Chiara Ambrosio and Chris Campbell – **The Chemistry of Relations**
Forthcoming in *Peirce on Perception and Reasoning: From Icons to Logic*, London: Routledge
Please cite from the published version

The Chemistry of *Relations*: Peirce, Perspicuous Representations and Experiments with Diagrams

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> "[…] 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).

In *Prolegomena to an Apology of Pragmatism* (c1906), Peirce describes the process of experimenting with diagrams through an intriguing comparison between chemistry and logic. Just like chemical experimentation, Peirce maintains, consists in "the putting of questions to Nature", so experimentation with diagrams consists in asking questions "to the Nature of the Relations concerned". Peirce scholars are relatively familiar with the meaning of "experimentation" that Peirce attributes to diagrams in this context. The idea that experimentation upon diagrams involves processes of visualization and thought manipulation analogous to the performance of an experiment in practice has been variously explored in recent studies of Peirce's system of Existential Graphs (Shin 2002; Pietarinen 2006; Stjernfelt 2007), as well as studies addressing the relations between abduction and diagrammatic reasoning (Hoffman 2007; Paavola 2011). More generally, scholars tend to agree that the quote is in line with the relationship that Peirce established between diagrams and Pragmaticism: "experimenting" in this particular context amounts to considering the conceivable practical effects that would follow from the adoption of the particular states of affairs (or hypotheses) represented in the diagram. Most of these studies have privileged the logical implications of diagrammatic reasoning – and rightly so, especially in light of the renewed attention that Peirce's system of Existential Graphs and its relation to Peirce's Pragmaticism has received in recent years.

Our contribution aims to offer a slightly different perspective on Peirce's general claim that experimenting with diagrams "take[s] the place of the experiments upon real things that one performs in Chemical and Physical research". We take Peirce's comparison with chemistry in particular very seriously, not merely as a pedagogical or descriptive device to lend concreteness to his otherwise rather abstract description of logical operations on diagrams, but rather as one of the material sources that informed and directed his thinking about the epistemic and logical value of diagrams and diagrammatic reasoning. Our work takes its cue from Kenneth Ketner's (1982) systematization of what “ought to be called Eisele’s Law” (Ketner 1982, 328): the idea, to which Carolyn Eisele devoted most of her scholarly work, that Peirce’s philosophy cannot be properly understood independently of his mathematics and science. Eisele herself, however, privileged the mathematical and physical applications of her own law, leaving the connections between Peirce’s scientific work beyond physics as a possibility open to her legacy for further investigation. In the introduction of her *Historical Perspectives on Peirce’s Logic of Science* (1985), for example, she appeals specifically to Peirce’s regular references to diagrammatic reasoning in her account of how his version of the doctrine of *exact philosophy* differed from contemporary positivistic accounts of the relations between mathematics, philosophy and science. Peirce’s effort to bring mathematical exactitude at the core of his philosophy, Eisele argues, revolves around an inherently diagrammatic conception of mathematical reasoning:

> “If one stops to examine the operation of this procedural mechanism in the ‘proof’ of a theorem from high school geometry, one would:
>
> 1. Construct an icon, the relation of whose parts is determined by the premises;
> 2. Experiment upon the *effects* of modifying this diagram. The probable modification is a construction;
> 3. Observe in this experiment certain relations between parts of the enlarged diagram over and above those which sufficed to determine its construction;
> 4. Satisfy oneself by inductive reasoning that these new relationships would always subsist where those in the premises existed”. (HP1,11)

Peirce’s general ability to think diagrammatically is often related *exclusively* to such a diagrammatic conception of mathematical reasoning, which occupied a very central place, of course, in his work. What we would like to suggest, however, is that a similar conception of diagrammatic thinking can be fleshed out from his early research, and lifelong interest, in chemistry. Thus, without underplaying the importance of logic and mathematics in the development of Peirce’s account of diagrammatic reasoning, we intend to suggest that chemistry played an equally important role - one that has been so far neglected in the literature. For one thing, the very text of the *Prolegomena to an Apology of Pragmatism* seems to substantiate this conjecture. After drawing the comparison between chemistry as a way of putting questions to nature and diagrams as ways of putting questions “to the Nature of the Relations involved”, Peirce moves on to consider a possible objection to this claim. One could argue, Peirce acknowledges, that there may be “a good deal of difference between experiments like the Chemist's, which are trials made upon the very substance whose behavior is in question, and experiments made upon diagrams, these latter having no physical connection with the things they represent” (CP 4.530). Thinking of chemical experimentation merely in terms of manipulation of particular samples of a certain substance, however, for Peirce would miss the point, resulting in a rather crude form of nominalism. The chemist’s quest, instead, is for Peirce a quest for generality: “For it was not the particular sample that the chemist was investigating; it was the molecular structure” (CP 4.530). Diagrammatic reasoning is ultimately a way of making visible “The Form of a Relation” (CP 4.530). In the same way, chemical experimentation makes visible the relations holding between elements in the molecular structure of a substance, independently of the individual characteristics of the particular sample a chemist is working with.

Our claim is that this comparison is not accidental. In what follows, we advance a conjecture on where it might have come from, and how, more broadly, chemical reasoning and chemical practice might have directed and informed Peirce's work with and on diagrams. Our hope is to open a new conceptual possibility in the study of Peirce's account of diagrams: that along with mathematics, chemistry contributed substantially to Peirce's way of thinking diagrammatically and in terms of *relations,* as well as in terms of conceivable consequences. Indeed, we hope to show that the combination of mathematical and chemical thinking in particular, as evidenced by Peirce's chemical training at Harvard, formed a solid conceptual basis for his account of diagrams. We will conclude with some suggestions for further investigation into the role of chemistry in Peirce's philosophical system more broadly, and the potential this new avenue of inquiry might have for the direction of Peircean scholarship.

Chemistry Teaching at Harvard

Two pieces of biographical information concerning Peirce and chemistry are well known among scholars: that in 1850, aged only eleven, Peirce bravely attempted to write a (now lost) "History of Chemistry" (W1, 2), and that Peirce's degree at Lawrence Scientific School, awarded *summa cum laude* in 1863, was in chemistry. These have been treated quite superficially by Peirce scholars, as mere biographical curiosities: in the introduction to the first volume of the *Writings of Charles Peirce,* for example, Max Fisch clearly accounts for Peirce's chemical training as a mere stepping stone toward his subsequent achievements in science and logic:

> "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 and to logic as a whole" (W1, xxi)

A completely different picture emerges if one pays greater attention to the nature of the chemistry curriculum in Harvard at the time, and in particular to the pedagogical innovations introduced by Peirce's chemistry teacher, Josiah Parsons Cooke.[1] Before plunging into the details of

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[1] The *Catalogue of the Officers and Students of Harvard University for the Academic Year 1861-62* lists Peirce's father, a founding force behind the Lawrence Scientific School, as 'Benjamin Peirce, LL.D., Parkman Professor of Astronomy and Mathematics' (p.6). His son's chemistry tutor, Josiah M Cooke, is listed as Erving Professor of Chemistry and Mineralogy. There are fifty seven 'scientific students' (pp.71-73), including 'Peirce, Charles S., A.B', studying chemistry. The catalogue outlines the curriculum for each subject. The entry 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' (p. 75). 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 Stöckhard's *Elements of Chemistry* (1858) in addition to Cooke's *Chemical Physics* (1860)

Cooke's teaching, it is worthwhile to give a brief overview of the roots of the pedagogical model that informed the teaching of chemistry in Harvard around Peirce's time more broadly.

Peirce's father, Benjamin, had been instrumental in reforming the science curriculum at Harvard. Part of his proposal resulted in the establishment of the Lawrence Scientific School in 1847. The school's primary aim was to provide training specifically in practical science, and indeed its teaching provision revolved around the Rumford Professorship for the Application of Science to the Practical Arts (James 1992, 68). In 1847 Eben Horsford was appointed Rumford professor, having previously graduated in civil engineering form the Rensselaer Institute at Troy, New York. This was also one of America's earliest colleges of science and civil engineering. After graduating, Horsford travelled to Europe and studied chemistry at Justus Liebig's laboratory in Giessen for the two years between 1844 and 1846. In an early account of the beginnings of laboratory teaching in America, Frank Whitman explains that it was indeed Horsford and "a favourite pupil of Liebig [who] brought to Cambridge the methods and ideas of the Giessen laboratory" (Whitman 1898, 203). Similarly, commenting on Horsford's studies under Liebig, H.S Van Klooster records him as stating that "the methods pursued under the guidance of that great teacher, were in many respects the methods I had been familiar with in the Rensselaer Institute" (Van Klooster 1949, 11).

The connection between the Lawrence school and the chemical tradition established by Liebig in Giessen is of crucial importance to understand the context of Peirce's own chemistry training. The foundation of the Lawrence Scientific School is part of a larger transition toward the establishment of institutional laboratories which would fulfil the precise aim of transferring a model of "division of labor" to science and replace the traditionally theoretical and conceptual model of training offered by universities at the time. Historians of science have investigated the rise of institutional scientific laboratories from a range of perspectives, and have unanimously highlighted how the rise of laboratories paralleled the rise of disciplinary specialization particularly in the natural sciences. An exhaustive account of this history is well beyond the scope of this chapter, but three landmark works on the subject deserve to be mentioned: David Cahan's (1985) study leading to the very concept of "institutional revolution" in physics, Graeme Gooday's (1990) work on the priority of training over pure research in the context of the institutional revolution, and Simon Schaffer's (1992) study of the role of the Cavendish laboratory in Cambridge (which Peirce himself visited during his travels in Europe) on the establishment of Victorian metrology in England and in setting the standards for laboratory training in physics more broadly. In contrast with these studies, which concentrate exclusively on the establishment of *physical* laboratories, Catherine Jackson (2011) has insightfully demonstrated that chemical laboratories, through a tradition established by Liebig himself, were well ahead of the physicists' game. "If the institutionalisation of physics (or any other discipline) *appears* to have been driven primarily by scholarly ideals", Jackson contends, " this is because chemistry had paved the way. Its 'craft tradition', far from characterising a merely empirical, mathematically unsophisticated science, not only drove the institutionalisation of chemistry but also enabled the *institutional revolution* in physics" (Jackson 2011, 62).

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and Regnault's *Elements of Chemistry* (1853). As we will show later on, these textbooks provide a glimpse into Cooke's pedagogical innovations at Harvard.

Why was Liebig's laboratory so important in driving this transition? Part of the answer lies precisely in the relation between teaching and research that Liebig himself helped establish. His idea of laboratory was a space where students and assistants could work side by side, and learn by doing rather than through mere rote learning. Historians of chemistry have repeatedly underlined this distinctive feature of Liebig's teaching more broadly, stressing how group research was a vital component of the experiential pedagogy of the Giessen laboratory model (Holmes 1989; Fruton 1988). The importance and extent of Liebig's pedagogical innovations is best understood in contrast to previous traditions. In the first half of the nineteenth century, chemistry teaching was divided over the very relation between theory and practice that Liebig himself tried to reconcile. On one hand, the "applied" aspect of chemistry was dismissed precisely because of its too practical nature, which assimilated it to a craft rather than an exact science like physics and mathematics. On the other hand, the status of the discipline was being reasserted, especially in Europe, by moving chemical professorships from medical faculties (where chemistry was primarily at the service of pharmaceutical applications) to philosophy faculties. As Alan Rocke (2003) points out, Liebig's primary aim was to resolve this tension: "Liebig and others who were 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" (Rocke 2003, 108). Even more importantly, Rocke stresses how an important peculiarity of Liebig's model was to turn chemistry into a whole mindset that would allow students to *think* differently: "Those 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" (ibid.). Among the crucial factors that contributed to the success of Liebig's pedagogy, Rocke identifies the discovery of isomers, the use of a particular kind of apparatus (the *Kalliapparat*) for the effective synthesis of organic compounds and the systematic use of chemical formulas as "paper tools".[2] As we will show later on, the idea of chemical notation as "paper tools" has particular semiotic connotations, and is conceptually and historiographically relevant in relation to Peirce.

Horsford's direct relationship with Liebig was one of the factors that contributed to persuading the manufacturer Abbot Lawrence to donate fifty-thousand dollars – a record amount at the time – for the foundation of the Lawrence Scientific School. As Keith Sheppard (2006) argues, "Eben Horsford was most influential in transplanting Liebig's methodology to the United States", with the new School being "modelled along Liebig's lines" (Sheppard 2006, 567). 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. This certainly had an adverse impact on Horsford's teaching, along with further impediments which were both financial and related to the cultural difficulties of adapting a German model to the teaching of chemistry in America. Indeed, Horsford (and Peirce's teacher Cooke after him) embarked on the ambitious project of establishing a "Giessen on the Charles", as the historians Alan Rocke and Margaret Rossiter described it (Rocke 2006, 112). Lawrence's initial gift of fifty thousand dollars was eventually divided, and only half of the initial amount went to support Horsford's laboratory. When Peirce entered the Lawrence Scientific School

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[2] The idea of Berzelian formulae (a modification of which is still in use in contemporary chemistry) as "paper tools" has been proposed by Ursula Klein (2001a; 2001b; 2003), and will be discussed later on.

Horsford and Cooke were engaged in keeping the Giessen tradition alive in spite of the financial constraints, but their attempt eventually proved unsuccessful. Horsford resigned from Harvard in 1863, the very year of Peirce's graduation.

Alan Rocke explains the failure of the Giessen experiment in Harvard as primarily determined by a dramatic lack of funds. "There can be little doubt", he claims, "that the endeavor *would* have succeeded… had the initial amount remained undivided" (Rocke 2006, 113). This suggests that Liebig's methodology *did* take root in Harvard in Peirce's time, and that indeed Peirce would have been trained in a research spirit very much modelled on the combination of theory and practice that was so distinctive of Liebig's pedagogical methodology. Moreover, while Horsford initially brought Liebig's laboratory method of teaching to Harvard, it was Peirce's teacher Cooke who, motivated by his contact with the French chemists Jean-Baptiste Dumas and Henri Regnault (themselves involved in building a similar laboratory tradition in France), resurrected the laboratory programme after its subsequent decline during Horsford's tenure. Stephen Weininger (2013) captures the twin effects of Horsford and Cooke on chemistry at Harvard by stating that while 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.' (Weininger 2013, 97). One of the students in that cramped room was very probably Peirce.

Cooke and Peirce on Chemistry and Mathematics

Having originally been appointed as a tutor in mathematics, Cooke was soon assigned a chemistry position and eventually advanced to the Erving Professorship of Chemistry and Mineralogy in 1850. The reason for this promotion was precisely to revive the chemistry curriculum in Harvard (Rosen 1982, 525), and for this purpose Cooke travelled to Europe in search of apparatus for his newly assigned Boylston Hall laboratory in Harvard. The trip allowed him to make contact with institutions that had already adopted Liebig's model and establish particularly close relationships with the Parisian chemists Henri Regnault and Jean-Baptiste Dumas, both engaged in introducing Liebig's ideas and pedagogical innovations in France.

The way in which Cooke revived the chemistry programme in Harvard resonates well with the mathematical mindset often attributed by scholars to Peirce. Indeed, mathematics was the primary route through which Cooke arrived at the teaching of chemistry, and this had an interesting effect on his application and adaptation of a Liebig-inspired pedagogy. On one hand, Cooke used mathematics as a way of lending rigor to the discipline of chemistry – a move that seems to suggest he embraced the rhetoric, typical of his time, that the matematisation of chemistry would allow chemists to present it as an exact science on equal footing with physics. On the other hand, however, Cooke's own approach to mathematics seems to suggest a more subtle position,[3] which

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[3] This is partly related to Cooke's Unitarian views, which developed in a sophisticated epistemological framework aimed at reconciling science and religion. Cooke worked at the very time in which the reception of

shares many important features with the views Peirce himself would develop on the subject later on in life. In a late apologia entitled *Religion and Chemistry, the Credentials of Science: Warrant of Faith* (1888), which also sums up his broader views on the relationship between science and natural theology, Cooke explains that for the application of the deductive method to science "mathematics is the most important tool" (Cooke, 1888, 94). More importantly, mathematics offers more than a tool to perform valid deductions, for Cooke: instead, he describes it as a means to visualize relations. "Mathematics", he states, "is the science of quantitative relations wholly independent of their material expression" (Cooke 1888, 101). This explains why, despite the emphasis on quantification, the actual mathematics in Cooke's lectures was ultimately not advanced and relatively manageable. Rather than a complex machinery (mastered by rote, mechanical learning) to achieve exactitude in chemistry, Cooke regarded mathematics as a way of grasping, through logic and thinking, relations between quantities. Even twenty five years after his first intake of students, Cooke comments that 'mathematical studies are peculiarly well adapted to train the logical faculties' (Cooke 1875, 528). Nonetheless, because of the widespread practice of rote learning found in many American schools, Cooke 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' (Cooke 1875, 530). The changes Cooke had made to the curriculum were in part an attempt to compensate for this perceived weakness in the American educational system, and in part were heading in the direction of developing a system of quantification that would also serve as a broader mode of chemical reasoning for the purpose of chemical research.

An example of how Cooke incorporated mathematics in his curriculum comes from one of the very textbooks he wrote specifically for his courses at Harvard. The book, published in 1857, has an interesting (albeit indirect) connection with the Peirce family. Titled *Chemical Problems and Reactions to Accompany* Stöckhardt's *Elements of Chemistry*, it was produced by Cooke specifically to support Julius Stöckhardt's chemistry textbook, which he adopted, mobilizing the entire Harvard Council for a formal endorsement, short after his appointment in 1850 (Eliot 1894, 532). Before showing how this contributed to the mathematisation of chemistry, it is first worth considering Stöckhardt's original book a little more in detail. The preface to the 1858 edition of Stöckhardt's *Elements of Chemistry* states that the work was recommended for translation by Eben Horsford. The translation was carried out by Peirce's uncle, Charles Henry Peirce, assisted by Peirce's aunt Charlotte Peirce - who, as Max Fish suggests, did most of the actual work (W1, xviii). It was from his uncle and aunt that Peirce inherited his first chemistry laboratory, and the very completion of their translation of Stöckhardt coincided with the writing of Peirce's (never found) History of Chemistry. It is therefore quite reasonable to assume that, either via his own family or via Cooke's teaching, Peirce had access to both Stöckhardt's book and Cooke's companion to Stöckhardt.

Darwin's *Origin of Species* in America prompted either the complete abandonment of traditional natural theologies or, as in the case of Peirce's own mentor Luis Agassiz, the production of explicit criticisms of Darwin's ideas. As shown by Contakes and Kyle (2011), Cooke saw science and religion as complementary epistemologies, and mathematics, in his account, offered an indispensable key to this complementarity.

The purpose of Cooke's book as an accompaniment to Stöckhardt's original text can be illustrated by comparing the two pages in fig. 1 and fig. 2. Cooke's book mirrors Stöckhardt's by setting problems to accompany the practical exercises, but an interesting process of translation takes place across the two. Cooke operationalises chemistry specifically to bring it in line with the Liebig-inspired combination of teaching and research, theory and practice he was trying to recreate in Harvard.

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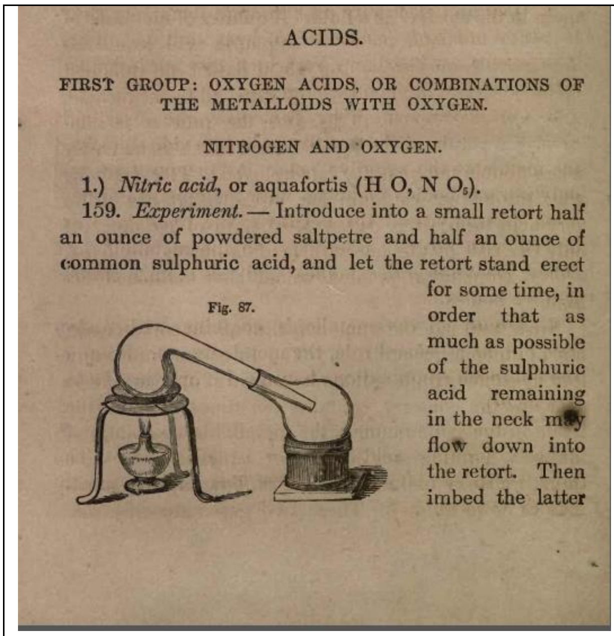

ACIDS.

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

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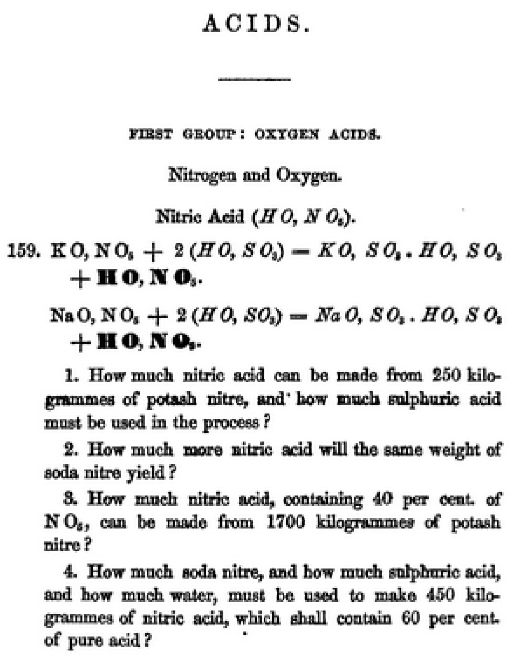

ACIDS.

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?
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<td>Fig. 1 Stöckhardt<i>'s Elements of Chemistry</i> 1858,152</td>
<td>Fig. 2 Cooke's <i>Chemical Problems and Reactions to Accompany</i> Stöckhardt<i>'s Elements of Chemistry</i> 1857, 63</td>
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In fig. 1 Stöckhardt describes an experiment to produce nitric acid, whilst Cooke, in fig. 2, sets his students 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.[4] 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 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, Cooke realized that "it did this at the sacrifice of all that is distinctive and peculiarly valuable in the study of an experimental science" (Jackson

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[4] 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 physical chemist Dutch chemist Jacobus van't Hoff in his book on chemical equlibrium *Étude de Dynamique Chemique* (*Studies in Chemical Dynamics*), where double reversed arrows were used to indicate reversible reactions and the dynamic nature of chemical equilibrium.

1894, 5126) - 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.

Cooke's operationalisation of chemical practice partly relies on the systematic use of chemical symbols and chemical formulae as "paper tools": not mere shorthand labels for elements and compounds (H for hydrogen, O for oxygen, H_2O for water), but generative tools that participated in the very justification and modelling of chemical reactions. As Ursula Klein (2001a) states:

> "The notion of paper tools implies the assertion that scientists often apply representations or signs systems in general for the same epistemic purpose and in a similar way to laboratory instruments in the strict sense: to produce new representations of invisible objects or processes…Paper tools are visible marks which can be manipulated on paper to create representations of a scientific object" (Klein 2001a, 97).

Klein's definition seems to suggest a distinctively pragmatic and semiotic function for paper tools in chemical practice, and it is indeed strange that her account does not capitalize on, or at least refer to, Peirce's semiotics. Applied to the case of Cooke's textbook, the inclusion of paper tools in operationalizing Stöckhardt's practical experiments has the double function of providing a shared common language for the quantitative aspects of laboratory practice, and a powerful mechanism to *visualize relations* between chemical phenomena. Cooke's problem-based approach demanded students to treat chemical formulas diagrammatically, and in this particular respect his application of simple mathematical operations to the study of chemistry went well beyond "mere mathematisation".

It may be useful, at this stage, to start outlining how even the simplest and most basic pedagogical assumptions developed by Cooke in the course of his teaching career at Harvard resonated with Peirce, and how they might have informed his treatment of diagrams in analogy with chemistry. The text of the *Prolegomena* is again a good place to start drawing this comparison, as it is there that Peirce very explicitly fleshes out the analogy between chemical, mathematical and logical diagrams. After insisting that a general quest for molecular structure informs even the chemist's isolated experiments on individual substances, and in substantiating his view that, along similar lines, the Object of Investigation of a diagram is "the Form of a Relation", Peirce switches back to a mathematical example:

> "Now this Form of Relation is the very form of the relation between the two corresponding parts of the diagram. For example, let f1 and f2 be the two distances of the two foci of a lens from the lens. Then,
>
> $1/f1 + 1/f2 = 1/f0$

> 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 f1, f2, f0 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).

Just like Cooke, Peirce is here pursuing the line of reflecting on the (diagrammatic) characteristics of mathematical *reasoning* broadly construed. It is in this particular sense that an equation can indeed function as a diagrammatic representation: Cooke's idea of mathematics as "the science of quantitative relations wholly independent of their material expression" (Cooke 1888, 101) finds a resonance in Peirce's statement that an equation exhibits a relation between quantities (in the case above the three focal distances expressed in the equation) regardless of the accidental significance of the very letters involved in its material notation. At the same time, Peirce tells us that the form of the relation thus obtained is "is the Very Same as the form of the relation between the three focal distances that these letters denote": experimenting with diagrams amounts to performing operations on the very objects of investigation that the diagram is supposed to represent. Incidentally, this is a further opportunity to think about how Peirce's account of diagrams could interestingly complement Klein's account of paper tools. In Klein's view, the literature on paper tools should be extended to diagrammatic representations as a case in point: " we may also think of other sign systems in modern physics, such as Feynman diagrams, as paper tools" (Klein, 2001b, 296). But what Peirce seems to suggest in his *Prolegomena* example is in fact the opposite: that a distinguishing characteristic of what counts as a "paper tool" (in chemistry, mathematics, physics or logic) is in fact their inherently diagrammatic nature.

An important aspect of Peirce's idea that diagrams make relations visible is inevitably related to his qualification of diagrams as iconic representations *par excellence*. Indeed, in reference to his own system of Existential Graphs, and in a manuscript (MS 293, c 1906) which probably served as a draft for what would become his *Prolegomena,* Peirce defines a diagram as "an Icon of a set of rationally related objects". By "rationally related" Peirce means "that there is between them, not merely one of those relations which we know by experience, but know not how to comprehend, but one of those relations which anybody who reasons must have an inward acquaintance with" (MS 293, pp. 10-11). This is in line with Peirce's dictum that all necessary reasoning is ultimately diagrammatic (ibid. p. 6), and in particular with his idea that necessary reasoning makes (or should make) its conclusions *evident*. Reasoning upon a diagram, Peirce explains, allows for the truth of the conclusion to be "perceived, in all its generality; and in the generality the how and why of the truth is perceived" (ibid. p. 11, emphasis in the text). His claim here is that only iconic representations such as diagrams can provide just this kind of evidence:

> "It is, therefore, a very extraordinary feature of diagrams that they show, - as literally show as a Percept shows the Perceptual Judgment to be true, - that a consequence does follow, and more marvellous yet, that it would follow under all varieties of circumstances accompanying the premises". (ibid. p.13, emphasis in the text)

This seems in line with the diagrammatic exemplification of mathematical reasoning that, as we showed in section 1, Carolyn Eisele placed at the core of Peirce's philosophy more broadly. It is also, however, very close to the role of mathematics as "peculiarly well adapted to train the logical faculties' (Cooke 1875, 528) envisioned by Cooke as central to his chemical training. It is important to note, at this stage, that we are not claiming any direct lineage between Cooke's and Peirce's ideas of mathematics. Nor are we claiming that Peirce inherited his diagrammatic approach to mathematical reasoning directly from Cooke. After all, Cooke was only one of Peirce's teachers, and he certainly was not primarily responsible for Peirce's *mathematical* education. We claim, however, that at least part of the justification for Peirce's treatment of *relations* lies beyond the scope of mathematics alone. Thus, the emphasis on Peirce's chemical training might substantiate a more modest, but still fruitful, line of argumentation: the combination of chemistry and mathematics had on Peirce the effects that Liebig (and Cooke) desired and aspired to in crafting their pedagogical innovations. In combining theory (the "form" of relations) with practice (actual research-driven experimental work), chemical thinking became part and parcel of Peirce's philosophy.

Chemical and Logical Diagrams

So far, we tried to prove that the combination of chemistry and mathematics developed by Peirce's teacher Josiah Cooke was well aligned with Peirce's own treatment of diagrams as ways of visualizing relations, so much so that it offers reasonable evidence to look for alternative sources, other than mathematics and logic alone, for his treatment of diagrams. It is our contention, a contention that we set out to substantiate further in this section, that there was more in Cooke's teaching that might have directed the young Peirce's attention toward the advantages of thinking in terms of relations and through diagrams. The very approach to chemical diagrams developed by Cooke for his lectures at Harvard might offer additional evidence that diagrammatic reasoning was part and parcel of Peirce's scientific training from the outset.

Harvard's *Catalogue of the Officers and Students of Harvard University for the Academic Year 1861-62* includes Cooke's newly published book *Chemical Physics* (1860) as one of the texts Peirce would have used as a student. 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. For one thing, Cooke's use of diagrams fulfils a distinctively "semiotic" function. With a somewhat transversal historiographical move, one could use Peirce's own semiotic categories to analyse his teacher's use of crystallographic representations as diagrams, and observe that the images fulfilled more than a mere illustrative purpose in the textbook. Cooke's crystallographic diagrams are intended to generate interpretive thoughts, and in the process the diagrams become indistinguishable from the crystal forms with which they share a number of significant characteristics. In what follows, we discuss how Cooke accomplished this.

The section on crystallography begins with Cooke advising his students to produce their own representations by 'prepar[ing] models of the more important forms' (Cooke 1860, 132). Interestingly, his discussion of the geometry of crystals is shaped in analogy with material models, which he advises students may purchase “from dealers in philosophical instruments” (ibid.).[5] Cooke even points out that models of various materials are available for the purpose, however “by far the most instructive models are made with glass faces fastened together by strips of colored paper pasted on the edges” (ibid.), which would facilitate the geometric understanding of the structure of the crystals thus modelled. He then considers the principal crystal systems, starting with holohedral forms of the monometric system. An example of his approach can then be seen in the way Cooke extracts geometric knowledge working directly with the diagrams (fig. 3).

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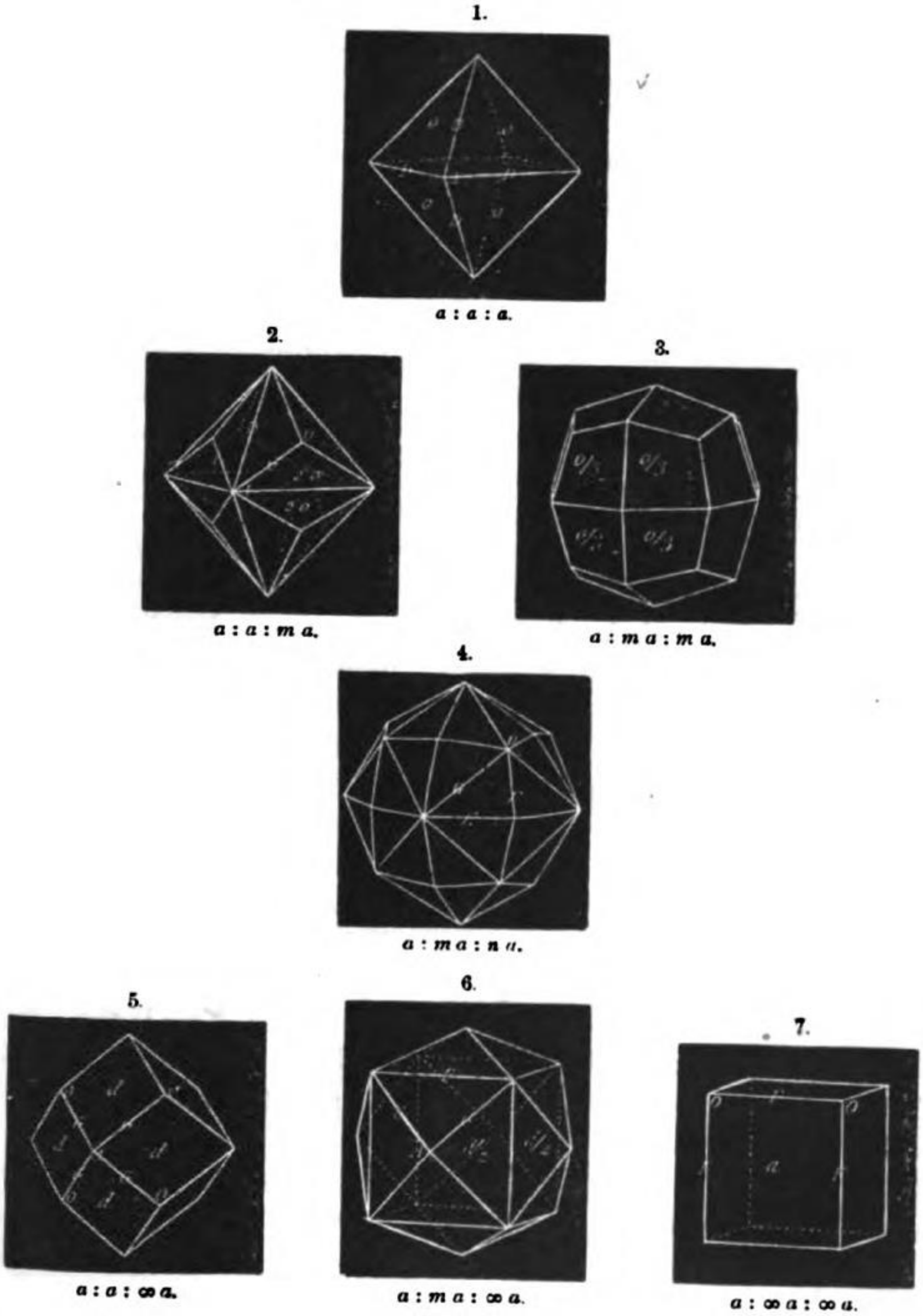
[5] Three dimensional models of the kind Cooke suggests to his students were ubiquitous in nineteenth century teaching and research. For a historical overview of the various uses of these kinds of models across scientific disciplines see De Chadarevian and Hopwood, 2004.

Simple Holohedral Forms.



1. a : a : a.
2. a : a : m a.
3. a : m a : m a.
4. a : m a : n a.
5. a : a : ∞ a.
6. a : m a : ∞ a.
7. a : ∞ a : ∞ a.

Fig. 85.

1. a : a : a.	Octahedron.	Solid	bounded by	8 equilateral triangles.
2. a : a : m a.	Trigonal triakis-octahedron.	"	"	3 × 8 isosceles "
3. a : m a : m a.	Tetragonal triakis-octahedron.	"	"	3 × 8 quadrilaterals.
4. a : m a : n a.	Hexakis-octahedron.	"	"	6 × 8 scalene triangles.
5. a : a : ∞ a.	Rhombic dodecahedron.	"	"	12 rhombs.
6. a : m a : ∞ a.	Tetrakis-hexahedron.	"	"	4 × 6 isosceles triangles.
7. a : ∞ a : ∞ a.	Hexahedron (cube).	"	"	6 squares.

Fig. 3. Cooke's Crystallography Diagrams, from Cooke, *Chemical Physics* (1860), p. 133.

Three solids among the seven shown on the page (the octahedron, the rhombic dodecahedron and the hexahedron), Cooke explains, have invariable parameters and do not admit any variation in the relative position of their planes. The remaining four, however, have variable parameters and the position of their planes depends on the values assigned to *m* (a simple rational number, giving the parameter value for a particular crystal axis). So, Cooke explains, in the case of the tetrakis-hexahedron (solid no. 6 in fig. 3), which is an intermediate form between the dodecahedron and the cube, "when $m=1$ the pair of faces meeting at *m* coincide, and we have the dodecahedron. As the value of *m* increases, the solid angle at A becomes more and more obtuse, until, when $m=\infty$ the four planes meeting at A coincide and we have a cube" (Cooke 1860, 134). Cooke then invites students to try analogous operations on other solids in the series represented in the figure, such as the hexakis-octahedron (solid no. 4 in fig. 3), but in doing so he points out that he will not spoonfeed the necessary information: "to trace out these relations, both in the symbols and the forms, is left for an exercise to the student" (ibid.).

There are two points of importance here that have crucial relevance for Peirce's subsequent treatment of diagrams. First, Cooke singles out the features (the four planes meeting at A, *m* and the values assigned to it etc.) that serve as pointers to perform relevant operations on the figures. This is analogous to what Peirce, later on, would define as the indexical component of diagrams. Secondly, the student is encouraged to experiment on the representation in order to fully engage with these relations – to consider, for instance, the geometric consequences of increasing the value of *m* until it approaches infinity. This approach, where Cooke presents crystallography in the language of relations between mathematical symbols and forms, is repeated many times throughout the chapter, as is the instruction for the student to comprehend these crystallographic relations by experimenting on the representations. Not all the crystal systems are set out in detail, for as Cooke 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]" (Cooke, 1860, 140).

In using geometric diagrams in this way, Cooke offers a conceptual image that seems to encourage the student to merge the representation as printed in the tex book with its object, the crystalline form found in nature. The result is that Cooke's geometric diagram is, for the student, the thing itself – the natural crystalline form under investigation. Cooke's approach enables the student to discover the relations between the natural crystalline form and its geometric representation, which captures the "form" of that relation independently of its material configuration. At the same time, the student comes to know the object – the crystalline form – by interacting with its representation. By viewing the representation through the lens of practice – the practice of crystallography, productively merged with geometry – the student synthesises a sense of meaning and understanding through the many relations at play.

We showed that Cooke's *Chemical Physics* was one of the textbooks used in Peirce's chemistry course at Harvard. It is easy to see how Cooke's pedagogical methods would have resonated with Peirce – and of course this judgment is far too easy to make in hindsight, with the knowledge we have today of Peirce's strong preference for visual thinking. Late in life, Peirce himself would acknowledge: "I do not think I ever reflect in words: I employ visual diagrams, firstly, because this way of thinking is my language of self-communion, and secondly because I am convinced that it is the best system for the purpose" (MS 619:8). Far too often Peirce's scholars have treated this ability as one of the many marvelous products of Peirce's unique mind, but visual thinking, as all other modes of knowing, is an ability that needs to be fostered and cultivated. In light of the historical evidence we presented so far, there is reason to believe that Cooke at least contributed to nourish Peirce's preferred mode of learning, and that his teaching of crystallography through diagrams could have been at least one of the many factors that allowed his inclination toward diagrammatic thinking to flourish. By approaching crystallography through Cooke's diagrammatic methods, Peirce experienced the iconic nature of diagrams in a way which he would later describe in one of his most evocative passages on the subject:

> "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'. (CP 3.362 1885)

Peirce scholars know that this is a passage from Peirce's 1885 *Algebra of Logic*, which considerably precedes his diagrammatic system of Existential Graphs (formally put forward only in 1896), and is especially known as his formal introduction of quantifiers in logic. But as Ahti Pietarinen (2006, 109ff) notes, Peirce's diagrammatic system of Existential Graphs was ultimately rooted in Peirce's previous investigations in logical algebra, and as Shin and Hammer (2013) point out "Peirce's mission for a new logic started with the question of how to represent relations" (Shin and Hammer 2013, n.p.), a question that partly marks the continuity between his discovery of logical quantifiers and his subsequent diagrammatic system of logic. It is therefore not too surprising that one of Peirce's most forceful discussions of the iconic nature of diagrams appears in a logical context such as the *Algebra of Logic*, and it is even less surprising that diagrams, having been such a crucial part of Peirce's scientific way of thinking even before the beginning of his formal career as a scientist, constituted a recurrent concern in his writings.

Later in life, and as we showed earlier on, Peirce used diagrams as an opportunity to reflect on the evidential status of logical relations. On the one hand, he claims, relations are discovered through the very process of constructing and inspecting a diagram. This process requires the diagram to be built in relation to an Interpretant – which for Peirce is the interpreting sign that a sign itself triggers in an interpreter's mind (or quasi-mind). Once a diagram has incorporated an intention to appeal to an Interpretant, its necessary conclusions become universally communicable and thus *evident* – that is, appealing to "those relations which anybody who reasons must have an inward acquaintance with" (MS 293, pp. 10-11). This is very much in line with the pedagogical approach to diagrams developed and pursued by Cooke in his teaching. Peirce was trained in a chemical tradition which placed diagrammatic reasoning at the core of experimental practice, and through Cooke's teaching he became acquainted with the process of discovering the relations governing chemical structure (through chemical formulas, stoichiometry and the application of geometry to crystallography, all used in a distinctively "diagrammatic" way). But Cooke's textbooks also emphasized that, once communicated or shared within a community, relations become *evident* and can be comprehended beyond what is merely experienced through singular observations.

Peirce's quote from the *Algebra of Logic* referred to above also reveals an (apparent) tension which would characterize his approach to diagrams more broadly, and which reappears in the passage from the *Prolegomena* that opened our chapter. On one hand, experimenting on a diagram is different from handling a pure icon because diagrams possess generality: they obey particular conventions, for example, and function through the indispensable aid of indices as pointers for relevant features to be manipulated and experimented upon. At the same time, Peirce explains, reasoning on a diagram is a way of coming into contact with the particular object of inquiry that the diagram is supposed to investigate. In transferring the discussion in the *Algebra of Logic* from diagrams to the iconic function of other kinds of representations, such as paintings, Peirce continues: "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" (CP 3.362). Once again, Peirce's quest for relations here offers the key: diagrams are ways of discovering relations (between the parts of the representation itself, independently of its material components), and at the same time extend those relations to particular, still uninvestigated instances. In this, Peirce's treatment of diagrams appears once again in line with the teachings of his teacher, Josiah Cooke, and particularly with his pedagogical use of diagrams to relate geometric and chemical structure.

The apparent tension between the generality of diagrams and their ability to place us into contact with the direct object of inquiry is smoothed even further by a passage from MS 293, in which Peirce draws an illuminating analogy between diagrams and Kantian Schemata:

> "Meantime, the Diagram remains in the field of perception or imagination; and so the Iconic Diagram and its Initial Symbolic Interpretant taken together constitute what we shall not too much wrench Kant's term in calling a Schema, which is on the one side an object capable of being observed, while on the other side it is a general"(MS 293, 13).

While this is not the appropriate place for a long exegetic discussion of the relations between Kant and Peirce,[6] a few remarks are here in place. Just like Schemata, Peirce states, diagrams have a twofold nature: on one hand they are objects "capable of being observed", while on the other they also possess generality. The most effective way of making sense of this statement is through Hookway's (2002) perceptive investigation of the relations between Schematism and iconicity, which can easily be extended to diagrammatic representations. As Hookway (2002) points out, Peirce drew on Kantian Schematism to advance a broader point on the generality of ideas. In this context, Hookway argues, Schemata appear to be "'templates' or stereotypes in applying concepts – or at least in applying some concepts" (Hookway 2002, 32). There is much that this characterization has in common with Peirce's treatment of diagrams. Diagrammatic representations appear to be somehow a materialization of Hookway's account of ideas on paper. Just like Kantian

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[6] The literature on Kant and Peirce is vast, and here we limit ourselves to point the reader to Gava (2014), as an excellent and up-to date source on the subject.

Schemata mediate between the faculty of understanding and experience, so diagrams mediate between the “inward acquaintance” that every reasoner has with the (general) nature of relations and the concrete phenomena the diagram is supposed to relate. Even more importantly, the parallel with Schemata allows us to account for the generative character of diagrams more broadly. Schemata, in Kant and Peirce, are indeed rules, methods, or procedures produced by the faculty of imagination that allow us to anticipate experience (and in doing so, to make sense of it conceptually). Similarly diagrams, by virtue of their iconic character, allow both the synthesis of a manifold of experienced ideas into a unified representation, *and* the discovery of relations not necessarily involved in the construction of the representation itself. With this in mind, it may also be productive to revisit the recent literature on Existential Graphs, which emphasizes how Peirce constructed his system of diagrammatic logic as “moving pictures of thought” (CP 4.8, c1905; Pietarinen 2006 pp. 103ff). Peirce’s quote on diagrams as Schemata adds a further tile in the mosaic of the logical system he developed in the 1890s. Schematism explains the generative and dynamic, general and observational nature of diagrams. As materialistions on paper of the faculty of imagination, diagrams offer a “moving picture of the action of the mind in thought”(MS 296, 6) and in doing so they serve as key mediators between understanding and experience.

Once again, a caveat is here in place. We are not arguing that Peirce inherited his philosophical application of Schematism to diagrams from Cooke: it is well established in the literature that Peirce’s Kantian training began in 1855 (W1, 2) and continued in parallel with his scientific training. What we are arguing, however, is that Peirce experienced the particular functions and properties he attributed to diagrams through the pedagogical innovations Cooke tried to introduce in his lectures at Harvard. In a Kantian spirit, Cooke acknowledged in his *Chemical Physics* textbook that we can have no knowledge of the *essential nature* of chemical substances. But in an equally Kantian spirit, Cooke also acknowledged that this limitation is the condition of possibility for chemical knowledge:

> “In regard to the essential nature of matter, or 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”. (Cooke 1860, 3)

It is this *relational* view of chemical knowledge, pursued diagrammatically, which we claim Peirce might have inherited from Cooke and turned into one of the bedrocks of his philosophical system.

Conclusions

Much remains to be investigated when it comes to understanding the impact of Peirce’s chemical training on his philosophical ideas. Peirce scholars often tend to neglect even the most basic results of Peirce’s chemical training – for example the fact that Peirce’s first published paper, “The chemical Theory of Interpenetration” (1863; W1, 95-100), was in fact a *chemical* paper, of a distinctively

Kantian flavor. Throughout his life, Peirce frequently drew on Dmitri Mendeleev's periodic table as an exemplary instance of inductive reasoning and, in 1869, he published his own contribution to the history of the periodic table. Peirce's paper, titled "The Pairing of the Elements" and published in the American edition of *Chemical News,* was praised by the American Association for the Advancement of Science as having "greatly added to the illustration of the fact of pairing by representing in a diagram the elements in positions determined by ordinates representing atomic numbers" (W1 xx). Several years later, reporting on the discovery of the Periodic Law for the *Nation* in 1892, Peirce makes what is possibly his most powerful claim in support of his old tutor as the foremost herald of Mendeleev:

> "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).

Only a few lines later, a cryptic comment suggests that Peirce inscribed himself in the very tradition Cooke and, subsequently, Mendeleev pursued in chemistry:

> "'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". (W8, 285)

The "obscure American chemist" in this case is Peirce himself, and the table he refers to is the very diagrammatic illustration of the pairing of elements praised by the American Association for the Advancement of Science in 1869.

Before concluding, we would like to trace some of the broader implications that the study of Peirce's work on chemistry can have on Peirce's scholarship. In a recent article, Richard Atkins (2010) traces an important difference between Peirce's *formal* , Cenopytagorean categories (Firtsness, Secondness and Thirdness) and his *material* categories, not reducible to their formal counterpart. In drawing this distinction, Atkins insightfully appeals to the relations between Peirce and Mendeleev, so much so that he redefines Peirce's 1908 re-systematisation of his categories as his "Mendeleevian period" (Atkins 2010, 101). We believe that more of this work is needed in Peircean scholarship, and that a historical study of the chemical context surrounding, directing, and informing Peirce's philosophy is an essential complement to the philosophical understanding of Peirce's chemical metaphors. Peirce's references to chemistry need to be taken seriously. Far from being a mere stepping stone toward his greater accomplishments in science, logic and philosophy, chemistry was for Peirce a whole mindset and a way of thinking that complemented epistemically, visually, materially and even metaphysically the development of his philosophy.

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