Structural Realism in Chemistry: The Periodic System of the Elements

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These divisions and definitions, namely 'cells,' 'molecules,' and 'electrons,' are possibly very imperfect; it may be that with time science will establish others, but the principle will remain always the same and lower cosmoses will always be in precisely such relation to the Microcosmos
George Gurdjieff, as quoted by Ouspensky (1949)

Abstract
Structural realism is the view that science provides knowledge of the relational patterns of the world, rather than the individual entities populating it. While widely applied in physics, its applications in chemistry have hitherto been scarce. Here, we examine the periodic system of the elements through the lens of structural realism, drawing from the history, philosophy, and practice of chemistry. First, we argue that Mendeleev's structuralist approach—emphasizing the relations between atomic weights of elements as abstract entities—was key to the development of the periodic system. Second, we argue that the periodic system has to be regarded as real, in that it represents a predictively successful structure that has remained intact through changes in the atomic theory. Third, we argue that a structural realist perspective can offer a guiding principle to adjudicate between competing proposals of the periodic table. Overall, our work demonstrates that chemistry is a promising domain for structural realism to thrive.

Keywords: Scientific realism, structural realism, chemistry, periodic system, Mendeleev

1. Structural realism and chemistry

Structural Realism. Structural realism holds that predictively successful science delivers knowledge of the relations inhabiting reality. This view, which is regarded as one of the most defensible forms of scientific realism, was introduced—or perhaps resurrected from previous incarnations—by Worrall (1989) in a highly influential article.

Worrall envisions structural realism as the "best of both worlds," a conciliatory position between realists, who commit to the existence of the entities posited by scientific theories, and anti-realists, who do not. Worrall presses his case by examining the transition from Fresnel's wave theory to Maxwell's electromagnetic theory. Fresnel developed a theory in which light waves propagate through aether, an all-pervading mechanical medium. Such a theory was later succeeded by that of Maxwell, for whom light was to be regarded as consisting of a disembodied electromagnetic field. Some of Fresnel's equations, however, were successfully retained in Maxwell's theory. Worrall concludes that whereas entities such as aether may come and go, the underlying mathematical structure survives across theory change. This motivates skepticism regarding unobservable entities, while licensing belief in the relational structure that connects them.

In doing so, Worrall is partly responding to Laudan (1981)'s pessimistic meta-induction, which points out that many previously posited scientific entities, such as phlogiston, aether, and caloric, have now been abandoned, even though they may have featured in what were successful theories at one time. If this is the case, so the meta-induction says, why should we believe that currently posited scientific entities should fare any better? Worrall acknowledges that theory change involve disruptions at the ontological level. Yet, these are confined to entities. The structure, though reinterpreted by the subsequent theory, remains conserved, supporting Putnam (1975)'s no-miracle argument that supports the inference from scientific success to approximate truth.

Worrall's proposal has spawned a veritable cottage industry, especially among philosophers of physics such as Ladyman and Ross (2009), French (2016), and Saunders (2003), who have successfully applied this intriguing idea in many areas of classical and quantum mechanics. However, suppose structural realism is to be of lasting value. In that case, one imagines that it should apply to other disciplines than physics, although one then runs across the problem that these other disciplines do not possess the same degree of mathematical structure that physics obviously does. Few authors have ventured to examine whether structural realism has any relevance to the discipline of chemistry, which is frequently described as being the central science. In addition, it may be said that chemistry is the next most mathematical of the sciences after physics and, therefore, the most fertile ground in which to attempt to enlarge the domain of structural realism.

Structural Realism and Chemistry. An earlier attempt to apply structural realism to chemistry is the historical case of phlogiston theory, as articulated by, e.g., Ladyman (2011) and Carrier (2004). Although the phlogiston theory posits the existence of an entity that had ceased to exist, the structural realist argues, it nonetheless revealed a set of relations that have persisted in subsequent science. Specifically, according to Ladyman (2011), "the one great truth" of phlogiston theory that was retained is its ability to recognize that "combustion, respiration, and calcination are all the same kind of reaction" (p. 90). Moreover, such reactions are described through the inverse processes of phlogistication and dephlogistication, a pair of relations that have endured in contemporary chemistry as the inverse processes of reduction and oxidation. Hence, Ladyman ascribes the empirical success of the phlogiston to its correct identification of the "causal/nomological structure of the world as expressed in the unification of reactions into phlogistication and dephlogistication" (p. 100), which "is retained in contemporary chemistry by the duality between oxidation and reduction reaction." (p. 89)

This structural correspondence between phlogiston theory and contemporary chemistry has been called into question. Doppelt (2011), for example, criticizes Ladyman's view by arguing that it fails to clearly identify "some unobservable underlying structure of relations" (p. 308) which is responsible for the success of phlogiston theory. The ability of phlogiston theory to unify phenomena "does not describe any underlying unobservable structure of relations, except to say "that there is some such structure" commonly responsible for, or manifest in, three kinds of observable phenomena" (p. 309). In addition, Pizzochero and Oldofredi (2025) have argued that the parallelism between phlogistication and dephlogistication on the one hand, and reduction and oxidation on the other, is plagued by an ambiguity. Phlogistication and dephlogistication are processes that pertain to chemical compounds as wholes, while reduction and oxidation are processes that pertain to individual chemical elements. If the structural correspondence is maintained, then one falls into the contradiction that a chemical compound can be simultaneously dephlogisticated and phlogisticated, depending on which chemical element is inspected. Even if accepted, such structural correspondence fails to support any form of scientific realism, which should aim to identify continuity across fundamental science, while oxidation and reduction are merely an instrumental framework.

Applications of structural realism to chemistry remain limited, and no consensus has emerged regarding their success. This gap needs to be bridged if structural realism is to establish itself as a general and comprehensive philosophical account of mature science. In what follows, we make progress by proposing that the periodic system—the set of recursive relations among the atomic weights of the elements—provides a successful realization of structural realism in chemistry. Importantly, the periodic system is qualitatively different from the structures pervading the physical sciences in that it cannot be expressed in a mathematical form. This is due to the fact that the properties of the elements do not repeat at a regular interval, unlike in ordinary periodic functions, as acknowledged by Mendeleev:

> *But in ordinary periodic functions one variable varies continuously, whilst the other increases to a limit, then a period of decrease begins, and having in turn reached its limit, a period of increase again begins. It is otherwise in the periodic function of the elements. Here the mass of the element does not increase continuously, but abruptly, by steps, as from magnesium to aluminium. So also, the valency or atomicity leaps directly from 1 to 2 to 3, &c, without intermediate quantities, and in my opinion, it is these properties which are the most important, and it is their periodicity which forms the substance of the periodic law* (Mendeleev, 1897, Part III, p. 21 n. 11).

The remainder of this essay is organized as follows. In Section 2, we set the stage by briefly outlining the historical development of the periodic system before Mendeleev. In Section 3, we argue that Mendeleev can be regarded as an earlier exponent of structural realism, in that his emphasis on the reality of relations between elements over their existence was essential to the development of the periodic system. In Section 4, we show that the periodic system qualifies as a successful realization of structural realism in chemistry, in that it is a structure that is both predictively successful and persistent over multiple theoretical discontinuities involving its content. In Section 5, we put structural realism to good use by adjudicating between competing proposals of the periodic table. Finally, in Section 5, we address potential objections and conclude our analysis.

2. Before Mendeleev: Elements and their arrangement

The nature of the elements. The true nature of elements has been debated since the dawn of human knowledge, starting from the time of the pre-Socratic philosophers, for whom four elements existed, namely earth, fire, water, and air. These four elements were considered as property bearers responsible for the observable features of all substances, while remaining intrinsically unobservable. Said in other words, they were regarded as abstract, immaterial qualities impressed on an otherwise undifferentiated primordial matter and which were present in all substances. Moving to the Middle Ages and the field of alchemy, more substances became regarded as elements, such as gold, silver, copper, iron, tin, lead, antimony, mercury, sulfur, and carbon.

While previous thinkers had viewed elements as abstract entities, Antoine Lavoisier is well known for emphasizing them as substances that could actually be isolated, thus reducing any metaphysical interpretation. Undoubtedly, these two perspectives greatly contributed to the development of modern chemistry and the decline of the ancient discipline of alchemy. The new 'operational' view drew upon the pre-Socratic tradition of elements as principles, but also made some important modifications. In particular, the new chemistry introduced the concept of a simple substance, meaning one that could not be decomposed by any *known* means. The inclusion of the word known is important, since the scheme proposed that simple substances were to be regarded as such only provisionally, because future refinements in analytical techniques might reveal that they were, in fact, decomposable. Lavoisier no longer talked of undifferentiated primordial matter, but the focus of attention became the many elementary constituents, or simple substances, each of which possessed observable properties. Over time, simple substances became regarded as the only form of an element, while the metaphysical counterpart to each simple substance was largely forgotten. On this philosophical basis, Lavoisier and his contemporaries created a list of the 33 simple substances known at the time,[1] which would soon be organized in tables.

Arranging the elements. One way to understand the nature of the periodic table, and the periodic system which it attempts to represent graphically, is to consider its historical development. Although tables of chemical affinity existed as many as 300 years ago, and even though Lavoisier produced a famous table of the 33 known 'elements' in 1789, none of these developments can be considered to be a periodic system for the simple reason that they did not feature periodicity among the properties of the elements.

Our brief historical survey begins with the rebirth of atomic theory in the early 1800s at the hands of the Manchester school teacher John Dalton. Dalton published his five postulates about the nature of atoms, including the fact that they were indestructible, in his view, and that the atoms of each element had a distinct weight. This development can be identified as the starting point of all the later steps, which culminated in the discovery of chemical periodicity and its representation in various periodic tables in the 1860s.

The first hint of chemical periodicity came from one Wolfgang Döbereiner, a German chemist who identified a remarkable property concerning several sets of three elements that behaved similarly in terms of chemical and, in some cases, physical properties. Using Dalton's atomic weights, Döbereiner noticed that the atoms of lithium, sodium, and potassium, to take the classic example of such a triad, had two important properties. First, the atomic weight of one of the atoms of these three elements was approximately the numerical average of that of the other two. The approximate weights of the atoms of these elements are as follows: lithium = 7, sodium = 23, and potassium = 39. Consequently, the weight of an atom of sodium, or 23, is the mathematical average of that of lithium + potassium or (7+39)/2 = 23. In addition, the chemical properties possessed by the element sodium are intermediate between those of lithium and potassium. For example, if one places small samples of equal size of each of these elements into basins of water, they show an increasing degree of reactivity, starting with lithium, which reacts slowly, sodium, which reacts moderately, and potassium, which reacts very vigorously. Döbereiner had discovered a numerical regularity that underlies and connects the behavior of three quite distinct elements. This can be regarded as the first hint of an underlying structure among the different elements and one which eventually morphed into the familiar periodic table that today hangs in chemistry lecture halls and laboratories throughout the world.

What followed were various attempts to discover other triads of elements, some of which research lapsed into mere numerology, in the sense that the numerical coincidences were seized upon while neglecting the fact that many claimed new triads concerned elements that did not display chemical similarities. While the notion of chemical triads fell into disrepute, the germ of the idea seems to have survived. In addition, many more elements were discovered following the initial publication of Döbereiner's triads in 1817. The eventual periodic system consisted of connecting the various legitimate triads that existed, but it is doubtful that the periodic table could have emerged by doing just that, since many elements still remained to be discovered.[2] Nevertheless, as Scerri (2022) has claimed, the discovery of triads essentially marks the discovery of chemical periodicity.

The next decisive development took place at the Karlsruhe conference of 1860, when the Italian chemist and physicist Stanislao Cannizzaro provided a definitive and consistent set of the atomic weights of the elements. Two chemists who attended this meeting were Lothar Meyer and Dmitri Mendeleev, each of whom was to produce versions of the periodic table a few years later, based on an increasing order of elemental atomic weights. We shall now turn to that story.

3. Mendeleev: A precursor to structural realism

Mendeleev and the elements. The culmination of the nineteenth-century element scheme was achieved with the discovery of the periodic system and, in particular, with the work of Mendeleev, who began his landmark book by paying tribute to Lavoisier. Interestingly, Mendeleev appears to have been more concerned with the philosophical nature of the term 'element' than any other of the six co-discoverers of the periodic system (Scerri and Ghibaudi, 2020), a trait that proved instrumental to his success.

Mendeleev goes to considerable lengths to emphasize the dual meaning of the notion of element. On the one hand, it denotes simple substances that can be isolated. On the other hand, it carries an abstract sense—reviving the idea from the pre-Socratic philosophers—of an entity that cannot itself be isolated or observed, yet persists throughout chemical reactions. In the words of Mendeleev,

> *It is useful in this sense to make a clear distinction between the conception of an element as a separate homogeneous substance and as a material but invisible part of a compound. 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 the 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* (Mendeleev, 1891, p. 23)

Mendeleev regarded an element as unobservable but forming the inner 'essence' of simple bodies, giving rise to all the variety of substances that are observed. Whereas any particular abstract element was thought of as unchanging, its corresponding simple body aspect could take many forms, such as diamond or graphite, in the case of the element carbon, for example.

Mendeleev recognized that the abstract sense of element survived intact in the course of compound formation, with its atomic weight being the only quantity that is conserved in the course of chemical reactions. Mendeleev, therefore, proceeded to associate these two meanings of the term 'element' together, as it has become known in the contemporary literature.[3] An abstract element, therefore, possessed a single, measurable, but not observable, attribute of atomic weight that would remain unchanged in the course of all its chemical combinations.[4] In so doing, Mendeleev was providing a fundamental justification for using atomic weight as the basis for the classification of the elements. Following this interpretation, it becomes possible to understand Mendeleev's otherwise rather naive-sounding claim that he had realized the need to order the elements according to atomic weight, given that several other pioneers of the periodic system had done so before him. Unlike the co-discoverers of the periodic system, Mendeleev provided a detailed philosophical account of why this was the correct approach to take.

But it would be incorrect to believe that the abstract sense of element is the only aspect to focus upon when classifying the elements, as some passages in Mendeleev's writings suggest, since periodicity also concerns properties in the observable sense.[5] Atomic weight alone can only provide the sequence of the elements and not the points at which they repeat approximately. The sole use of atomic weight would therefore not reveal the chemical and physical periodicity among the elements. Kaji (2003) has argued that Mendeleev began his textbook by using the concept of valency as a means of ordering the elements. This is clearly seen in the fact that Mendeleev considered the elements in the order of hydrogen, oxygen, nitrogen, and carbon, whose valences are 1, 2, 3, and 4, respectively. Mendeleev then turned to the halogens, beginning again with the valence of 1, followed by a consideration of the alkali metals, also of valence 1, and then the alkaline earths, which show a valence of 2. It appears that, while making the transition between the alkali metals and the alkaline earths, Mendeleev made the crucial discovery that led to publishing his periodic table. It was at this point that he realized that the key to classifying the elements lay in atomic weight rather than valence. As Mendeleev writes,

> *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* (Mendeleev 1889, p. 626)

There is currently an extensive literature that aims to understand why Mendeleev was able to make such striking predictions rather than Lothar Meyer or others (Gordin, 2012). Some authors have claimed that the other chemists lacked the courage to do so; others have proposed a sociological explanation concerning the contrasting academic climates in Russia compared to those in Germany. Meanwhile, Scerri (2020) has suggested that Mendeleev's advantage was due to his philosophical attitude regarding the nature of the elements, which provided him with the insight that his less philosophically minded contemporary chemists lacked. As was argued above, Mendeleev believed that the abstract sense of elements should be regarded as more foundational than their simple substance aspects. Consequently, if the periodic system were to be of fundamental importance, it would primarily have to classify the abstract elements and not simple substances. In making predictions, Mendeleev considered the abstract aspect of elements more than their concrete instatiations. For example, the halogen elements (fluorine, chlorine, bromine, and iodine) appear to be very different from each other if one focuses on the simple substances, since they consist of two gases, a liquid, and a solid, respectively. But if one considers the similarities between the compounds that each forms with sodium, all of which are crystalline white powders, their kinship becomes clearer. The main point is that fluorine, chlorine, bromine, and iodine, in these compounds, are present not as simple substances but in their latent, or abstract, form as basic substances.

Mendeleev as a structural realist. Armed with his belief that the periodic law applied to the abstract elements, Mendeleev could maintain the validity of the periodic law even in cases where observational evidence seemed to point in a different direction. Mendeleev also held that this law was as fundamental and equal in status to Newton's laws of mechanics, a claim which he expressed in several of his writings. Had he been more of a positivist and had he focused on elements as simple substances, Mendeleev might have lost confidence in the priority of the periodic system over the elements and might have harbored doubts about his predictions.

In view of this, we suggest that Mendeleev can be seen as an early exponent of structural realism who regarded the periodic system realistically, but not the entities that populate it. On the one hand, Mendeleev (1889) was committed to "those relations which *exist* between the atomic weights of dissimilar elements" (p. 626, emphasis added). As noted by Scerri (2020), this commitment was indeed his distinctive insight, as other "co-discoverers could in principle have made predictions about unknown elements had they believed deeply enough in the underlying pattern in their periodic system" (p. 89). On the other hand, Mendeleev may also be said to have promoted a 'thingless ontology' which focuses on abstract, rather than concrete, elements, as previously discussed. This can be further supported by examining Mendeleev's negative views about the reality of atoms. A frequently neglected fact about Mendeleev, and one that surprises modern readers, is that he remained steadfastly opposed to the reality of atoms, which some chemists had been willing to embrace since Dalton published his work on the subject in the early 1800s.[6.] Many passages in his writings clearly express this view, including the following two examples,[7]

One may replace the term atomic weight by elementary weight in order to avoid recourse to the atom, which in any case is purely conventional (Mendeleev, 1968, p. 694).

The atomic hypothesis seems to me to be useless, if only because it does not lead to any general law and because it is not assured of a solid basis (ibid, p. 733)."

Mendeleev and Paneth. Even though Mendeleev upheld a view of elements as abstract entities, the prevailing positivist attitude among chemists and physicists of the years that followed resulted in the erosion of such a notion. Nevertheless, the Austrian-born radiochemist Friedrich Paneth redirected the attention of chemists to an accompanying abstract view of elements. While some of his contemporaries, like Kasimir Fajans, were in favor of defining an element entirely through atomic physics, Paneth insisted on the need to retain an abstract, some might say even a metaphysical, conception alongside the more concrete and operational notion. Paneth (2023)'s dual definition was as follows,

1. Element a simple substance (einfacher Stoff), the material form of an element that can be isolated and studied in the laboratory.

2. Element as basic substance (Grundstoff), the abstract principle or kind common to all forms of that element; it persists through chemical change but is never found in pure form.

Once again, one sees the underlying structure of the elements being taken to be equally, if not more, fundamental than their concrete or more realistic aspects. Stated otherwise, Paneth appears to be ascribing realism to the underlying structure of elements and affirming that the metaphysical nature of elements has a role to play in attempts to understand the field of chemistry.

Paneth's return to Mendeleev's dual view of elements has been partly enshrined in the current official definition of the term element, as given in the IUPAC Gold Book (International Union of Pure and Applied Chemistry, 2019). More specifically, following several changes carried out by successive committees of chemists, the IUPAC organization has maintained the spirit of Paneth's desire for a dual definition, although it has become distorted to the point of effectively eradicating any mention of the abstract sense of any element.[8] The current Gold book definition reads as,

1. A species of atoms; all atoms with the same number of protons in the atomic nucleus.

2. A pure chemical substance composed of atoms with the same number of protons in the atomic nucleus. Sometimes this concept is called the elementary substance but mostly the term chemical element is used for both concepts.

4. The periodic system as a real structure

Predictive success. The periodic system provides a structural entity that has proven successful and has not been refuted in spite of many challenges. As Scerri (2012) wrote, the periodic system of the chemical elements offers a good candidate for structural realism in that it is literally, as well as metaphorically, the underlying structure for much of the discipline of chemistry.

Scientific realists of various strands have customarily distinguished between 'working' and 'idle' posits to discriminate between those theoretical constituents that are essential or irrelevant to its success. Votsis (2010) has extended this idea to structural realism, distinguishing between 'operative' and 'inoperative' structures, where the former entail genuine predictive success—and are thus to be regarded realistically—whereas the latter do not. We argue that the periodic system is an 'operative' structure, as demonstrated by Mendeleev's ability to generate a number of novel predictions based on it (Campbell and Pulkkinen, 2020), with the most notable including

1. Unknown chemical elements,
2. Physical properties of unknown elements,
3. Chemical properties of unknown elements.

Although the periodic system proposed by Mendeleev displayed remarkable regularity, certain discontinuities remained. In 1871, Mendeleev proposed that these apparent gaps were to be filled with elements yet to be discovered. To these, he assigned the provisional names of eka-aluminium, eka-boron, and eka-silicon, to reflect their proximity to known elements that were the closest in the periodic system. These predictions received full confirmation within fifteen years. In 1875, Lecoq de Boisbaudran isolated a new element, gallium, whose properties corresponded closely to those of eka-aluminium. In 1879, Lard Fredrik Nilsson identified scandium, corresponding to eka-boron. Finally, in 1886, Clemens Winkler discovered germanium, fulfilling Mendeleev's prediction of eka-silicon.

Mendeleev issued quantitative predictions of the physical properties of these then-unknown elements, such as their atomic weights and volumes, by systematically combining the periodic system with the known values of neighboring elements, which he referred to as 'atom analogs.' According to Mendeleev,

> *The position of an element, R, in the system is determined by the series and the group to which R belongs, and hence by neighbouring elements, X and Y, in the same series, as well as by the two elements in the same group with the next lowest (R') and next highest (R") atomic weights. The properties of R may be determined from the known properties of X, Y, R' and R"* (Mendeleev, 1872, p. 66).

Mendeleev predicted the atomic weights and volumes by linearly interpolating from the corresponding values of neighboring elements. For instance, he estimated the atomic weight of unknown eka-boron by averaging the atomic weights of the known surrounding elements potassium (K = 39), calcium (Ca = 40), titanium (Ti = 48), and vanadium (V = 51). As a result of this approach, he obtained predicted atomic weights of eka-aluminium, eka-boron, and eka-silicon of 68, 44, and 72, respectively. When compared with the currently accepted empirical values of 69.72, 44.96, and 72.63 for gallium, scandium, and germanium, Mendeleev's predictions exhibit an excellent accuracy, within approximately 2%. Using a similar approach, Mendeleev predicted the atomic volumes of eka-aluminium and eka-silicon to be 11.5 and 13, respectively, in striking agreement with the currently accepted values of 11.8 and 13.6 for gallium and germanium. Besides these temporal-novel predictions, Mendeleev issued 'contra-predictions' whereby he corrected the atomic weights of several known elements, including beryllium, uranium, and tellurium.

Further to physical properties, Mendeleev was able to predict the chemical properties of unknown (and little-known) elements—particularly the properties of their oxides. To that end, he introduced an additional row into his system, representing the stoichiometry of the higher saline oxides of known elements for each of the eight groups. For a given element R, the row took the form R_2O, R_2O_2 (or RO), R_2O_3, R_2O_4 (or RO_2), R_2O_5, R_2O_6 (or RO_3), and R_2O_7, where each formula corresponds to one of the eight groups. For instance, for the second period, the sequence reads Na_2O, Mg_2O_2 (or MgO), Al_2O_3, Si_2O_4 (or SiO_2), P_2O_5, S_2O_6 (or SO_3), and Cl_2O_7. By examining these known compounds, Mendeleev identified two patterns. As one moves from left to right across a period (i.e., from R_2O to R_2O_7), both the oxygen content and the acidic character increase. Within a given group, the acidic character decreases with increasing atomic weight.

Through these patterns, Mendeleev predicted the chemical properties of the oxides of eka-elements. For example, he anticipated that eka-boron (Eb) would form a higher saline oxide with chemical formula Eb_2O_3, in line with the chemical formula of gallium oxide, Ga_2O_3. This oxide, he proposed, would exhibit chemical properties intermediate between those of the oxides of the elements preceding and following eka-boron, namely CaO and TiO_2. Furthermore, Mendeleev suggested that the relationship between Eb2O3 and Al_2O_3 would mirror that between the pairs CaO and MgO, as well as TiO_2 and SiO_2. At the same time, Eb_2O_3 would be more basic than Al_2O_3, yet more acidic than MgO.

These illustrations emphasize that the periodic system is an operative structure that, by establishing analogical relations, is key to successful predictions. As Campbell and Pulkkinen (2020) noted, the system supported "interpolating the atomic weights of undiscovered elements by placing analogical elements together" and "predicting the properties of little-known and undiscovered elements by visualising and encoding the analogies between the elements" (p. 214).

Stability across theory change. The periodic system is a relation that has survived many changes in the underlying physical theory that purports to describe its relata (i.e., the chemical elements) and explain it, effectively realizing Worrall (1989)'s claim that "the continuity is one of form or structure, not of content" (p. 117). These changes have included the following, arranged in historical order,

1. At the time of Mendeleev's discovery, there was no explanation,
2. J.J. Thomson's classical theory of electrons ,
3. Bohr's old quantum theory,
4. Non-relativistic modern quantum mechanics,
5. Quantum relativistic explanations for superheavy elements.

It took a period of about forty years before anybody produced an explanation for why the periodic table has the form that it has, or more specifically, why some particular elements, such as lithium, sodium, and potassium, for example, behave in chemically similar ways. Such an explanation was first offered by the discoverer of the electron J.J. Thomson, who suggested that electrons, which were embedded in the main body of the positive atom, were located in a number of concentric rings. By assigning particular numbers of electrons to each ring, Thomson hypothesized that atoms of the elements that shared chemical properties did so because of analogous electron ring arrangements. In providing this explanation, Thomson used arguments entirely arising from classical physics since quantum theory had not yet been applied to the structure of the atom. Thomson had provided a rudimentary form of an explanation that essentially stands to this day, namely that the analogous behavior in the atoms of certain elements lies in their analogous electron arrangements. However, his explanation failed in a significant manner since he claimed that the atoms of elements with 5 electrons would be chemically similar to those having 16 electrons. In modern terms, this amounts to claiming that the element boron would be similar to sulfur, which is incorrect.

Next came the important contribution from Niels Bohr, who began to use the old quantum theory in order to attempt to explain the atomic structure by introducing quantized, semi-classical orbits. According to Bohr, an atom of boron has an electron arrangement, or configuration, of 2,3, meaning two electrons in the first shell and three in the second one. In the case of the element aluminum, which does belong in the same group of the periodic table as boron, Bohr assigned a configuration of 8,2,3. However, Bohr's explanation consisted of a judicious use of semi-empirical arguments rather than an appeal to the first principles of the old quantum theory. In many ways, Bohr was led to his assignment of electron configurations by a consideration of chemical properties and spectral evidence instead of a strict derivation from theory. In the years 1925-26, the modern version of the quantum theory was developed by a number of contributors, including Heisenberg, Schrodinger, and Pauli. It then became possible to specify a more detailed set of electronic configurations and to resolve a number of remaining anomalies arising from Bohr's assignments. The more recent development has been the application of relativistic quantum mechanics, which is required to account for the apparent anomalous behavior of the superheavy elements.

The main point we wish to stress is that the periodic system has not been altered by any of these successive theoretical developments, despite the fact that each of them involved conceptual disruptions in the description of the entities populating it. This emphasizes the resilience of the periodic system, lending support to our claim that it provides an example in favor of structural realism.

Further historical challenges from chemistry. In addition to these discontinuities in the atomic theories, the history of chemistry has posed challenges to the periodic system and the periodic table, including the following,

1. The case of pair reversals,
2. The discovery of the noble gases,
3. The discovery of isotopes,
4. The discovery and accommodation of the rare earth elements,
5. The relativistic effects that occur in the atoms of elements with high atomic weights.

Pair reversals consist of several pairs of elements that would appear in an incorrect order if one adheres strictly to ordering the elements according to their atomic weights. The best-known example is the case of iodine and tellurium. The atomic weight of iodine is less than that of tellurium. However, the chemical properties of the two elements require that the elements should be reversed in the way that they are placed in the periodic table to be consistent with their chemical properties. Iodine is a halogen that should be grouped with the elements fluorine, chlorine, and bromine, while tellurium has many properties in common with the preceding group of the periodic table, which includes oxygen, sulfur, and selenium. To their credit, Mendeleev and other discoverers of the periodic system reversed these elements but also recognized the challenge that this situation posed for the underlying ordering principle. Matters were eventually resolved more than 40 years later when it was discovered that a better ordering principle was provided by the atomic number of each element, rather than its atomic weight. As a consequence of this change, the reversal of iodine and tellurium was placed on a secure foundation, given that tellurium has a lower atomic number (52) than iodine (53).

The first noble gas to be discovered was argon, which had an atomic weight of 40. This posed a problem for the periodic table since there was already an element, namely calcium, which possessed the same value, and it therefore appeared that argon could not be accommodated into the table. Over the course of a few years, a total of four further noble gas elements were discovered, which meant that the periodic table seemed incapable of accommodating a total of five elements, thus leading to something of a crisis in the chemistry and physics community, some of whose members began to think that the periodic table was in danger of being overthrown. However, one of the co-discoverers of these elements, William Ramsay, eventually solved the problem by creating an entirely new column on the table, between the halogens and the alkali metals (Scerri, 2020).

Another major challenge to the very existence of the periodic table occurred in the 1910s when Frederick Soddy and others discovered what appeared to be many new elements, each having a particular atomic weight. As in the previous challenging events already mentioned, some chemists reacted by doubting the validity of the periodic table, given the rapid profusion of what seemed to be new elements that could not be accommodated in the body of the traditional table. But it was also discovered that the more accurate criterion for the identification of any element was given by its atomic number as mentioned above, with the result that the newly discovered species were not in fact new elements but variations or isotopes of those that already existed.

An important challenge that was successfully overcome was the case of the rare earth elements, which for many years seemed to defy all attempts at placing them correctly into the periodic table. The solution came from the recognition that chemical periodicity involves period lengths of varying length and that the rare earth elements required an expansion of the periodic table to encompass periods consisting of 32 elements (Scerri, 2025a).

Yet another challenge to the periodic table comes in the form of relativistic effects, which result in the profound modification of the properties of elements that have high atomic numbers and which require the application of relativistic quantum mechanics in order for their properties to be successfully explained. Briefly put, as the number of electrons in an atom increases, the innermost electrons begin to move at a speed which approaches that of light and therefore need to be considered from the perspective of Einstein's special theory of relativity. These effects were first detected in the superheavy elements of rutherfordium (element 104) and dubnium (element 105). It was discovered that rutherfordium atoms behaved unlike the elements that belong in the same group of the table, but more like plutonium, which falls quite far removed from the position of rutherfordium. Meanwhile, atoms of the element dubnium behaved similarly to atoms of protactinium rather than the elements niobium and tantalum with which it is grouped in the periodic table. The upshot of these and several subsequent studies has been that relativistic effects need to be invoked to explain what at first sight appear to be anomalies and thus further apparent challenges to the robustness of the periodic table.

The simple fact is that the periodic table has withstood all five of these challenges, which leads one to think that it represents a secure underlying structural foundation for chemistry.

5. Structural realism and the periodic table

There are a number of long-standing debates among chemists regarding the optimal arrangement of several elements in the periodic table, which cannot be answered based on currently known science. It should also be stressed that when we speak of optimal arrangement, we are not speaking of the shape of the periodic table or whether it is represented as a spiral, in a clockwise fashion, or in three dimensions. These forms of arrangement are indeed arbitrary and a matter of taste. We are referring to the disputed placement of certain elements such as hydrogen, helium, lanthanum, actinium, lutetium, and lawrencium. We argue that some of these disputes could benefit from a structural realist approach to the periodic system, which places more emphasis on the existence of the underlying structure rather than on the individual elements regarded as simple substances.

For example, the element hydrogen is typically placed in group 1 of the periodic table, where it sits somewhat uncomfortably along with several reactive metals such as sodium, potassium, and rubidium. Meanwhile, some designers of periodic tables place hydrogen among the halogen elements due to its ability to form singly negatively charged ions, its gaseous state under normal conditions, and its occurrence as diatomic molecules. Yet others place hydrogen on its own, floating above the main body of the periodic table in view of its anomalous status.

The element helium is typically placed at the head of the noble gas group of the periodic table in view of its highly unreactive chemical nature, like the other members of the group that include neon, argon, krypton, and xenon. Other authors prefer to locate helium at the head of group 2 of the table in view of its two electrons and the fact that this feature is analogous to the members of group two, all of which possess two outer electrons in their atoms.

																													H	He	2
																													Li	Be	2
																							B	C	N	O	F	Ne	Na	Mg	8
																							Al	Si	P	S	Cl	Ar	K	Ca	8
													Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	18
													Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	18
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	32
Ac	Th	Pa	U	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	119	120	32

Figure 1. Janet's left-step periodic table, showing all period lengths, including the first one, repeating.

One way to solve this issue categorically is to consider the adoption of the left-step periodic table shown in Figure 1, in which the emphasis is very much on the regularity of the periodic table, which, among other things, features the repetition of all period lengths whereas the conventional table is anomalous in not incorporating the repetition of the very first period of two elements (Janet, 1928; Stewart, 2010; Scerri, 2007).

The dispute concerning the placement of the elements lanthanum, actinium, lutetium, and lawrencium appears to remain completely unsettled if chemists restrict themselves to the chemical or physical properties of these elements or even their electronic configurations. A categorical resolution to this question is available if one places more emphasis on the regularity of the entire periodic table in terms of smoothly increasing atomic number ordering, rather than on the individual properties of the four elements in question regarded as simple substances (Scerri, 2021).

If one regards the periodic system in a structural realist manner, one is more likely to believe that there is a fact of the matter about chemical periodicity and that it is not merely a matter of human classification. The classification is rather viewed as resulting from 'Nature being carved at its joints'. Periodic classification is, in fact, frequently regarded as the finest example of a natural system of classification. Nevertheless, many chemists balk at the notion that one optimal system of periodic classification might exist and revert to the view that one can arrange the system in many ways and claim that there is no one 'best system' of classification. We submit that this view is incorrect, if the goal of the periodic table is to reflect the reality of the relations in Nature.

5. Concluding remarks

Potential objections. A possible objection to the claim that structural realism applies to the periodic system might be that the periodic table is merely a compilation of the observable properties of the elements. Structural realism, as it has been discussed in physics, is of course a view concerning theories, while the periodic system is seldom regarded as a theory.[9] Our response to such a rebuttal would be to point out that the periodic system draws on the observed properties of the elements but goes well beyond tabulating and organizing observations of individual elements. Instead, the periodic system expresses the relationship between completely diverse elements in a pattern of regularities.

Another concern may be that the periodic system deals in entities. It should be pointed out that this is not necessarily the case since the periodic system applies equally well to entities on a microscopic level as it does to macroscopic samples of elements. There are therefore no particular entities in question, but perhaps elements in the abstract sense that subsumes all possible entities spanning from the microscopic atoms, to nanoscopic samples, and to macroscopic observable samples of the 'elements.' Indeed, there is a rich and well-developed literature on the nature of elements that needs to be brought to bear on the question being discussed in the present article (Scerri and Ghibaudi, 2020).

Conclusions. In summary, we have presented a comprehensive analysis of the periodic system through the lens of structural realism, examining its implications for the history, philosophy, and practice of chemistry. First, we have shown that Mendeleev can be regarded as an early structural realist, whose commitment to the relations among the atomic weights of the elements —understood in abstract rather than concrete terms—was central to his discovery of the periodic system. This approach promoted a 'thingless ontology' that places stronger emphasis on the pattern of relationships persisting through chemical change. Second, we have argued that the periodic system, and its tabular representation, may be viewed as a vivid manifestation of structural realism in chemistry, insofar it encodes a successful structure, as illustrated by Mendeleev's novel predictions of undiscovered elements and their properties, that has remained preserved across theoretical discontinuities involving the entities populating them, such as atomic and sub-atomic components. Third, we have employed this structural realist priority of structure over entities to adjudicate between competing designs of the periodic table, advocating for the superiority of Janet's left-step periodic table owing to its stronger emphasis on the periodicity.

To conclude, our work not only articulates a structural realist reading of the periodic system but also demonstrates that structural realism can meaningfully engage with chemistry, thereby addressing one of the "most pressing challenges" identified by Votsis and Frigg (2011)— namely, that "structural realism cannot continue ignoring sciences other than physics" (p. 269-270).

Notes

1 This statement represents something of an oversimplification, given that Lavoisier's list of elements also included some principles such as heat and light.

2 A total of 16 elements were discovered between the time of Döbereiner's first recognition of triads of elements (1817) and the discovery of the mature periodic table by Mendeleev in 1869. These elements were lithium, selenium, cadmium, silicon, aluminum, bromine, thorium, lanthanum, terbium, erbium, ruthenium, cesium, rubidium, thallium, indium and helium.

3 The terminology in the contemporary literature is one of element as basic substance (the abstract sense of element) and element as simple substance (the observable and isolable or even

the everyday sense of element). The terms simple and basic are due to the philosopher-historian Heinz Post who translated the work of his father, Fritz Paneth, who used the words ‘grundschtoff’ and ‘einfacherstoff,’ respectively.

[4] The reader should note the difference between observable and measurable in this context. Atomic weight is clearly not observable but can be measured or deduced from some complicated procedures.

[5] Some authors have pointed out this apparent contradiction in Mendeleev’s writings.

[6] This is an oversimplification since there were major disagreements and debates on the question of whether atoms were to be regarded realistically or as useful fictions (Brock and Knight, 1965; Rocke, 1984).

[7] Thyssen (2025) has written an excellent analysis of Mendeleev’s view on atomism in which he argues that Mendeleev was indeed against the literal existence of atoms as entities but that he may have veered towards a realistic view in his later life when confronted with the problem of classifying the rare earth elements.

[8] This is unfortunate, but thankfully, this state of affairs is currently under review within the IUPAC community (Scerri, 2025b).

[9] With the possible exception of Weisberg (2007), who has claimed that the periodic table should be considered as a theory; a critique of this view has been articulated by Scerri (2012b).

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