014:147) argues that her extensive researches into the periodic law, 'reveals some naiveté in the literature concerning the role of accommodation versus prediction in theory acceptance'. Part of Woody's reasoning here is that the periodic law, represented by its corresponding table, is not a law in the traditional sense – not being cast as a logical conditional and rarely as an exact mathematical relation. This lack of mathematical exactitude, which Peirce sought unsuccessfully to find, is perhaps also the basis of Scerri's (2012:328) view that the periodic table does not fit the traditional mode for philosophical discussion for, 'it is neither a theory, nor a model nor perhaps even a law of nature in the traditional sense' (Scerri offers no reasons for this view).

The points Woody and Scerri make here can be illustrated by considering of the mathematics of periodic motion – sometimes described as simple harmonic motion – described by an oscillating system, such as an object suspended from a spring. An analysis of this periodic form of motion requires two laws, both of which are in Woody's words, cast as an 'exact mathematical relation' – a condition that would likely satisfy Scerri's concept of a traditional law. The two laws operating here are,

a) Hooke's law
   $F = -kx$;
   F = force, x = displacement, k = the spring constant)

b) Newton's second law of motion
   $F = ma$
   F = force, m = mass, a = acceleration

Without delving into the mathematics, the following representation and associated formulae of this form of periodic motion is common to many physics texts.



y = displacement
k = force constant for the spring
t = time
A = amplitude
T = period of oscillation
ω = angular frequency
m = mass of the object

Figure 47: Simple Harmonic Motion
Source: taken from *HyperPhysics*, Department of Physics and Astronomy, Georgia State University[77]

When Mendeleev (1875:218) claims that the properties of the chemical elements and the formulae and properties of their compounds are, 'periodic functions of the atomic weights of the elements' he was alluding to the mathematically exact form of periodic motion demonstrated the example of simple harmonic motion shown in figure 47. Writing some fourteen year later Mendeleev (1888:181) makes a clear link between his periodic law and the laws of physics when he states, '[t]he periodic law has shown that our chemical individuals display a *harmonic periodicity* of properties, dependent on their masses (emphasis added). In his *Principles of Chemistry*, Mendeleev (1901:215 n321) states that, 'Newton laid the foundation of a truly scientific theoretical mechanics of external visible motion' and that whilst 'a Newton has not yet appeared in the molecular world; when he does, I think that he will find the fundamental laws of the mechanics of invisible motions of matter…in the chemical structure of matter'. I would suggest that Mendeleev's use of 'periodic' to describe the relations between the chemical elements arranged in order of atomic weight was a direct allusion to Newtonian mechanics and perhaps the beginnings of its emergence in 'the chemical structure of matter'. Mendeleev (1901b:453) makes many references to both Lavoisier and Newton in his *Principles of Chemistry;* Appendix 1 being titled 'An Attempt to Apply to Chemistry One of the Principles of Newton's Natural Philosophy'. It is Gordin's (1998:110) view that Mendeleev sought 'desperately' to be a successor to Newton and Lavoisier. Nevertheless, the exact form of periodicity demonstrated by the mechanical system of an oscillating spring, modelled with the aid of Hooke's and Newton's respective laws, is not demonstrated by Mendeleev's periodic law. The atomic weights of the chemical elements as arranged in the periodic table increase but

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[77] URL: http://hyperphysics.phy-astr.gsu.edu/hbase/shm2.html last visited 20/03/2017

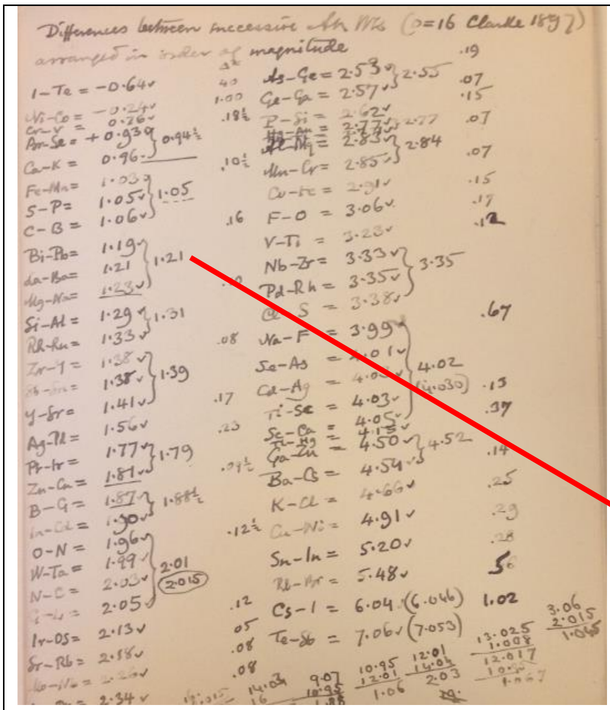
not in a regular fashion. The formulae and properties of their compounds are not a mathematically exact periodic function of their atomic weights. It is for reasons such as this - and also for reasons related to what philosophers of science usually define as a law - that Woody and Scerri question the periodic law, on which the periodic table is founded, as being a law 'in the traditional sense'.

Whilst Scerri (2012:329) argues that the periodic table may not be grounded on a law in the 'traditional sense', he accepts that 'the periodic system is capable of rationalizing vast amounts of information, and capable of making successful predictions'. Debates around whether the periodic table is founded on a 'traditional' law and whether its acceptance is founded on its capacity to 'accommodate' or to 'predict', are likely to continue – see for example Niaz's (2016) study on the reasons given in recent text books (1966 – 2002) for the acceptance of the periodic table. As suggested earlier, such debates are unlikely to be settled any time soon. However, by taking the substance of competing claims made under the categories of *accommodation* and under *prediction* there is, I would argue, a more coherent account of the periodic table to be had, if we connect these claims from the perspective of Mendeleev's *representational practice* and by way of Peirce's formulation of iconicity. In taking this approach the aim is to demonstrate Mendeleev's *articulated awareness* of relations between the chemical elements as represented by the periodic table.

As part of his account of the study of scientific *practice* Chang (2014: 67) argues 'that a serious study of science must be concerned with what it is that we actually *do* in scientific work' (emphasis in the original). I will argue in the coming section that aspects of what Mendeleev *did* are captured by his representational practice whereby he both *accommodates* and *predicts* the relations between the chemical elements. Furthermore that Mendeleev's *representational practice* – or *doing* – is captured by Peirce's formulation of iconicity. For as Chang (2014:76) argues, '[i]nstead of thinking about the abstract nature of a definition, we can consider what one has to *do* in order to define a scientific term' (emphasis in the original): in my case by reformulating the arguments around 'accommodation' and prediction' and through the lens of Peirce's iconicity. Furthermore there is further encouragement in this approach in Chang's (2014:77) claim that, '[m]ost standard philosophical topics can receive a new lease of life by being re-conceptualized fully in terms of activities'.

In chapter four I argued that the periodic table functioned as an iconic sign which, when mediated by Mendeleev's mental processes, stimulates thoughts on the relations between the chemical elements. Mendeleev's engagement with the iconic periodic table was also a practical activity: experimenting with relations on paper in order to disclose new relations as evidenced by an examination of the proto forms of the periodic table (figures 36 and 37). In chapter three, we saw how Peirce sought unsuccessfully to fathom the mathematical relationship underpinning the periodic table. In this next section Peirce too can be seen to be engaging practically as a paper and pencil exercise in order to explore and ultimately reveal this relationship. In this next example of Peirce's quest we can perhaps see a glimpse of the end point he was seeking in his sketch of a periodic curve similar to the one described above. This curve sketch follows another of Peirce's series of calculations looking at the pattern of change in atomic weights for the chemical elements arranged according to Mendeleev's scheme.

This unpublished manuscript (MS 1039, c1898), written around five years after Peirce's submission to *The Nation* on *The Periodic Law* (1892), opens as a chemistry text book might in describing a number of key terms such as 'substance' – materials where 'their smallest sensible parts have the same physical properties'. In the style of a text book, Peirce continues to expand on other important concepts such as the nature of a chemical compound and atomic weights. This is followed by a couple of pages describing the properties of a series of potassium compounds. The descriptive chemistry then comes to an abrupt halt as Peirce switches his attention to a multitude of calculations on the atomic weights of the elements. Here is an example:



Differences between successive At Wts (O=16 Clarke 1897) arranged in order of magnitude

As the title states, Peirce is calculating the differences in atomic weights between successive elements within the periodic table. The data is based on ‘O=16 Clarke[78] 1897’

The differences in atomic weights are arranged in order of magnitude. Having ranked the differences Peirce then calculates the average difference between successive pairs or triads of ordered pairs of elements – this represents the second column of numbers.

For example,

Bi – Pb 1.19

Li – Be 1.21

Mg – Na 1.23

Average of all three = 1.21

Figure 48: Peirce’s calculation of atomic weight differences
Source: taken from Peirce’s MS 1039 v8 c1898

Peirce makes no introduction to these calculations and offers no conclusions. My suggestion is that he broke off from his earlier descriptive account of chemistry to embark on one of his many searches for an exact mathematical relationship between the atomic weights of successive elements within Mendeleev’s scheme. This next page of calculations is taken from the same MS and again there is nothing by way of description to assess what Peirce was up to:

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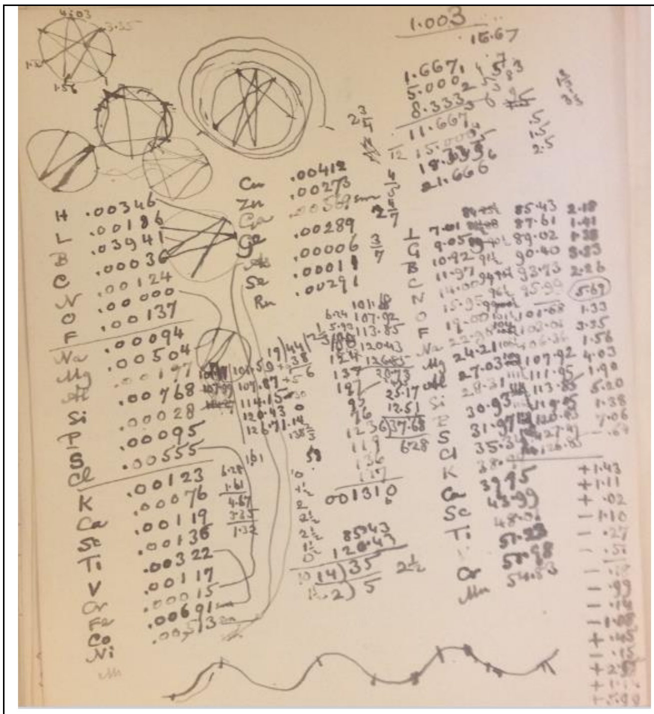
[78] The American chemist Frank W. Clarke, graduated from the Lawrence Scientific School in 1867 and later founded the American Chemistry Society published his *Recalculation of the Atomic Weights* in 1882.



The column on the left shows the first twenty elements listed with horizontal lines between F and Na, Cl and K thereby identifying successive rows or periods of elements. The element Be is omitted from the first period. Peirce gives no indication of what the five-figure decimal fractions refer to but the connecting lines suggest a search for the numerical relations between the elements concerned. The values appear to be relative to oxygen as the entry for oxygen is zero. The atomic weights (Clarke 1897) were all relative to O=16. The column of data on the right lists the atomic weights of the elements: Li=7.01, G[79]=9.05, C=11.97 etc. Curiously the values do not correspond to the values by Clarke (1897:364/5) where, for example Li = 7.03 and G = 9.08

Figure 49: Peirce's calculation of atomic weight differences and periodic curve
Source: taken from Peirce's MS 1039 v8 c1898

What is most intriguing is his sketch at the bottom of the page of a typical periodic curve – subject to the exact mathematical formalism Peirce is seeking – with a number of points marked off. Regrettably Peirce gives no indication as to how this curve – or the circular diagrams - relates to the atomic weight calculations. I believe however that we are able to make a number of speculations around Peirce's methods here. In particular I will attempt to show that figure 49 is an example of Peirce experimenting on paper with the relations between the atomic weights of the chemical elements in order to disclose new relations. Looking again we can see that in addition to the periodic curve and the circular diagrams Peirce has divided the data in to the form of a table: a line drawn between fluorine (F) and

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[79] G (glucinium) later renamed beryllium

sodium (Na) and also between chlorine (Cl) and potassium (K) separates the elements of what today would be known as period 1 (Li – F[80]), period 2 (Na – Cl) and period 3 (K – Ni[81]). It is perhaps surprising that argon and helium are not included; the manuscript is dated 1898 and three years after Ramsay and Rayleigh published on these elements[82]. Before attempting to offer any view on how Peirce might have been using the information he has assembled (figure 49) it is worth recalling three points made in earlier chapters. Firstly the emphasis Hookway places on the capacity of an iconic representation to reveal new discoveries by engaging with the sign itself. Secondly Peirce's emphasis that the process of reasoning is founded on the construction of iconic diagrams and that these diagrams make relations visible. It is through the act of representation – such as constructing tables – that new information is revealed. Thirdly that iconicity is intrinsically linked with the process of surrogative reasoning. Looking again at figure 49 we can see how Peirce has drawn connecting lines between several of the elements. For example lines are drawn from the calculations as decimal fractions associated with the first five elements (H – N) and that these are related to a position on the sketch of a circle. It would seem reasonable to state that in the act of constructing this table where periods of elements seem blocked together, making the various calculations and then attempting to connect points of significance and to transpose these in some way onto the circular and periodic curve, Peirce is trying to surface new relations between the chemical elements. Peirce's practice in this case is an experiment on paper - the foundation of his surrogative reasoning - to disclose new relations between the chemical elements.

Earlier in chapter four I argued that Mendeleev's use of the term 'periodic' – and alluded to in Peirce's curve (figure 49) – was an appeal to mathematics and the exactness of Newtonian mechanics. I also demonstrated how for Peirce a mathematical function is able to operate iconically in facilitating the disclosure of a novel relation. By taking an example from mathematics I should like to make an initial case for engagement with an iconic sign being a practical activity; one involving both the accommodation of existing information as well as the disclosure of novel facts.

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[80] Peirce omits beryllium (Be)

[81] Peirce does not include all the elements of period 3

[82] Lord Rayleigh, Ramsay, W. 1895. 'Argon, a New Constituent of the Atmosphere'. *Philosophical Transactions of the Royal Society of London* **186** :187-241 & Ramsay, W. 1895a. 'Helium, a Gaseous Constituent of Certain Minerals'. *Proceedings of the Royal Society of London* **58**:80-89

Consider now the problem to show that $\cos(\sin^{-1} x) = \sqrt{(1 - x^2)}$.

One means of tackling this problem involves a couple of practical activities:

1. Applying the rules of trigonometry we can *write*: let $\theta = \sin^{-1} x$, then $\sin(\theta) = x$, then
2. *Draw* a right angled triangle and label as shown in figure 50

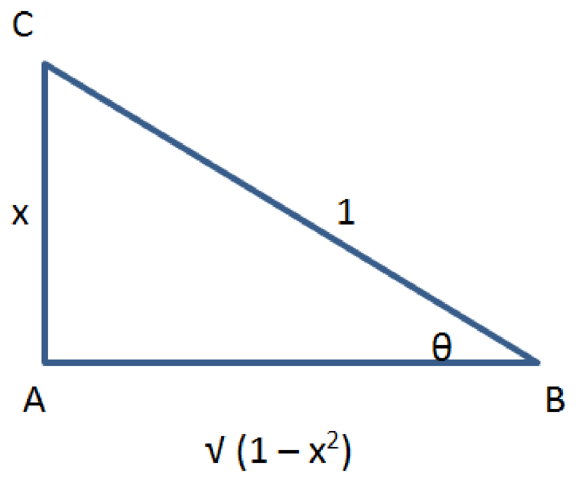
	There follows what might be characterised as a number of steps of mental reasoning: Applying the rules of trigonometry $\sin(\theta) = x/1$ Applying Pythagoras's theorem $AB = \sqrt{(1 - x^2)}$. Applying the rules of trigonometry $\cos(\sin^{-1} x) = \cos(\theta)$ $= AB/BC$ $= \sqrt{(1 - x^2)}$. Therefore $\cos(\sin^{-1} x) = \sqrt{(1 - x^2)}$.

Figure 50: trigonometric proof for $\cos(\sin^{-1} x) = \sqrt{(1 - x^2)}$

This is first a practical activity involving the mathematician first rearranging the problem into a more convenient form. There then follows the pencil and paper (and ruler) exercise of drawing out and labelling the right-angled triangle. In this way the relation embodied in the expression '$\sin(\theta) = x$' is represented as a geometrical diagram – the right-angled triangle - above (Figure 50). By the practical activity of constructing and acting on the diagram accompanied by mental acts of reasoning, the proof that $\cos(\sin^{-1} x) = \sqrt{(1 - x^2)}$ is discovered. The diagram is an icon of the relations contained with the expression $\sin(\theta) = x$ and our reasoning is grounded on the iconic representation in order to arrive at the proof. The iconic diagram embodies – or *accommodates* – the relations given in $\sin(\theta) = x$. The practical activity of acting on the diagram reveals new knowledge: $\cos(\sin^{-1} x)$ is equal to $\sqrt{(1 - x^2)}$ – the answer being a form of newly discovered relation – analogous to a Mendeleevian *prediction.* The iconicity of the geometric diagram is revealed in the mathematician's practice of experimenting on paper, on a representation of her problem, in the form of a right-angled triangle. By this process an answer to the original problem is discovered. I would argue that by analogy with this example from geometry, the periodic table is an icon which embodies or *accommodates* the physiochemical relations between the chemical elements and which has the capacity to reveal or *predict* novel facts – e.g.

corrected atomic weight values and the prediction of novel elements. To extend the analogy, for Mendeleev – as for a mathematician – this is a practical activity of representing existing relations on paper in order to discover novel relations.

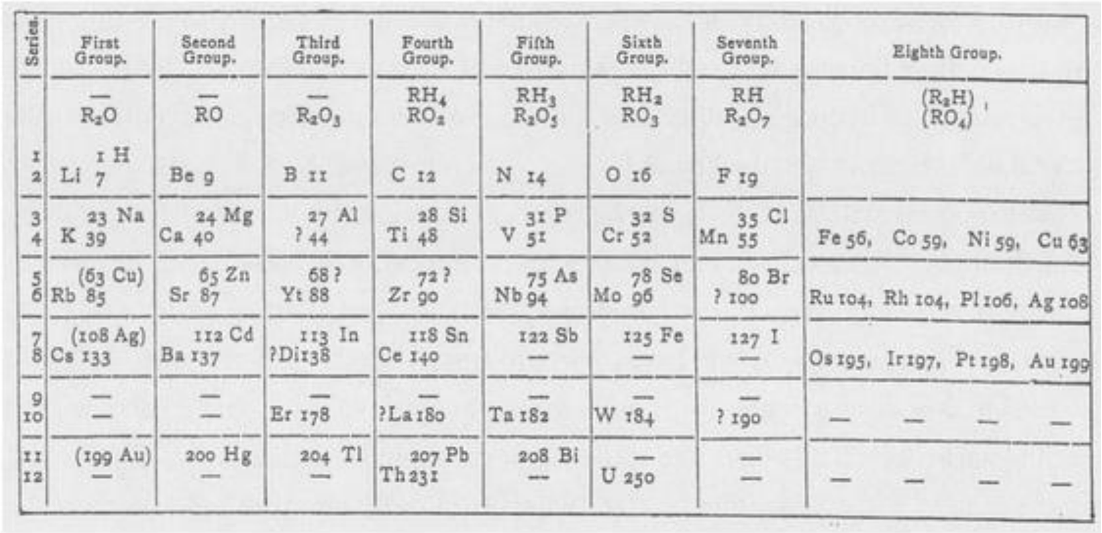
6.5 Bringing together aspects of 'accommodation' and 'prediction' from the view point of Mendeleev's representational practice

Woody (2014:123) argues that accounts that focus on *practice* are 'based on [an] examination of the reasoning invoked by scientists in particular contexts that arise in their ongoing work'. I should like to consider Mendeleev's *practice* by examining the reasoning he appealed to in an account that has not until now featured in this project: *Remarks Concerning the Discovery of Gallium* (1875). I hope to reveal Mendeleev's representational practice by the way he demonstrates an *articulated awareness* of the nature of the relations operating between his chemical objects. This might be evidenced in two ways. Firstly in Mendeleev's understanding of the periodic law in terms of the physiochemical relations existing between the elements accommodated within his scheme. Secondly, in the way Mendeleev used the periodic table – its iconicity – to infer novel relations between the chemical elements. I hope to show that by taking Mendeleev's representational practice from the view point of Woody's *articulated awareness* we can bring together aspects from the 'accommodation and 'prediction debate' into a single narrative. This is offered as a novel attempt to go beyond this long-running dispute in the philosophy of science as it applies to the periodic table.

In 1875 the French chemist Emile Lecoq De Boisbaudran (1875:159) reported on the 'indications of the probable existence of a new elementary body in the products of the chemical examination of a [zinc] blende…for which I propose the name of Gallium'. De Boisbaudran's discovery was not, states Scerri (2006:135), 'a result of testing Mendeleev's prediction…[De Boisbaudran]…operated quite independently by empirical means, in ignorance of Mendeleev's prediction, and proceeded to characterize the new element spectroscopically'. Mendeleev's (1875:144) paper, written in response to De Boisbaudran's discovery, begins with a statement of the periodic law:

> The properties of simple substances, the constitution of their combinations, as well as the properties of the latter, are periodic functions of the atomic weights of the elements.

Also included is a representation of the law in the form of the periodic table (figure 51), evidence contributing to Mendeleev's deep understanding – *articulated awareness* – of the relations between the chemical elements.



Series.	First Group.	Second Group.	Third Group.	Fourth Group.	Fifth Group.	Sixth Group.	Seventh Group.	Eighth Group.
	— R_2O	— RO	— R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	(R_2H), (RO_4)
1 2	1 H Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3 4	23 Na K 39	24 Mg Ca 40	27 Al ? 44	28 Si Ti 48	31 P V 51	32 S Cr 52	35 Cl Mn 55	Fe 56, Co 59, Ni 59, Cu 63
5 6	(63 Cu) Rb 85	65 Zn Sr 87	68 ? Yt 88	72 ? Zr 90	75 As Nb 94	78 Se Mo 96	80 Br ? 100	Ru 104, Rh 104, Pl 106, Ag 108
7 8	(108 Ag) Cs 133	112 Cd Ba 137	113 In ?Di 138	118 Sn Ce 140	122 Sb —	125 Fe —	127 I —	Os 195, Ir 197, Pt 198, Au 199
9 10	— —	— —	— Er 178	— ?La 180	— Ta 182	— W 184	— ? 190	— — — —
11 12	(199 Au) —	200 Hg —	204 Tl —	207 Pb Th 231	208 Bi —	— U 250	— —	— — — —

Figure 51: Mendeleev's periodic table of 1875
Source: taken from Jensen, W. 2002. *Mendeleev on the Periodic Law: Selected Writings, 1869–1905*. Dover Publications, Mineola, NY, page 144

Drawing the reader's attention to the table Mendeleev (1875:128) makes three claims. The first might be described as one of *accommodation*, for Mendeleev claims the representation of the periodic law 'constitutes the basis of the complete system of the elements'. That is to say it accommodates all the known elements arranged by atomic weight. This is followed by Mendeleev's (1875:128) two further claims that would fall within the *predictivist* camp as set out in the earlier discussion. The second is that the arrangement of the elements as represented by the table 'requires some revision of the atomic weights of some metals not yet sufficiently studied'. The third of Mendeleev's predictivist claims is that the gaps in the table 'enables us to predict the properties of the unknown elements…*eka-aluminium, El, and eka-silicon, Es'* (emphasis in the original). By acting on and experimenting with the periodic table as part of his reasoning process (the second criterion of iconicity described in chapter four) Mendeleev (1875:128) further predicts successfully a number of properties for eka-aluminium (El). The inferences Mendeleev draws here in terms of the likely need to revise a number of atomic weights and the likely existance to two undiscovered elements are further evidence of his *atriculated awareness* of the relations between the chemical elements. Furthermore, and echoing Chang's (2012) earlier point that a serious approach to scientific practice is concerned with what scientists *do*, I would argue that a study of the practice of representation must have a concern for what practitioners – here Mendeleev – *do* with them. Here we see Menddeleev using his representation of the relations between the chemical elements – the periodic table – to predict novel facts interms of corrected atomic weights and two more eka-elements. These claims come with Mendeleev's statement that the periodic law, and its representation, contain or accommodate all the known elements – a complete system. Mendeleev's representational practice encoprporates both *accommodation* and *prediction*. The degree to which Mendeleev's representational practice demonstrates an articulated awareness of the relations between the chemical elements might be seen by the accuracy of the inferences he drew for the properties of eka-aluminium (later shown to be gallium). The following table sums up Mendeleev's (1875:128) predictions and compares these with those later determined for gallium:

Property	**Predicted (eka-aluminium, El)**	**Actual (gallium, Ga)**	**Difference from experimental result**
Atomic weight	68	69.2	1.7%
Atomic volume	11.5	11.8	2.5%
Specific gravity	5.5 ('thereabouts')	5.9	6.8%
Chloride	$ElCl_3$	$GaCl_3$	Correct
Oxide	El_2O_3	Ga_2O_3	Correct
Sulphide	El_2S_3	Ga_2S_3	Correct
Alum	$ElK(SO_4)_2$	$KAl(SO_4)_2$	Correct
Reaction with acids/alkalis	Slow	Slow	Correct

Looking at Mendeleev's fourth column, where the degree of concurrence between the predicted and experimentally determined results are given, then we might agree with Scerri's earlier remark that Mendeleev's predictions are 'astonishing' in their accuracy.

From the perspective of this particular 1875 paper I would claim that Mendeleev's representational practice involves a combination of activities that fall under the previously described accounts of 'accommodation' and of 'prediction'. I would suggest that this view from practice goes beyond the bipartisan debate around accommodation and prediction outlined earlier. By drawing also on the work of chapter four we can take a broader view of Mendeleev's practice than is afforded by a study of Mendeleev's relatively short paper from 1875. Chapter four made the case for the periodic table being an icon, its iconicity being integrated into Mendeleev's process of reasoning. Implicit in Mendeleev's representational practice, one formulated on iconicity, are the core aspects of the arguments labelled under ‘accommodation’ and ‘prediction’. In chapter three I argued for the concept of *relations* being important to both Peirce and to Mendeleev. With Mendeleev’s periodic table, physio-chemical relations underpin the accommodation of the elements of its construction. Looking back to Mendeleev’s table of 1875 (Figure 51) relations founded on atomic weight and valency determine an element’s position and the overall structure of the table. For example consider the relations between the elements lithium, fluorine and sodium. Sodium (Na = 23) follows on from after fluorine (F = 19). It makes sense to place sodium in the same group as lithium (Li = 7) as they are chemically similar – soft reactive metals – are both monovalent forming compounds with identical combining ratios (e.g. LiF and NaF; Li_2O and Na_2O). In recognising relations such as these, Mendeleev was able to *accommodate* the chemical elements into his iconic table. In chapter four I argued that an important property of an icon was its epistemic fruitfulness. That, as Peirce explains, by experimenting on the icon in the form of thought experiments novel facts can be discovered. By engaging with the iconicity of the periodic table, Mendeleev was able to *predict* the possibility of novel elements. Mendeleev’s representational practice, as captured by Peirce’s working of iconicity, is an integrated process. It involves forming an iconic diagram founded on the relations at play between the *accommodated* chemical elements and then to both mentally and physically engage (pen on paper) with this – Mendeleev’s representational practice - to *predict* novel facts. I would argue that Mendeleev’s representational practice brings together aspects of both prediction and accommodation, both aspects being unified within Peirce’s account of iconicity.

6.6 Conclusion

From the perspective of Peirce’s iconicity set out during the course of this project I would argue that elements of ‘accommodation’ and ‘prediction’ have been alloyed together on other occasions. In chapter four we saw how Mendeleev engaged with sketched proto-forms of the periodic table both mentally as well as practically as he experimented on paper in order to disclose new relations between the chemical elements. His early tables both accommodated existing elements and left gaps for projected novel elements. In chapter five the term iconic robustness was developed as an attempt to capture the periodic table’s continuing iconic fruitfulness against a background of nature’s resistance in the form of the challenge to accommodate novel elements.

The way which Mendeleev arrived at the periodic table is summed up by Robin Hendry (2012:259) as follows,

> First came a preliminary list of the elements by atomic weight. Next came a careful noting of the trends and patterns in their chemical behaviour, including the stoichiometry and physical properties of their compounds. Through reflective equilibrium[83] between data and hypothesis, Mendeleev was able to revise some atomic weights, and to recognise where gaps must be left for undiscovered elements.

Hendry captures something here of Mendeleev's *representational practice*. Firstly in *accommodating* the available elements into his construction of the periodic table by their atomic weights and supported by their physiochemical properties (compounds included). Secondly by emphasising the table's epistemic fruitfulness in *predicting* revised atomic weights and new elements awaiting discovery. I would argue that Mendeleev's representational practice, mediated by the periodic table's iconicity, provided a pathway or process that mediated between 'data and hypothesis' – data relating to the accommodation of existing elements and hypotheses that include novel predictions. This chapter attempted to show how Peirce's theory of iconicity weaves together filaments from both sides of the accommodation/prediction debate. I believe that this approach, construed in terms of Mendeleev's representational practice, offers a more holistic approach to the epistemology of the periodic system than the 'accommodation/prediction' debate set out earlier. The predictive power of Mendeleev's table in discovering new relations between the chemical elements, and its construction through accommodating known elements are revealed as integrated functions of his practice of representing when viewed through the lens of Peirce's formulation of iconicity.

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[83] Hendry's term 'reflective equilibrium' is one associated with Nelson Goodman (1965) and the moral philosophy of John Rawls (1971). In his influential *Theory of Justice* Rawls (1971:43) describes *reflective equlibrium* as the position, 'reached after a person has weighed various proposed conceptions and he has either revised his judgements to accord with one of them or held fast to his original convictions'.

Conclusion

The aim of this dissertation was to show that aspects of the works of Charles Peirce and Dimitri Mendeleev are illumined by the insights and perceptions of the other. My thesis was motivated initially by Peirce's many references to Mendeleev's periodic table and to the chemical concept of valency. I noted there was little in the secondary literature that connected Peirce's philosophy to his study of chemistry. There seemed to be a widely held view that Peirce's philosophy and logic are better understood within the context of his mathematics; any mention of chemistry was usually by way of biographical detail. I also noted that the literature was rich in discussions on the relative evidential weight to be attributed to Mendeleev's periodic law in terms of its capacity to accommodate known elements against its predictive capacity. There was far less on how the periodic table featured as part of Mendeleev's practice in terms of its fruitful capacity to accommodate existing data, assign new values, and point the way towards novel knowledge. I noted too that Peirce's formulation of iconicity was rarely used in analysing how scientific representations function in scientific practice. Even one rare mention – Ursula Klein in her study of Berzelian formula as *paper tools* – led to the eventual rejection of Peirce's iconicity.

My aim in **chapter one** was to set out the context of Peirce's study of chemistry at Harvard's Lawrence Scientific School under the direction of Josiah Cooke. I discussed the reforms Cooke introduced to the teaching of chemistry. This included Cooke's move away from rote learning towards a more laboratory based problem-solving curriculum with a greater emphasis on mathematical rigour. With regard to Peirce's later philosophy Cooke, in common with Mendeleev, framed the study of chemistry in terms of the *relations* between substances and their empirically determined properties. Secondly Cooke devised a diagrammatic process of reasoning to enable his students to understand the structural relations embodied within the study of crystallography. In chapter one I sought to establish that Peirce's training as a chemist at Harvard made a contribution to his thinking on the epistemic and logical value of diagrams, ways of thinking diagrammatically and in terms of *relations.*

The aim of **chapter two** was to explore Peirce's early publications in chemistry for an insight into his chemical interests and to see how these map on to his philosophical position at the time. I showed that Peirce shared a number of interests in common with his contemporaries: the atomic theory and systemising the chemical elements by atomic weight. Where Peirce differed was in his readiness to ground his arguments in metaphysics. His contemporaries, including Cooke, tended to dismiss metaphysics as irrelevant to their empirical work in the laboratory. I also connected Peirce's chemistry to his early Kantianism which, scholars agree, features in his wider philosophy at the time. This chapter also demonstrated Peirce's interests in the value of classifying the chemical elements by their atomic weights, an interest that develops in to a life-long fascination with Mendeleev's periodic table. Whilst publishing a diagrammatic attempt to demonstrate a degree of order to the chemical elements, Peirce was at the same time arguing against JS Mill's justification of inductive reasoning founded on the inherent orderliness of nature. I was able to map Peirce's justification of inductive logic onto his chemistry where he sets out an orderly scheme for chemical elements based on their atomic weights. I argued that Peirce's chemistry was not in conflict with his philosophical position at the time: Peirce does not deny the possible discoverability of regularities in the world; rather, the insufficiency of an appeal to order to justify induction.

I began **chapter three** by exploring the connections between Peirce and Mendeleev. Whilst Mendeleev was most probably unaware of Peirce's work, Peirce had a great knowledge of and interest in Mendeleev's achievements in chemistry. I demonstrated that both these philosopher-chemists framed their approach to the periodic arrangement of the chemical elements in terms of the *relation* between their atomic weights and physiochemical properties. My aim in this chapter was also to examine Peirce's reception of Mendeleev's scheme. Using a number of Peirce's published works and manuscripts I revealed his dissatisfaction and frustration at not being able to discover an exact mathematical pattern to Mendeleev's system. A number of Peirce's manuscripts are littered with attempts to discover a mathematical key to the periodic table. My aim in this chapter was also to show that an additional insight is afforded by viewing Peirce's phenomenology through the lens of his chemistry. I examined the concept of valency as deployed in chemical graphs of the period as well as Mendeleev's periodic table in relation to Peirce's phenomenology. I was able to show that Peirce's chemistry carries across to his phenomenology. Both valency and the periodic table are the basis for diagrammatic forms that depict relations. The periodic table represents the physiochemical relations between the chemical elements. Chemical graphs - molecular diagrams - depict relations between atoms which are in turn dependent upon their respective valencies. I showed how, using these visual forms from chemistry, Peirce created a diagrammatic pathway to an understanding of phaneroscopy.

In **chapter four** I went on to investigate Mendeleev's periodic table as an iconic representation. I began by presenting Peirce's three orders of signs: icon, index and symbol. I then focussed on the icon in terms of its epistemic fruitfulness; the possibility of making new discoveries about an object by observing and experimenting on its iconic representation. Ahead of a detailed treatment of the periodic table I further developed Peirce's concept of iconicity in relation to chemical graphs as developed by Edward Franklin and Alexander Crum Brown. I argued that chemical graphs functioned as icons by facilitating reasoning: the bonds affected during the course of a chemical reaction and assigning isomer types. By using chemical graphs I demonstrated that an icon need not resemble its chemical object in looks but only with respect to the relations between their parts. Also ahead of dealing with the periodic table I set up and then offered a number of counter-arguments to some of the objections to iconicity on the grounds of *resemblance*. This was followed by a detailed consideration of the different strength of relations – eg isomorphism and homomorphism – sometimes posited between a representation and its target. I argued that iconicity is founded on homomorphism – a partial but structure preserving mapping from source to target – which surfaces through the process of representing. I then took Ursula Klein's (2001) study of Berzelian formulae, where she rejects Peirce's formulation of iconicity, preferring instead her own neologism *iconic symbol.* Klein rejected Peirce's formulation of the *icon* as she believed this required an isomorphic relationship between source (Berzelian formulae) and target (chemical substances). I argued that homomorphism better characterises this situation and that Klein missed the opportunity of using Peirce's iconicity as part of her analysis in arriving at Berzelian formulae as *paper tools.*

I set out three key functions of Peirce's formulation of iconicity which when mapped on to the periodic table demonstrated its function as an *icon:*-

a) epistemic fruitfulness
a) surrogative reasoning
b) a system of relations.

I showed how, through a series of practical pencil-and-paper exercises, Mendeleev experimented on a number of early proto-sketches. Through a series of reconstructions of these preliminary sketch diagrams Mendeleev arrived at his first periodic table of 1869: an arrangement of the chemical elements in atomic weight order such that they displayed a periodic variation in their physiochemical properties. I argued that these early proto-sketches were at the heart of Mendeleev's surrogative reasoning. I argued that the periodic table was a system of relations and noted how Mendeleev expressed the connection between the properties of the elements and their atomic weight in terms of *relations.* I argued that the iconic character of the periodic table was realised through the process of Mendeleev's representative practice: in constructing his diagrammatic table, founded on the relations between the atomic weights and the properties of the chemical elements, it was possible to point towards the possibility of new knowledge: novel elements and revised atomic weight values. I argued that in papers published after the first arrangement of 1869, Mendeleev continued to exploit the fruitfulness of his table – its iconicity – in terms of the eka-elements and new atomic weight values. I also showed how Mendeleev's early sketches and his later published schemes also acted as *construals*: in presenting an interpretation of the relations between atomic weight and chemical properties and placing these ideas into the wider chemical community for discussion.

Having established the periodic table as an iconic representation, in **chapter five** I went on to investigate how its iconicity was affected by the problem of the rare earth elements and the noble gases, elements that failed initially to be assimilated within Mendeleev's scheme. I began by characterising these elements as offering resistance – that is *nature's resistance* – to the periodic table, a term borrowed from Hasok Chang's (2012) formulation of *active realism.* I set out two case studies where the periodic table encountered *nature's resistance*: the *rare earth crisis* (Thyssen and Binnemans, 2015) and the discovery of the noble gases and their eventual placing into the periodic table, the result of work carried out by Sir William Ramsay, Lord Rayleigh and Morris Travers. By combining these two case studies within the context of Peirce's account of fallibilism, I argued that the periodic table demonstrated iconic robustness in retaining its capacity to promote thought experiments and to generate new knowledge, whilst undergoing structural changes in response to *nature's resistance*. I concluded chapter five by defining iconic robustness in the context of the periodic table: the continuing capacity to generate knowledge of novel relations between the chemical elements without being thwarted by nature's resistance and within the context of a fallible inquiry. This is, I believe, a term new to Peirce studies.

In **chapter six** I built on the case for the periodic table as an iconic sign as well as Mendeleev's practice of representing, so as to offer a new insight into its epistemology. My aim was to move beyond the long-running and dyadic debate around whether Mendeleev's prediction of new elements had a greater impact on the chemical community than the accommodation of existing elements. I first examined the wider historiography of the ‘accommodation/prediction’ debate before focussing on the periodic table. I argued that Mendeleev’s practice of representing, mediated by the periodic table and from the vantage point of Peirce’s formulation of iconicity, provided a creative pathway of thought that brought together threads from both the ‘accommodation’ and ‘prediction’ debates as a single narrative.

Finally, I hope to have shown that Peirce’s chemistry is worth more to the HPS community than as a simple biographical note: I believe it provided Peirce with a thought pathway or mind-set that enabled him to develop a diagrammatic approach to aspects of his philosophy. At the same time, through the study of Mendeleev’s periodic table, I hope to have demonstrated the value of Peirce’s formulation of iconicity as an analytical framework for scientific representations and representational practice.

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