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Essays

Periodic Table

Challenges for the Periodic Systems of Elements: Chemical, Historical and Mathematical Perspectives

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Dedicated to the memory of José Luis Villaveces

Abstract: We celebrate 150 years of periodic systems that reached their maturity in the 1860s. They began as pedagogical efforts to project corpuses of substances on the similarity and order relationships of the chemical elements. However, these elements are not the canned substances wrongly displayed in many periodic tables, but rather the abstract preserved entities in compound transformations. We celebrate the systems, rather than their tables or ultimate table. The periodic law, we argue, is not an all-encompassing achievement, as it does not apply to every property of all elements and compounds. Periodic systems have been generalised as ordered hypergraphs, which solves the long-lasting question on the mathematical structure of the systems. In this essay, it is shown that these hypergraphs may solve current issues such as order reversals in super-heavy elements and lack of system predictive power. We discuss research in extending the limits of the systems in the super-heavy-atom region and draw attention to other limits: the antimatter region and the limit arising from compounds under extreme conditions. As systems depend on the known chemical substances (chemical space) and such a space grows exponentially, we wonder whether systems still aim at projecting knowledge of compounds on the relationships among the elements. We claim that systems are not based on compounds anymore, rather on 20th century projections of the 1860s systems of elements on systems of atoms. These projections bring about oversimplifications based on entities far from being related to compounds. A linked oversimplification is the myth of vertical group similarity, which raises questions on the approaches to locate new elements in the system. Finally, we propose bringing back chemistry to the systems by exploring similarity and order relationships of elements using the current information of the chemical space. We ponder whether 19th century periodic systems are still there or whether they have faded away, leaving us with an empty 150th celebration.

Prolegomenon

Unveiling numerical trends among either atomic or equivalent weights that somehow preserved resemblances among elements was frequent in the first two thirds of the 19th century.[1] Standing out from the crowd, Meyer and Mendeleev went beyond numerical relationships, certainly motivated by a pedagogical aim. Both were after systems synthesizing the chemical knowledge of their times in an appealing way to be presented to chemistry students.[3,4] Chemical knowledge spans known chemical substances and their properties, which Meyer and Mendeleev sought to relate with chemical elements, these latter as the basic matter constituents at their times. In sections 1 and 2 we discuss the concepts of the chemical elements and of sets of chemical compounds, dubbed chemical spaces, and their relationships with the periodic systems. Section 3 delves into the mathematical structure of the systems and the open questions it may solve. The limits of the systems are analysed in section 4 and the essay concludes with a plea to bring back chemistry to the study of periodic systems.

1. Chemical element

There is no unified concept of chemical element, as seen in the double definition of the IUPAC Gold book, one atomistic and the other at the level of substances:[5] "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 as distinct from the chemical element as defined under (1), but mostly the term chemical element is used for both concepts."[8]

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In celebration of the International Year of the Periodic Table.

1.1 Dualistic stuff

The substance or stuff definition comes from the chemical experience built upon chemical reactions. At this level, element refers to simple substances chemists work with, which give place to basic substances that result by abstraction from chemical operations carried out with simple substances. Simple substances are, for example charcoal, diamond, graphene, graphite, fullerenes, carbon nanotubes and 18-atom cyclocarbon,[9] which turn out to be different allotropic forms of the basic substance carbon. Methane and carbon dioxide are also simple substances of carbon, simultaneously contributing to building up the basic substances hydrogen and oxygen.[10] Meyer and Mendeleev formulated periodic systems of elements as basic substances, taking into account the accumulated knowledge that they had of compounds (simple substances) as bearers of chemical and physical properties.[11] Hence, the systems arose as abstractions of the known chemical compounds in the 1860s.

1.2 Atomistic

The atomistic definition of chemical element arose from research on the inner structure of matter at the turn of the 20th century, which introduced new entities and concepts such as electron, proton, radioactivity, isotopes and others.[6] The boom of atoms of different sorts suggested more boxes on the periodic table to accommodate these particles. The issue was solved in a thoughtful way by recurring to basic substances. The claim was: no matter whether hydrogen has no neutrons, or one or two, the chemistry of hydrogen, as a basic substance, is invariant to the number of neutrons hydrogen atoms have.[13,14] It was thoughtful but problematic as the widespread idea that isotopes have the same chemistry does not always hold.[15] If isotopes of the same element are chemically distinct, do we, after all, need to expand the periodic systems to accommodate the current more than 3,000 isotopes and foresee the room for the 3,000 to 4,000 additional ones that are expected? The answer depends on the level of detail sought after. If we want systems gauging the generality of chemistry, keeping the current boxes, one for each element, suffices. However, if we aim at including particular details of the chemistry of isotopes, we would need much bigger systems. This makes us recall Jorge Luis Borges' story "*Del rigor en la ciencia*" (On rigour in science)[17] in which he analyses how cartographers, eager for more details in their maps, end up with maps of the size of the charted land. How accurate is the chemical map we are after?

The atomistic view of chemical element entails an ontological shift, which historically coincides with a shift from stuffs, for light elements, to atomic species, for heavy elements. By 1869 there were a bit more than ten thousand known substances; a large proportion of which were O-, H-, C- and N-based.[18] This dramatic concentration of compounds based on light elements has not changed with the discovery of heavier elements.[19] Most of the new compounds keep being synthesized in wet-labs at the level of stuffs, the reactivity and physical properties of which are then analysed. However, it is currently impossible to address super-heavy elements at the level of bulk substances, as is typical for lighter elements. Given the difficulty of making long lasting super-heavy isotopes, one-atom-at-a-time chemistry approaches have been devised for which only a limited number of chemical properties can be experimentally investigated.[20] One-atom-at-a-time chemistry requires half-lives of the order of 1–2 s and production rates of at least a few atoms per day.[21] In spite of these difficulties, there has been progress in the chemical characterisation of transactinides, with flerovium ($Z=114$) marking the super-heavy limit of chemistry today.[22]

The ontological shift is evident in the current requirement of detecting "at least a nuclide with an atomic number Z [...] existing for at least 10^{-14} s,"[23] for claiming the discovery of a new element. This minimum lifetime is selected taking into account the time it takes for a nucleus to acquire its outer electrons; which brings up subtle consequences. For example, that periodic systems based on chemical compounds *a la* 1860s are a romantic idea, as forming bonds requires for an atom to have ten thousand times the time it spends completing its valence shell.[24] Thus, there is no room for chemical experiments for these very short-lived atoms and the systems are then left to the theoretical arenas, lacking experimental evidence to test hypothesis.

2. Systems Based upon the Chemical Space

The role of compounds for the 1860s systems is evident, for example, in Mendeleev's idea of a chemical element as an object characterised by the elements it forms compounds with and the proportions of those combinations.[25] He wrote in 1905: "if CO_2 and SO_2 are two gases which closely resemble each other both in their physical and chemical properties, the reason of this must be looked for not in an analogy of sulphur and carbon but in that identity of the type of combination, RX_4, which both oxides assume."[28,29] He concludes: "The elements, which are most chemically analogous, are characterized by the fact of their giving compounds of similar form RX_n."[28] If we call the set of known compounds as the chemical space,

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the question arising is, how can one end up with systems of elements based on such a space?

2.1 Order and similarity

Of capital importance for the periodic systems is that they are actually "systems," as called in the 1860s[32,33] but currently replaced by "periodic tables" (in English), which are representations of the systems.[34] A system is based on relations among its objects.[37] The tenets of Meyer's and Mendeleev's systems were two relations: order and similarity, which came from compounds. Atomic weights resulted from relative measurements among compounds, in fact from determining the smallest common weight of large sets of substances containing the reference element. Besides acidity and alkalinity of oxides and several other properties of compounds, composition was central for Meyer and Mendeleev. From the proportions of combinations of elements into compounds the current "valency" arose, which proved essential to find resemblances among elements.[38]

Today, emphasis is frequently on one of the two relations, thereby misrepresenting the periodic systems as either classifications or as orderings. However, they are not classifications, as Mendeleev originally understood them[41] and as stated in references [36,43–46]. Nor are they an ordered set of elements, as claimed in references [21,43,47,48], let alone an ordering leading to a classification[49,50] or the other way round.[51,52] If they were a mere classification, one could produce periodic tables with alkali metals lying in between chalcogens and halogens, for example (Figure 1 A). If they were an ordering, instead of tables displayed at chemistry classrooms and labs, there would be fancy strings of elements, from hydrogen to oganesson (Figure 1 B) hanging at those chemistry places. So, what are the periodic systems of chemical elements? They are neither a classification, nor an ordering of elements, they are both! They are the interweaving of order and similarity relationships of the chemical elements (Figure 1 C). We have recently shown that such a structure corresponds to an ordered hypergraph (Figure 1 D),[54,55] which can be used to define periodic systems of elements, a lack of definition highlighted by Karol.[56] A periodic system of chemical elements results from ordering and classifying chemical elements by some of their properties.[57]

The atomic discoveries of the early 20th century overhauled atomic weight as the ordering principle in favour of atomic number. A similar fate underwent similarity, now based on electronic properties of atoms.[6] A connection was found, a mapping, between families of similar elements and the similarity of electronic configurations of the valence electrons.[64] Even if the mapping did not preserve the structure of the system based on compound information,[66] it was considered more fundamental, following the physicalistic philosophy of science still in vogue in the 20th century. This facilitated the oversimplification of chemical resemblance to similarity of electronic configurations. Traditionally, electronic configurations refer to isolated atoms in their ground state energy levels.[69] However, atoms in such states have little to do with chemistry, for the interesting chemical atoms are bonded.[6,69] As Pyykkö clearly states: "The chemical behaviour of the elements […] is mostly driven by the orbitals, occupied in the atomic ground state […]. Sometimes also other orbitals, which are unoccupied in the atomic ground state but energetically accessible for bond formation, can participate. […] The atomic ground state does not always explain the molecular outcome."[69] There is no problem in relying on electronic configurations, the problem is relying on the wrong ones.

Changing similarity criteria brought up another misinterpretation, which is now part of the chemistry folklore: vertical similarities. The fact is that there is no one-to-one relationship between groups of elements (columns in the conventional periodic table) and families of similar elements, not even at the level of electronic configurations.[69] That is, having a column of the table does not always imply that the elements of the column are similar. Likewise, taking similar elements does not always lead to a column of the table. The heuristic works well at the extremes of the table, that is, for alkali metals, noble gases and halogens. However, it is not generally applicable to the other columns.

Surprisingly, from the very beginning (1869) Mendeleev showed that "in certain parts of the system the similarity between members of the horizontal rows will have to be considered, but in other parts, the similarity between members of the vertical columns."[70] Further examples of non vertical similarities are the ferrous metals, the lanthanoids, the resemblances of heavier *p*-block elements with transition metals,[71] of actinoids with transition metals,[21] not to mention those of super-heavy elements with transition metals,[21] the diagonal relationships,[72] those of hydrogen and halogens in crystal structures[73] and the so-called secondary periodicities.[69] Not only similarities go beyond verticality, also some elements vertically related are dissimilar! For example, second period elements are different from the members of their columns,[74] flerovium does not resemble lead (both in group 14),[75] oganesson is not akin to noble gases,[22,75,76] copernicium does not resemble group 12 elements, dubnium is not alike to group 5 elements.[79] To make matters worse, lack of vertical similarities is foreseen for elements beyond $Z=120$.[79]

Verticality, taken for granted, has led to compare properties of superheavy elements with those of their vertical congeners.[21,80] The question is, are we really comparing homologues or just chalk and cheese? Moreover, reliance on verticality has led to believe that if one knows the position of an element in a periodic system, estimating properties of the element is straightforward.[43] Although there are historical reasons to rely on the position of the elements to make estimations, as evident by Mendeleev's successful predictions; there is still a lot to do in determining the rational grounds Mendeleev used to map his structure to the properties of unknown elements.[82] At any rate, he did not consider only verticality or only horizontality.[39,83]

To conclude this section and the topic of misinterpretations, we briefly mention the confusion between periodic system, periodic table and periodic law, which although related concepts, they are different.[10] As stated, a system is the structure based

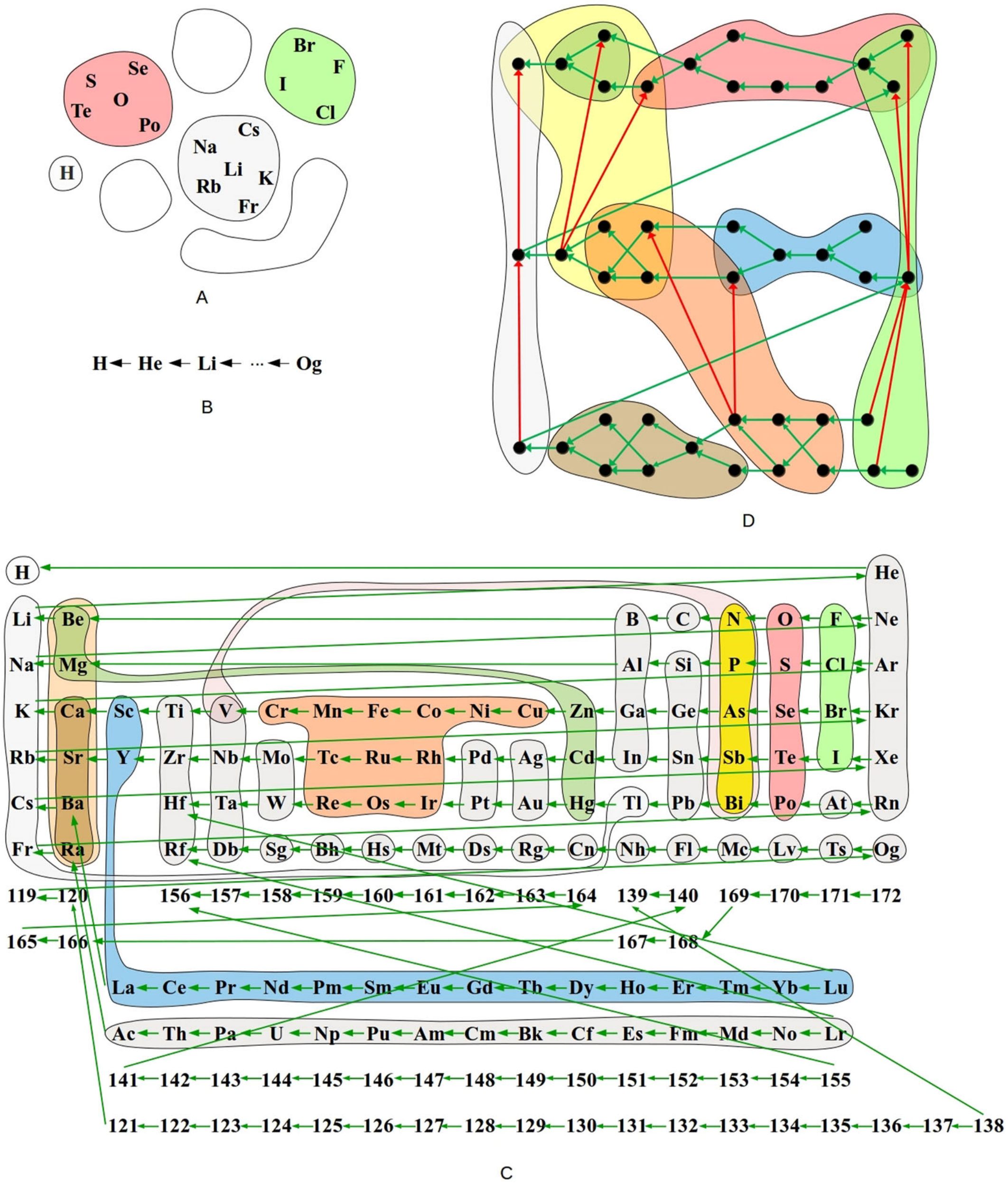

Figure 1. Systems of elements. A) System where only similarity is regarded. This corresponds to any disposition or reshuffling of classes of similar elements. Here the position of the classes is irrelevant, as well as the internal position of similar elements, that is, elements within a class.[58] B) System based only on an order relation of its elements. The selected property to order is atomic number Z and $x \leftarrow y$ indicates that $Z(x) \leq Z(y)$. The lack of similarity is the cause of not obtaining the traditional classes of elements, for example, alkali metals, halogens, etc. C) System based, simultaneously, on similarity and ordering. Here elements are not only encapsulated in their similarity classes as in A, nor are they forming the ordered string as in B, they rather form a structure, where elements within classes are ordered, therefore classes too. Ordering relationships come from reference [61], where order reversals are evident by the crossing arrows. Similarity classes of this plot come from several studies discussed in the current paper. Note that for elements with $Z > 118$, atomic numbers label elements rather than the three-letter symbol used for non synthesized elements. D) General system as an ordered hypergraph, where chemical elements are abstracted to objects holding similarities, represented as subsets of objects; and order relationships are indicated by arrows. Green arrows correspond to the order between objects and red arrows to the order for objects of different classes. Red arrows are obtained from green arrows.[62]

on order and similarity, a periodic table is any representation of such a structure and the periodic law was an overstatement, mainly championed by Mendeleev.[84,85] The periodic law, as defined by Mendeleev in 1875, states that "the properties of simple substances, the constitution of their combinations, as well as the properties of the latter, are periodic functions of the atomic weights of the elements."[86,87] It is an overstatement for two reasons. i) Not every property of the elements is periodic, not even a regular oscillating function of the atomic weight (or of the atomic number, in modern terms);[10] counter-examples include aggregation state at room temperature, colour, various conductivities and several others. ii) The domain of the periodic function is the set of basic substances, but actually most properties require a domain of simple substances.[10] What is the density of carbon? When we say it is 2.267 g cm^{-3}, we mean carbon's simple substance graphite. Other allotropes have different values.[90]

3. The Structure of Periodic Systems

Following Gordin, when pondering over the nature of periodic systems, we claim it is the "abstract idea of a system;"[3] originally attached to substances known in the 1860s. Once formulated, several scientists dwelt on its underlying mathematics. For example, Mendeleev and others sought for algebraic expressions encoding the essence of the systems. Discouraged, Mendeleev realised that the mathematics of his time was not ready to cope with the complexity of the systems.[91] He claimed in 1899: "In my opinion, the reason one has so far been unable to represent the law using an analytical function is because the law relates to a field too little explored to allow for mathematical elaboration. The reason for the absence of any explanation concerning the nature of the periodic law resides entirely in the fact that not a single rigorous, abstract expression of the law has been discovered."[93] In particular, Mendeleev found it troublesome to treat chemical properties mathematically. "Science does not as yet possess the means by which these properties can be measured, but they are still counted among the qualitative characteristics which distinguish the elements,"[39] he claimed in 1871. Today, some of the suitable mathematics to model these properties are part of (hyper)graph and order theories and, more generally, category theory. These are some of the mathematical branches handling relations, which is what chemical properties are.[26,94,95]

The ordered hypergraph structure we found for periodic systems is made of a set of objects, a classification of the objects, and an order relation that may come from more than one property of the objects.[54] When objects correspond to chemical elements, the order relation is given by their atomic weight (currently by atomic number) and the classification comes from chemical similarity; a periodic system of chemical elements results. However, there is no reason to rely on a single property to order the elements, one could use more than one, for example, atomic number and electronegativity or any other set of properties. The classification could also come from other criteria, not necessarily chemical resemblance. In this sense, tailored periodic systems can be devised and it is here that questions of adequate periodic tables for each purpose may have sense. That is, when the properties to order and to classify the elements are explicitly stated following a particular end. What do periodic systems (and their associated tables) look like for geochemical properties? How are they for organometallic properties?[96]

The ordered hypergraph structure is general enough to allow also changing objects, that is, it is not only restricted to chemical elements. The hypergraph structure is therefore the most general structure encompassing all possible periodic systems, not only of chemical objects, but of any other nature, even outside the chemistry realm.[54] One could even envision periodic systems in other disciplines, where the only requirement is to have orderable and classifiable objects. Time will tell about the use of these systems to better understand and estimate the objects of the systems and their properties, as well as their pedagogical reaches.

3.1 Problems the structure may solve

3.1.1 Order reversals in super-heavy elements

Besides the irregular presence of vertical similarities, especially for super-heavy elements;[79] order, the other tenet of the systems, also faces problems. When the periodic systems were originally formulated, elements were ordered by atomic weight and distributed on the table to make similarities evident. In such an arrangement there are famous order reversals to avoid blurring resemblances among elements as occurred with tellurium and iodine.[98] The issue of reversals was solved once atomic number took over as ordering criterion. However, order reversals are back. Pyykkö's relativistic quantum chemical calculations indicate that the systems may be extended up to 172 elements, which when ordered by atomic number and trying to maximise the resemblance of electronic configurations, include reversals (Figure 1 C), such as elements with $Z=$ 156 to 164 being located in period eight before elements with $Z=139$ and 140, which are followed by elements with $Z=169$ to 172. More jarring is that elements with $Z=165$ to 168 are part of the ninth period.[61]

Pyykkö's approach starts by relying on the order by atomic number and on similarities of electronic configurations. In such a setting, elements having similar electronic configurations are brought together without hurting the order (following a similar balance of similarity and order as the one of Meyer and Mendeleev). However, the approach departs from this balance when applied to heavy elements, where similarity of electronic configurations receives more importance. Trying to accommodate elements with similar configurations hurts the order. Had Pyykkö followed the other approach, that is, giving more relevance to order, then he would have ended up with a system without order reversals, but with a much more awkward panorama of similarities, where similar elements (normally neighbours on the table) would appear far apart. As Kean asks: "where should anomalous elements go? In the column where their atomic numbers say they should go or in a column with elements of similar properties?"[75] In other words, should we follow either the order or the similarity to place elements in the systems? We have argued that order and similarity hold equal importance and one should not give preference to one over the other. If vertical resemblance is not the rule and if the order by atomic number does not match the estimations of resemblance; has the time not come to reconsider the way of assessing resemblance and of overhauling atomic number as the order criterion? Note that modifications of the ordering or similarity criteria do not affect the underlying structure of the systems. It remains as the interweaving of order and similarity.[100]

3.1.2 Ultimate periodic table

Another issue is whether there is a definitive periodic table of chemical elements able to encompass the whole richness of chemistry. The structure shows that as long as the properties used for ordering the elements and those for classifying them are set up, one has a system. Hence, at the level of possible structures there are many, depending on the properties used to order and classify the elements. The several possibilities for classifying and ordering bring up different periodic systems[101] and their relationships form a super structure.[54] All possible periodic systems lie in that super structure and their relationships are worth exploring.[54] Now comes the question of the possible periodic tables. For a given structure all possible mappings or projections of the structure turn out to be periodic tables. So, there is no definitive periodic table, what is definitive is the super structure containing all possible periodic systems.

Thus, the claim that there must exist a definitive periodic table[97,102] is too narrow-minded.[103] We recently spoke about the periodic system as a sculpture, where each of its shadows is a periodic table.[105] It is difficult to have an idea of the sculpture just with one of its shadows. This is like staring at the wall in Plato's allegory of the cave. We actually think that chemists, unconsciously, in their daily work, use different periodic systems, tailored to their needs. That is perhaps the reason why we have had about 150 years to celebrate. We are not celebrating a singular periodic table,[106,107] rather we are celebrating the achievement of an underlying structure full of chemical relations. We actually celebrate an attempt to systematise chemical knowledge and to bring it down to the level of chemical elements. Perhaps more interesting than the question on the system of elements is how it is related to other chemical systems, for example of families of compounds, of quasi-molecular species, to name but a few. Can we better understand the complexities of chemistry by exploring those relationships? Can we predict something for chemistry, out of it? Can we complete the book of chemistry Meyer and Mendeleev started to sketch in the 1860s?

3.1.3 Relations between and among the groups

Much of the research on periodic systems has dealt with binary comparisons of elements and in some rare cases of sets of elements. A typical statement is "fluorine is more electronegative than bromine," but troubles pop up when comparing halogens with other sets of elements. This enters the realm of comparing sets. A chemical question of this sort is: are chalcogens more reactive than pnitcogens regarding ferrous metals? Alike questions were sketched out by Mendeleev,[108] but little research in that direction has been carried out. A possible reason is the underlying binary way of thinking in which we have grown up. We normally make an idea of something by binary assessments. A house is close to the other, that other to the next one, etc. In such a manner we build up an idea of our neighbourhood. Would it not be interesting to know the combined effect of having, simultaneously, halogens, chalcogens and lanthanoids in a particular new material? Shall we always look at the relationships between halogens and chalcogens, on the one hand; chalcogens and lanthanoids, on the other, and finally at those between lanthanoids and halogens? Is that a complete picture? Contemporary mathematics is equipped with hypergraphs and simplices, which are formal devices to treat *n*-ary relations, which are the relations we are referring to.[110] An initial step in that direction was using the hypergraph structure of the systems to address order relationships among classes of similar single-covalent bonds.[54]

3.1.4 Bringing back predictions

Mendeleev's successful predictions of elements using the structure of the systems required interpolations,[112] which are not any longer possible, as the unknowns of the systems lie at its super-heavy edge. Nevertheless, the structure can still be used as a predictive tool. Klein and co-workers[114–116] devised algorithms based on ordered structures to estimate properties of the ordered objects. Some examples of these structures are the partially ordered sets of molecules related by the suitability of one to be obtained by H-substitution of the other. These structures have been used to foresee physico-chemical properties of the associated substances to the ordered molecules. Methods of this sort can be framed in the general setting of ordered hypergraphs and suitably applied to estimating properties of classes of similar objects or of individual ones.

Another instance of the relevance of the structure as a predictive tool is its recent use in the estimation of enthalpies of formation of several compounds using neural networks and the order structure of the systems.[117] Likewise, machine learning methods can be used to estimate properties and there are already results where learning is defined and developed based upon ordered hypergraphs.[118] The mathematics of ordered hypergraphs is rather new, its future developments may bring up more predictive tools for chemistry. We envision this as a fruitful field of research with implications for the periodic systems.

Another sort of prediction was posed by Philip Ball, who asked us "if there is some sense in which it could be useful to "reverse-engineer" a particular graphical representation of the periodic table into its hypergraph form so that we might more clearly see which relationships it includes and which it ignores."[119] Our reply, including Wilmer Leal's thoughts (as co-author of the paper on the structure of the systems[54]), was that it is actually possible. By taking on the one hand a periodic table and, on the other a collection of several properties of the elements, the "reverse-engineering" boils down to know which properties produce the order and which others the similarity classes of the table, therefore of its underlying system. To know the properties leading to the order one must find which properties of the elements correlate with the order of the system and several approaches from order theory may be applied.[120] To detect the properties producing the observed similarity classes, several methods from machine learning can be used.

Thus, time has come to use the periodic systems of elements not only as a mnemotechnic of some well-behaved (oscillating) properties, but as predictive mathematical devices fed by chemical experimental information. The real challenge in terms of predictions is finding the right mappings from the systems to the whole empirical facts of chemistry. Each particular property requires the mapping connecting the property to the structure of the system. Thence, periodic systems may remain as an introductory chart to the chemical garden of the chemical space. The predictive power of the systems, masterfully explored by Mendeleev, is full of opportunities for chemistry and mathematics.

4. Limits of the Periodic Systems

The current understanding of the systems makes one wonders about their limits, which is normally considered in singular and makes reference to the region of super-heavy elements. There, scientists struggle to create/detect and incorporate transient elements to the systems. By definition, these elements must hold a measured atomic number,[23] that is, their atoms must have a whole number of protons. However, there is another extreme, namely before hydrogen.[121] Note that we do not mean the continuous and infinite possibilities between one proton (hydrogen) and zero protons.[123] We mean the discrete, but still theoretically infinite region lying before $Z=0$, the antimatter part of the systems made of anti-elements, which on an atomistic level requires anti-atoms with a whole number of anti-protons. At a substance level, anti-elements require, at least theoretically, a chemical space of anti-chemical compounds. Currently we only know two elements of this antipodes of the systems: anti-hydrogen[124] and anti-helium.[125] Hopefully, more anti-elements and, for the first time, their compounds, will feed the systems. The question that arises is whether the current systems based on the matter part of the chemical space may be used to know something about their antipodes. Perhaps, in the same way that Newton extended Pascal's triangle backwards and found expressions for negative values (and even fractions) of n in binomial expressions $(a+b)^n$,[126] the structure of the systems could be used to extend the systems to their antimatter region backwards. A third limit can be added, namely the one determined by the conditions attached to the chemical space to build up the systems. Most of the available chemical space has been explored at ambient conditions of temperature and pressure. Although there are indications that some properties of elements, like atomic volumes, abandon periodicity under extreme high pressures, for example, terapascals,[127] further research on the behaviour of compounds at these conditions is needed. Oganov, for instance, has shown that NaCl gives place to unconventional stoichiometries such as Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$ and $NaCl_7$ at high pressures.[128] Which compounds populate the chemical space at extreme conditions? We wonder whether we still have periodic systems as we know them at extreme conditions.

5. Can Periodic Systems Come Back to Chemistry?

The extension of the systems to super-heavy elements and its experimental and theoretical frameworks have brought up controversies among chemists and physicists about the disciplinary boundaries of the systems.[129] Are periodic systems devices originally formulated by chemists but currently the toy of physicists with little room for chemistry? How to chemically handle new elements not lasting long enough to form compounds? What we claim is that although it is true that the extensions of the systems are beyond the chemical domain, the region where compounds abound, or where they can be synthesized with our current technical possibilities, is still uncharted land with possible surprises for the stability of the periodic systems.

Periodic systems condense the knowledge of compounds in the 1860s, that is, an available chemical space of about 12 thousand substances involving 60 elements. By using Mendeleev's approach to chemical similarity based on the resemblance of compositions and by using the atomic weight as ordering criterion, we found the periodic system allowed by such space, which matches, to a large extent, Meyer's and Mendeleev's systems.[18]

But the number of new substances has grown exponentially, in fact about every 16 years chemists double their reported substances.[19] In such a rapidly expanding space, do we still have remains of the periodic systems of the 1860s or something stable after adding new elements and millions of new substances?

Once, Roald Hoffmann said to us that "While crank and outsider science focuses on proving relativity theory, second law of thermodynamics, and quantum mechanics wrong, when it comes to the same all too human proclivities relative to the periodic table, no one in my experience tries to prove it wrong, they just want to find some underlying reason why it is right."[130] We claim that the current chemical space becomes indispensable to test whether the systems are wrong/right. Some years ago we took a small sample of the available space (4700 binary compounds) and found the 1860s systems in good shape.[67] In a most recent study analysing the chemical space by 1869, we found a system displaying most of the similarities reported by Meyer and Mendeleev.[18] The chemical space turned out to be strongly concentrated on compounds of organogenic elements. This organogenic bias made that Meyer's and Mendeleev's systems were very likely obtained even with partial knowledge of the 1869 space. We currently conduct a study of the systems by considering the more than 20 million chemical substances reported all over the history of chemistry. Should that result in totally different systems, would it be the end of the romantic systems and tables hanging in millions of chemistry classrooms? Would it show that chemistry needs a new icon? Should it be something similar to the 1860s system, this could correspond to the "law" Mendeleev was after. Not an algebraic expression, but an invariance of the structure through the evolution of the chemical space. It is not, after all, any "law" an invariant of the field explored? Further tests of the systems involve, for example, to pinpoint the conditions of the space at which the known systems fade away. We wonder what the shape of the system would be if chemistry evolution change drastically its conservative way of extending the chemical space.[19]

Whatever the result of considering the current size of the chemical space is, periodic systems, either historically stable or unstable, are the sought depiction of chemistry, the map including all gathered chemical knowledge over the history of chemistry. Such a map must be explored and analysed on a regular basis to keep track of the expansion of the chemical space.

What we suggest is coming back to chemical information of compounds to devise periodic systems at different levels, for example using all the explored chemical space to come up with the most chemically general periodic system of elements. Or using particular compounds or regions of the chemical space to assess their effect upon the system. This return to compounds has also implications in teaching.[131] We have indeed claimed elsewhere that introducing the systems through the chemical space has advantages over the current atomistic approach based on electronic configurations of atoms in the ground state of energy.[131] The suggested compound approach requires curating and storing the chemical space on a regular basis by scanning all publications where scientists report new substances. This is currently done by Reaxys and SciFinder, for instance.[132] Moreover, the approach to the system through the space requires data analysis techniques to extract knowledge. Likely, chemical databases will include the possibility of running data analysis studies on the cloud in such a way that clicking on "give me the current system of elements" button, one can retrieve the shape of the system with the available chemical knowledge.[134]

In the meantime, a more realistic approach to the systems based on compounds is through random samples of the space, easy to handle in personal computers.[136] Another option is to run studies with enough computational facilities, able to store the whole chemical space at a given time and to process its information. This approach is currently followed in our research group, whose initial results show the evolution of the growth of the chemical space since 1800 up to date.[19] A third option is through classification of compounds in such a manner that one can select representative compounds of the classes to run similarity studies. This approach requires further research on the chemical space and on its mathematics.

All in all, Mendeleev's 1889 statement fits perfectly well with the current status of the system: the periodic system "appears as an instrument of thought which has not yet been compelled to undergo modification. But it needs not only new applications, but also improvements, further development, and plenty of fresh energy."[138]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: chemical space · mathematics · periodic system · periodic table · structure

[1] Döbereiner is famous for his triads. Some others were Graham, Gmelin, Gibbs, Pettenkofer, Gladstone, Lenssen, Dumas, Béguyer de Chancourtois, Newlands, Williamson, Meyer, Odling, Hinrichs and Mendeleev. In this regard Bensaude-Vincent claims that "the atomic weight had often been a pretext for pythagorean speculations on the primary matter."[2]
[2] B. Bensaude-Vincent, *Br. J. Hist. Sci.* **1986**, *19*, 3–17.
[3] M. D. Gordin in *Nature Engaged: Science in Practice from the Renaissance to the Present* (Ed.: M. Biagioli), Palgrave Macmillan US, New York, **2012**, Chapter 3, pp. 59–82.
[4] Note that we say "periodic systems," in plural and it will be explained in detail in the coming sections. Here it suffices to say that Meyer and Mendeleev produced more than one periodic system. Although both used the same criteria to address similarity among elements and to arrange them, the two chemists produced slightly different arrangements of elements and considered different similarities. Moreover, they considered different number of elements in their systems.
[5] Ontological details of those definitions are found in references [6,7]. Chemical elements are the subject of a forthcoming book on philosophy of chemistry edited by Elena Ghibaudi and Eric Scerri.
[6] G. Restrepo in *What Is a Chemical Element? A Collection of Essays by Chemists, Philosophers, Historians, and Educators* (Eds.: E. Scerri, E. Ghibaudi), Oxford University Press, New York, **2019** (forthcoming).
[7] G. Restrepo, R. Harré, *HYLE Int. J. Phil. Chem.* **2015**, *21*, 19–38.
[8] IUPAC Gold Book. https://goldbook.iupac.org/html/C/C01022.html (Accessed June 6th **2019**).
[9] K. Kaiser, L. M. Scriven, F. Schulz, P. Gawel, L. Gross, H. L. Anderson, *Science* **2019**, *365*, 1299–1301.
[10] G. Restrepo in *Mendeleev to Oganesson: A Multidisciplinary Perspective on the Periodic Table* (Eds.: E. Scerri, G. Restrepo), Oxford University Press, New York, **2018**, Chapter 4, pp. 80–103.
[11] However, Meyer in his "*Curve der Atomvolumina*," included in his 1870 paper on the system,[12] selected simple substances of the elements to measure their volumes. For example, he considered diamond and graphite as simple substances for carbon.
[12] L. Meyer, *Ann. Chem. Pharm. Supplementband* **1870**, *VII*, 354–364.
[13] The chemical equivalence of isotopes of the same element was championed by Georg Hevesy and Friedrich Paneth from electrochemical experiments of lead isotopes.[14]
[14] B. F. Thornton, S. C. Burdette, *Nat. Chem.* **2013**, *5*, 979–981.
[15] Harold Urey, right after the discovery of deuterium, showed that it behaves chemically different from protium.[14] Urey also showed variations in equilibrium properties of exchange reactions involving O^{16} and O^{18}. Further variations for other elements were analysed by Urey as well.[16]
[16] H. C. Urey, *J. Chem. Soc.* **1947**, 562–581.
[17] J. L. Borges, *El hacedor*, Emecé, Buenos Aires, **1960**.
[18] W. Leal, E. J. Llanos, P. F. Stadler, J. Jost, G. Restrepo, *ChemRxiv* **2019**, https://doi.org/10.26434/chemrxiv.9698888.v1.
[19] E. J. Llanos, W. Leal, D. H. Luu, J. Jost, P. F. Stadler, G. Restrepo, *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 12660–12665.
[20] These are, for example, formation and behaviour of complexes in aqueous solutions and their interaction with a second phase, mainly with organic complexing solutions or with ion-exchange resins.[21]
[21] M. Schädel, *Angew. Chem. Int. Ed.* **2006**, *45*, 368–401; *Angew. Chem.* **2006**, *118*, 378–414.
[22] W. Nazarewicz, *Nat. Phys.* **2018**, *14*, 537–541.
[23] A. H. Wapstra, *Pure Appl. Chem.* **1991**, *63*, 879–886.
[24] Data taken from Eugen Schwarz's presentation at the International Society for the Philosophy of Chemistry, held in Bristol in **2018**.

[25] Although a chemical element defined in terms of chemical elements sounds circular, Schummer shows that the apparent circularity actually underlies a network of chemical relations.[26] Formally, a chemical element is better described in terms of category theory,[27] where objects are not determined by their inherent properties but rather by the relations objects establish among them.
[26] J. Schummer, *HYLE Int. J. Phil. Chem.* **1998**, *4*, 129–162.
[27] A. Bernal, E. Llanos, W. Leal, G. Restrepo in *Advances in Mathematical Chemistry and Applications* (Eds.: S. C. Basak, G. Restrepo, J. L. Villaveces), Bentham-Elsevier, Sharjah, **2015**, Chapter 2, pp. 24–54.
[28] D. Mendeleev in *Mendeleev on the Periodic Law: Selected Writings, 1869–1905* (Ed.: W. B. Jensen), Dover, New York, **2002**; Paper 13, pp. 253–314.
[29] It may be confusing finding that Mendeleev associates CO_2 and SO_2 to RX_4. For Mendeleev, X stands for a univalent element,[28] therefore each oxygen in CO_2 and SO_2 replaces two univalent elements; thus, two oxygens replace four univalent elements. In Mendeleev's non-chemistry writings of 1877 and 1905 one sees that his notion of *individual* is very similar to that of *element*. For him an individual was determined by his/her relations with the others.[30] As Gordin claimed in reference [31], p. 161, for Mendeleev "the state was not composed of the people, but that it created them.".
[30] M. D. Gordin in *Mendeleev to Oganesson: A Multidisciplinary Perspective on the Periodic Table* (Eds.: E. Scerri, G. Restrepo), Oxford University Press, New York, **2018**, Chapter 14, pp. 266–278.
[31] M. D. Gordin, *A Well-Ordered Thing*, Basic Books, New York, **2004**.
[32] For example, Meyer talked about "*System der Elemente*"[33] and Mendeleev referred to a "*system of elements*" (translation from Russian), as seen in reference [31], p. 28. See also reference [41].
[33] K. Seubert, *Z. Anorg. Chem.* **1895**, *9*, 334–338.
[34] This "replacement" is yet not a worldwide trend, which is presumably related to national disciplinary traditions and other cultural factors. For example, the fading away of "periodic system" and the surge of "periodic table" is evident in the Ngrams of Google,[35] as we found that the system was popular before 1920 and that the table became the preponderant term ever since. However, in German, "*Periodensystem*," considering all its declinations, has been the most popular term since mid 1920s. Interestingly, "*Periodentabelle*" or "*Periodentafel*" have never caught on. Likewise, in Russian "Periodic system" has been more popular than "Periodic table." These results, nonetheless, are to be taken with caution, for they depend on the various corpuses in different languages Google uses, which may be biased. Similar conclusions are drawn in reference [36] for the languages here discussed, plus Danish and Dutch.
[35] Ngram viewer. https://books.google.com/ngrams (Accessed June 6th **2019**).
[36] J. Reedijk, N. Tarasova, *Chem. Int.* **2019**, *41*, 2–5.
[37] L. Bertalanffy, *General System Theory*, George Braziller, New York, **1968**.
[38] Yet, Mendeleev remained hostile to the concept of valency for most of his life. Valency was attached to the atomic concept, which Mendeleev rejected as a physical entity constituting matter (see reference [3]). Nevertheless, elemental composition and proportions of combination led to valency, which was further used by him, as noted in the labelling of some of the families of similar compounds using R^xO^y and R^uH^v.[39] Likewise, Meyer used valency as the label of his groups.[40]
[39] D. Mendeleev in *Mendeleev on the Periodic Law: Selected Writings, 1869–1905* (Ed.: W. B. Jensen), Dover, New York, **2002**, Paper 3, pp. 38–109.
[40] L. Meyer, *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik*, Verlag von Maruschke & Berendt, Breslau, **1864**, pp. 137–138.
[41] Mendeleev's first publication on the systems was a printed sheet of a preliminary table, with the title translated from Russian being "*Attempt at a system of elements, based on their atomic weights and chemical affinity*" (Gordin's translation[42]). Aiming at reaching European chemists, he translated it into French making a mistake with the indefinite article he used for "system."[42] Gordin claims that the error comes from Mendeleev's desire to have a classification of elements, rather than a system.[42] The hypothesis of an initial classification fits with Mendeleev's aim of grouping together elements to complete the second volume of his *Principles of Chemistry* textbook. The first volume had covered hydrogen, carbon, oxygen, and nitrogen, as well as the halogen family.[3]
[42] M. D. Gordin, *Ab Imperio* **2013**, *3*, 53–82.
[43] M. D. Gordin, *Science* **2019**, *363*, 471–473.
[44] Cambridge dictionary. http://dictionary.cambridge.org/dictionary/english/periodic-table. (Accessed September 11th **2017**).
[45] E. Scerri, *Nat. Chem.* **2009**, *1*, 679–680.
[46] E. Scerri in *Handbook of the Philosophy of Science* (Eds.: R. F. Hendry, P. Needham, A. I. Woody), Elsevier, Oxford, **2012**, Volume 6: Philosophy of chemistry, Part 4, pp. 329–338.
[47] U. Neubauer, *Neue Zürcher Zeitung*, **2019**. https://www.nzz.ch/wissenschaft/periodensystem-der-elemente-150-jahre-ordnung-im-reich-der-chemie-ld.1456162 (Accessed June 6th **2019**).
[48] Wikipedia. https://en.wikipedia.org/wiki/Periodic table. (Accessed September 11th **2017**).
[49] Encyclopaedia Britannica. https://www.britannica.com/science/periodic-table-of-the-elements. (Accessed September 11th **2017**).
[50] E. Scerri, *A Tale of Seven Elements*, Oxford University Press, New York, **2013**, p. 2.
[51] N. W. Ashcroft, *Angew. Chem. Int. Ed.* **2017**, *56*, 10224–10227; *Angew. Chem.* **2017**, *129*, 10358–10361.
[52] An exception to the emphasis either on order or similarity is the definition of periodic table by the Oxford Dictionary: "A table of the chemical elements arranged in order of atomic number, usually in rows, so that elements with similar atomic structure (and hence similar chemical properties) appear in vertical columns."[53] Despite the balance of this definition, we criticise its reliance on atomic structure as the source of similarity. We further elaborate on this point in the coming sections.
[53] Oxford dictionary. https://en.oxforddictionaries.com/definition/periodic_table. (Accessed September 11th **2017**).
[54] W. Leal, G. Restrepo, *Proc. R. Soc. A* **2019**, *475*, 20180581.
[55] A hypergraph is a collection of subsets of objects (or vertices in the graph theoretical jargon). Each subset is called a hyperedge. Hence, Figure 1 A is a hypergraph, where chalcogens, alkali metals, halogens and the other indicated subsets are hyperedges. An ordered hypergraph is a hypergraph whose objects hold an order relationship. This is the case of Figure 1 D, where arrows indicate order relationships.
[56] P. J. Karol in *Mendeleev to Oganesson: A Multidisciplinary Perspective on the Periodic Table* (Eds.: E. Scerri, G. Restrepo), Oxford University Press, New York, **2018**, Chapter 1, pp. 8–42.
[57] Looking for optimal representations preserving the order and maximizing the nearness of similar elements is worth mathematically exploring. Here, force fields approaches could be applied to similarity and order relationships. In this setting, every couple of related elements is modelled as a spring. Optimal representations of the system correspond to configurations of minimal energy of collections of springs.
[58] Similarity is a tolerant relation (reflexive and symmetric),[59] therefore similarity classes can be modelled as graphs, with any pair of similar elements becoming an edge (this makes that each edge can be regarded as a spring according to reference [57]). Although similarity is not a transitive relation,[59] similarity classes are customarily regarded as holding transitivity.[60] Therefore, similarity classes are treated as equivalence classes, which can be modelled as complete graphs. As we showed in reference [18], by assessing similarity between elements through chemical compounds, similarity turns out to be a non-symmetric relation. For example, Li holds certain similarity regarding Na, but this does not imply that Na holds the same similarity for Li. In this case a directed graph model for the similarities can be applied. Here the springs of reference [57] need to account for the direction of the relation.
[59] J. A. Schreider, *Equality, Resemblance and Order*; Mir publishers, Moscow, **1975**, p. 6.
[60] G. Restrepo, H. Mesa, *Curr. Comput. Aid Drug.* **2011**, *7*, 90–97.
[61] P. Pyykkö, *Phys. Chem. Chem. Phys.* **2011**, *13*, 161–168.
[62] Figure 1 D is a modification of Figure 4 of reference [54], motivated by the redrawing published in 63.
[63] H. Park, Y. Seungmin, *Donga Science* **2019**, *120*, 38–43.
[64] This is a historical mapping between the 1860s structure and another one where elements are ordered by atomic number and grouped to-

gether by electronic configuration resemblance. Another mapping from the families of similar elements is to the set of suffixes involved in the names of chemical elements, e.g.-*ium* or -*um* for metals, -*on* or -*ine* for non-metals (except helium and selenium), -*on* for carbon alike elements, and -*ine* for halogens.[65]

[65] B. F. Thornton, S. C. Burdette, *Nat. Chem.* **2013**, *5*, 350 – 352.

[66] For example, the electronic configuration of hydrogen indicates its similarity with alkali metals. However, chemical evidence shows that such a similarity does not always hold.[18,67–69]

[67] W. Leal, G. Restrepo, A. Bernal, *MATCH* **2012**, *68*, 417 – 442.

[68] G. Restrepo in *Elements Old and New: Discoveries, Developments, Challenges, and Environmental Implications* (Eds.: M. A. Benvenuto, T. Williamson), ACS Symposium Series; American Chemical Society, Washington, DC, **2017**, Chapter 5, pp. 95 – 110.

[69] P. Pyykkö, *Pure Appl. Chem.* **2019** https://doi.org/10.1515/pac-2019-0801.

[70] D. Mendeleev in *Mendeleev on the Periodic Law: Selected Writings, 1869 – 1905* (Ed.: W. B. Jensen), Dover, New York, **2002**, Paper 2, pp. 18 – 37.

[71] R. L. Melen, *Science* **2019**, *363*, 479 – 484.

[72] G. Rayner-Canham, *J. Chem. Educ.* **2000**, *77*, 1053 – 1056.

[73] H. Glawe, A. Sanna, E. K. U. Gross, M. A. L. Marques, *New J. Phys.* **2016**, *19*, 093011.

[74] This is the so-called singularity principle.

[75] S. Kean, *Science* **2019**, *363*, 466 – 470.

[76] In fact, calculations on oganesson are not that crystal clear, for one prediction suggests that oganesson is akin to noble gases with an electron affinity, while another study foresees a condensed phase standard state, with semi-conducting properties.[77,78]

[77] A. Türler, *Chimia* **2019**, *73*, 173 – 178.

[78] J.-M. Mewes, O. R. Smits, P. Jerabek, P. Schwerdtfeger, *Angew. Chem. Int. Ed.* **2019**, *58*, 14260; *Angew. Chem.* **2019**, *131*, 14398 – 14402.

[79] P. Ball, *Nature* **2019**, *565*, 552 – 555.

[80] These comparisons are mainly based on the resemblance of properties like ionic radii and the stability of oxidation states. The reliance on verticality also reaches theoretical shores, as evident, for example, in the claiming that “yet undiscovered, 119 and 120 are predicted to possess $8s^1$ and $8s^2$ electron configurations, respectively. Thus, they should be alkali and alkaline earth elements in groups 1 and 2, respectively.”[81]

[81] H. Haba, *Nat. Chem.* **2019**, *11*, 10 – 13.

[82] K. Pulkkinen, Abstract 23, ISPC 2018. https://www.bristol.ac.uk/arts/events/2018/philosophy-of-chemistry-conference.html (Accessed June 6^{th} **2019**).

[83] In reference [52] we celebrated an equilibrated definition of periodic system. However, it relies on vertical similarities.

[84] D. Mendelejeff, *Ber. Dtsch. Chem. Ges.* **1871**, *4*, 348 – 352.

[85] When “periodic law” is added to the Ngram search in English of reference [34], the law is the dominant term until about Mendeleev’s death (1907), afterwards it has had little use. In German, “*Periodische Gesetz*” (periodic law) and is declinations were only popular in the 1890s. In Russian, the term “*periodic law*” was a bit more popular than the system since 1930 until 1990, when the system became again slightly more popular than the law.

[86] D. Mendeleev in *Mendeleev on the Periodic Law: Selected Writings, 1869 – 1905* (Ed.: W. B. Jensen), Dover, New York, **2002**; Paper 6, pp. 135 – 137.

[87] The problem with the “law” lies in its supposed underlying “periodic function.” Laying the function aside, the remaining target of relating substances with compounds and properties entails a whole research programme, which in contemporary terms fits well with the aims of mathematical chemistry.[88] Note, for instance, how quantitative structure–activity relationship approaches look for connections between substances, at the level of quasi-molecular species, and physicochemical, environmental or medicinal properties.[7] Another instance is the sought grammar of chemistry, based upon rewrite rules of molecular graphs. Here the sought property is chemical reactivity based on molecular structures.[89]

[88] G. Restrepo in *Essays in the philosophy of chemistry* (Eds.: E. Scerri, G. Fisher), Oxford University Press, New York, **2016**; Chapter 15, pp. 332 – 351.

[89] J. L. Andersen, C. Flamm, D. Merkle, P. F. Stadler, *J. Syst. Chem.* **2013**, *4*, 4.

[90] A less pronounced overstatement was formulated by Meyer when claiming “the properties of the elements are mostly periodic functions of the atomic weights” ([…] *die Eigenschaften der Elemente großentheils periodische Functionen des Atomgewichtes sind*).[12]

[91] Others interested in algebraic expressions were Bazarov, Chicherin, Flavitskii, Haughton, Mills and Rydberg, to name but a few.[92]

[92] J. R. Smith, Persistence and Periodicity: A Study of Mendeleev’s Contribution to the Foundations of Chemistry. Doctoral thesis. **1976**, King’s College, London, p. 298.

[93] D. Mendeleev in *Mendeleev on the Periodic Law: Selected Writings, 1869 – 1905* (Ed.: W. B. Jensen), Dover, New York, **2002**, Paper 11, pp. 192 – 226.

[94] A. Bernal, E. E. Daza, *HYLE Int. J. Phil. Chem.* **2010**, *16*, 80 – 103.

[95] Chemical properties are relational properties among chemical species.[26] Another relational property is molecular structure, where atoms are related via bonds. This is modelled with graphs.

[96] The discussion on a “more correct” periodic table,[97] entailing a more correct periodic system, requires, therefore, clearly declaring which properties are to be optimised to end up with a correct periodic system. We doubt that properties of importance for organic chemists are the same than for new material scientists, for example. More about this in Section 3.1.2.

[97] E. Scerri, *Chem. Eur. J.* **2019**, *25*, 7410.

[98] Tellurium’s atomic weight is greater than iodine’s. However, Meyer[40] and Mendeleev[99] placed tellurium before iodine in the ordering of elements by atomic weight.

[99] D. Mendelejeff, *Z. Chem.* **1869**, *12*, 405 – 406.

[100] A more suitable table-like (bidimensional) depiction of the current systems is by clearly stating the order relationships between consecutive elements (cover relationships), for example as arrows,[54] as shown in Figure 1 C. If similarities are to be regarded as non-symmetric relationships, as mentioned in referene [57], then these directed similarities could also be represented by arrows as in reference [18].

[101] This was clear to Mendeleev, who wrote in his 1869 extended paper on the system: “I shall now give one of the many systems of elements which are based upon the atomic weight.”[70] Mendeleev’s awareness of the generality of his device is evident when suggesting alternative tables for his 1869 system. He wrote: “Similar arrangements can be imagined in great numbers, but they do not change the essentials of the system.”[70]

[102] E. Scerri, *Chem. Int.* **2019**, *41*, 16 – 20.

[103] Quoting Marguerite Yourcenar: “Peace was my aim, but not at all my idol; even to call it my ideal would displease me as too remote from reality.”[104] The problem is turning a table into an idol, even at the cost of being drifted further and further away from reality. As near-sighted as these efforts to freeze the periodic table in one standardised visual representation, are the attempts to link it exclusively to the name of Mendeleev, and dub “the” periodic table as Mendeleev’s table, as submitted in 2013 to IUPAC and more recently as a general motion to UNESCO. This latter was proposed during a scientific meeting, the 21st Mendeleev Congress in St. Petersburg, 9–13 September 2019.

[104] M. Yourcenar, *Memoirs of Hadria*, Secker & Warburg, London, **1964**, p. 105.

[105] S. Lemonick, *Chem. Eng. News* **2019**, *97*, 26 – 29.

[106] Besides having hundreds of periodic tables, some emphasizing certain properties over others, the discussion is often mixed with aesthetics, which leads to claim that one table is “better” than the other because of its colours and fancy symmetrical shapes. Pekka Pyykkö summarised the subjectivism in the generation of tables as: “It is a human right to make your own Periodic Table. Don’t let anyone take that right from you.”[107]

[107] P. Pyykkö, Lecture at Mendeleev-150, St. Petersburg, 26 July **2019**.

[108] He wrote in 1871 that systems “lack a general expression for the reciprocal relationships of the individual groups to one another”[39] (*Es fehlt an einem allgemeinen Ausdruck für die gegenseitigen Verhältnisse der einzelnen Gruppen zu einander.*)[109]

[109] D. Mendelejeff, *Ann. Chem. Pharm. Supplementband* **1871**, *VIII*, 133 – 229.

[110] Hypergraphs were mentioned in reference [55]. Simplices are regarded as multi-dimensional polygonal shapes built up from vertices (objects), edges (couples of objects), triangles, tetrahedra, etc.[111]
[111] D. I. Spivak. **2009**, *arXiv*:0909.4314v1.
[112] He also, unsuccessfully, tried estimations by extrapolation, for example when analysing coronium and ether and their incorporation into the systems.[113]
[113] D. Mendeleev in *Mendeleev on the Periodic Law: Selected Writings, 1869–1905* (Ed.: W. B. Jensen), Dover, New York, **2002**, Paper 12, pp. 227–252.
[114] D. J. Klein, *J. Math. Chem.* **1995**, *18*, 321–348.
[115] G. Restrepo, D. J. Klein, *J. Math. Chem.* **2011**, *49*, 1311–1321.
[116] A. Panda, S. Vijayakumar, D. J. Klein, A. Ryzhov, *J. Phys. Org. Chem.* **2013**, *26*, 917–926.
[117] X. Zheng, P. Zheng, R. Z. Zhang, *Chem. Sci.* **2018**, *9*, 8426–8432.
[118] F. Feng, X. He, Y. Liu, L. Nie, T. S. Chua, **2018**, Proceedings of the 2018 World Wide Web conference, WWW '18, pp. 1523–1532. Republic and Canton of Geneva, Switzerland: International World Wide Web Conferences Steering Committee.
[119] Personal communication (March 27th **2019**).
[120] R. Brüggemann, G. P. Patil, *Ranking and Prioritization for Multi-Indicator Systems*, Springer, Berlin, New York, **2011**.
[121] The idea of limits was early mentioned by Vincent in a 1902 paper on attempts to reproduce atomic weights, using algebraic equations.[122]
[122] J. H. Vincent, *Philos. Mag.* **1902**, *4*, 103–115.
[123] This was Mendeleev's setting based on atomic weight (considered as a real number), which led him to ponder over coronium and ether in 1904.[113]
[124] S. Reich, *Nature* **2010**, *468*, 355.
[125] R. Arsenescu, C. Baglin, H. P. Beck, K. Borer, A. Bussière, K. Elsener, P. Gorodetzky, J. P. Guillaud, S. Kabana, R. Klingenberg, G. Lehmann, T. Lindén, K. D. Lohmann, R. Mommsen, U. Moser, K. Pretzl, J. Schacher, R. Spiwoks, J. Tuominiemi, M. Weber, *New J. Phys.* **2003**, *6*, 1.
[126] J. Stedall, *Mathematics Emerging: A sourcebook 1540–1900*, Oxford University Press, Oxford, **2008**, p. 190.
[127] L. B. Altschuler, R. F. Trunin, V. D. Urlin, V. E. Fortov, A. I. Funtikov, *UFN* **1999**, *169*, 3, 323–344 https://doi.org/10.3367/UFNr.0169.199903g.0323 (in Russian).
[128] W. Zhang, A. R. Oganov, A. F. Goncharov, Q. Zhu, S. E. Boulfelfel, A. O. Lyakhov, E. Stavrou, M. Somayazulu, V. B. Prakapenka, Z. Konopkova, *Science* **2013**, *342*, 1502–1505.
[129] E. Cartlidge, *Nature* **2018**, *558*, 175–176.
[130] Personal communication (November 10th **2015**).
[131] G. Restrepo, *Substantia*, in press.
[132] The time is ripe for this data driven approach, as there is a worldwide move to adopt policies recognising and promoting data sharing.[133]
[133] *Sci. Data* **2019**, *6*, 72; https://doi.org/10.1038/s41597-019-0065-y
[134] A recent example of how data analysis techniques are making their way in contemporary chemistry is the publication of the first chemistry book written entirely by a machine.[135]
[135] B. Writer, *Lithium-Ion Batteries*, Springer **2019**.
[136] A similar approach was followed by Schummer when analysing the growth of chemical compounds at the end of the 1990s.[137]
[137] J. Schummer, *Scientometrics* **1997**, *39*, 107–123.
[138] D. Mendeleev in *Mendeleev on the Periodic Law: Selected Writings, 1869–1905* (Ed.: W. B. Jensen), Dover, New York, **2002**, Paper 9, pp. 162–188.

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Periodic Table

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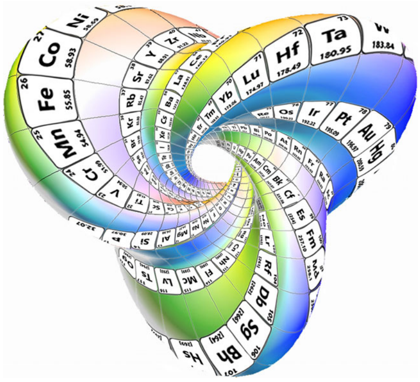
Challenges for the Periodic Systems of Elements: Chemical, Historical and Mathematical Perspectives



Systems through time: This Essay discusses the Periodic Table and as it celebrates its 150th year. Discussions include its powers and limitations, inherent generalizations as well as the ordering and inter-element relationships that exist in it currently and the previous periodic systems that have led to the Table as we know it today.