CHAPTER 4

The Periodic System

A Mathematical Approach

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THE PERIODIC TABLE, DESPITE its near 150 years, is still a vital scientific construct. Two instances of this vitality are the recent formulation of a periodic table of protein complexes (Ahnert et al. 2015) and the announcement of four new chemical elements (Van Noorden 2016). "Interestingly, there is no formal definition of 'Periodic Table'," claims Karol[1] (2017) in his chapter of the current volume. And even worse, the related concepts that come into play when referring to the periodic table (such as periodic law, chemical element, periodic system, and some others) overlap, leading to confusion.

In this chapter we explore the meaning of the periodic table and of some of its related terms. In so doing we highlight a few common mistakes that arise from confusion of those terms and from misinterpretation of others. By exploring the periodic table, we analyze its mathematics and discuss a recent comment by Hoffmann (2015): "No one in my experience tries to prove [the periodic table] wrong, they just want to find some underlying reason why it is right." We claim that if the periodic table were "wrong," its structure would be variable; however the test of the time, including similarity studies, show that it is rather invariable.

An approach to the structure of the periodic system we follow in this chapter is through similarity. In so doing we review seven works addressing the similarity of chemical elements accounting for different number of elements and using different properties, either chemical or physical ones.

1 Incidentally Paul J. Karol is the IUPAC committee chair for the project that analyzed the evidence of existence for the new elements.

Element and Its Relation to Basic and Simple Substance

The concept of "chemical element" has raised the interest of several scholars such as Paneth (1962) and is still a matter of discussion given the double meaning it has (see, e.g., Scerri 2007, Earley 2009, Ruthenberg 2009, Ghibaudi et al. 2013, van Brakel 2014, Restrepo & Harré 2015), which is confusing, leading to misconceptions. The two meanings of the concept of chemical element are basic and simple substance.

According to Paneth (1962), a *basic substance* belongs to the transcendental world and it is devoid of qualities, and therefore is not perceptible to our senses. It is the "indestructible substance present in compounds and simple substances"[2] (Paneth 1962), the "elementness" of some substances. It is, for example, the "boron-ness" of all substances whose chemical analysis yields boron as a constitutive part of them. In turn, a *simple substance* is *a* realization of an uncombined basic substance[3] (Fig. 4.1); that is, simple substances are allotropic forms of a basic substance. Thus, carbon, tellurium, and boron are basic substances whose respective realizations as simple substances are charcoal, diamond, fullerenes, and so on; amorphous and crystalline tellurium; and amorphous-, α-rhombohedral-, β-rhombohedral-, and so on, boron. Hence, *each box or position for an element in a periodic table represents a basic substance*, which is represented by a symbol.[4]

In the realm of properties of the elements, basic substances do not possess properties, but simple substances do. Hence, it is a mistake to state that carbon is black, for carbon, as a ~~simple~~ basic substance, is devoid of color; what is actually black is the charcoal realization of the basic substance carbon. Likewise, claiming that the density of carbon is 2.267 g/cm^3 is an error as the particular simple substance of carbon exhibiting such density needs to be declared. In fact, the different allotropic forms of carbon have different densities. Thus, *it is a mistake to write down properties for chemical elements on the periodic table*, unless the respective box of the element can be expanded into its different simple substances (allotropes). By the same token, Paneth (1962) criticizes approaching similarity of chemical elements through similarities of their simple substances. Paneth (1962, 152) asserts: "we need only recall how little resemblance there is between gaseous nitrogen and pure antimony"; and stresses the importance of compounds for similarity.

[2] We do not agree with van Brakel's (2014) interpretation of basic substance as IUPAC's "'chemical element' [. . .]A species of atoms; all atoms with the same number of protons in the atomic nucleus." As Paneth (1962) stated and as van Brakel (2014) also mentions, "the concept of basic substance as such does not in itself contain any idea of atomism."

[3] Restrepo & Harré (2015) have shown a mereological (part/whole) relationship between basic and simple substance, where simple substances are the whole and basic substances the parts.

[4] There is a connection between the association of symbols to elements and to variables in the mathematical way of thinking postulated by Weyl (1940). The very assignment of the label Fe to all iron realizations, even under different conditions, requires abstraction and generalization, which are worth studying from a mathematical and philosophical view point.

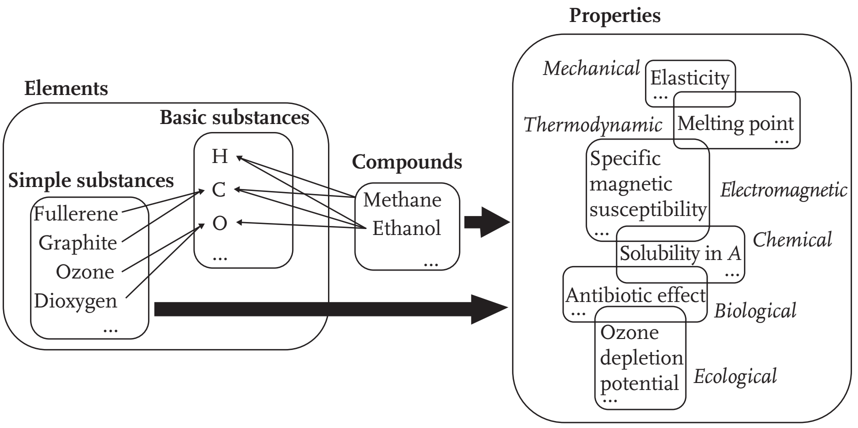

FIGURE 4.1 Basic and simple substances and their relationships with elements, compounds and material properties.

Compounds have played an important role in providing knowledge about chemical elements as basic substances; hence, there is something in each compound encoding information on its transcendental elements. That is why Paneth calls attention to the fallacious claim that "the properties of sulphur are just those properties which it exhibits to us in the special case when it is not combined with any other basic substance"[5] (Paneth 1962, 150). Our point here is that *a holistic representation of chemical elements as basic substances needs to consider their different simple substances as well as their compounds.*[6]

Periodic System, Table, and Law: How Different Are They?

If X represents the set of chemical elements (basic substances) and S the structure of similarity classes of chemical elements, then (X, S) is called a *periodic system*. As with any mathematical structure (Potter 2004), S is defined as $S = (X, R)$, with R a relation for the elements of X. What is the nature of such a relation? Is that relation unique or are there multiple relations? What are the causes of that relation? Those are questions that have driven research and interest on the periodic system since its discovery and which still need further

[5] This is a typical mistake when teaching the periodic system. Most, if not all, chemistry textbooks show electronic affinities and ionization energies as properties of chemical elements, disregarding valuable information on chemical reactivity and of compounds.

[6] Paneth has asserted "behind the 'simple substances' and 'compounds' endowed with constant properties, there stand the transcendental 'basic substances'" (Paneth 1962). This opens the question on the number of simple substances and compounds needed for such a description. Including them all is impossible, as the number of synthesized substances grows exponentially. Though, even if such a number were fixed, would all those substances be needed? Are some substances more important than others? Are binary compounds more important for representing elements than proteins?

research. For example, the nature of *R* can be analyzed by looking at Mendeleev's seminal statement (Mendeleev 1869, Jensen 2005, 16): "If one arranges the elements in vertical columns according to increasing atomic weight, such that the horizontal rows contain analogous elements, also arranged according to increasing atomic weight, one obtains the following table,"[7] where, remarkably, Mendeleev refers to arrangements and analogies. Thus, a periodic system is what results from taking chemical elements and ordering and classifying them in an entangled manner (Fig. 4.2).[8] Note that we refer to *a* periodic system rather than to *the* periodic system, for depending on the properties of the elements used for their characterization, different *S* may show up, therefore different periodic systems may also. Mendeleev ordered the elements by selecting as leading property the atomic weight (attaching a property to basic substances).[9] The similarity was based on different properties of simple substances and of compounds, such as oxides, hydrides, halides, and so on (Jensen 2005).

A mapping of the periodic system onto another space, normally a bi-dimensional space, is called a *periodic table*. As there may be different periodic systems and different spaces on which to map, the periodic table is not unique. Another widespread term when talking about chemical elements is *periodic law*, understood as the oscillating variation of some properties of chemical elements (simple substances) as a function of the atomic number Z ($f(Z)$).[10] Formally, it can be expressed as $(Z, f(Z))$. In this sense, there would be *a periodic law for each property of simple substances*, therefore no unique periodic table

[7] Current depictions of the table have interchanged Mendeleev's columns and rows and the "arranging" criteria has been changed to the atomic number.

[8] These ideas and their formal definitions are the subject of a paper with Wilmer Leal that is currently in preparation. Schwarz (2004) is one of the few researchers who has mentioned the importance of ordering *and* classification for the periodic system. Ordering was so important to Mendeleev that he criticized Chancourtuois and Newlands for their approaches to the periodic system lacking that relation (Mendeleev 1899, Jensen 2005 paper 11). Often claims about periodic systems of other entities different to chemical elements are found in the scientific literature, e.g., hydrocarbons, diatomic and triatomic molecules, fullerenes and protein complexes to name but a few. Do actually they meet the conditions of similarity and ordering of a periodic system?

[9] Mendeleev believed in the transcendental character of chemical elements as Paneth (1962) later did and championed the concept of basic substance. Mendeleev regarded chemical elements as devoid of properties; however he relied on the atomic weight as *the* invariant property. Perhaps Mendeleev drew a distinction between properties of one sort, for example, density or melting point, for they may result from the direct measurement upon substances; this contrasts with the atomic weight, which comes from comparison of, however, measured properties, e.g., of vapor densities of gases containing the common element whose atomic weight is to be determined. A historical account of ways to determine atomic weights is found in Scerri (2007). Hence, Mendeleev could have regarded atomic weight as a more complex property than others such as density or melting point. By doing so he perhaps thought he was not hurting the transcendental character of chemical elements as basic substances.

[10] Originally, Mendeleev mooted it using atomic weight but it is currently stated through atomic number.

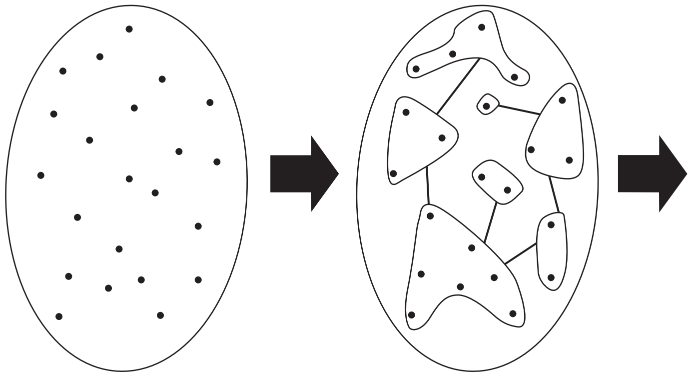

FIGURE 4.2 Relationship between chemical elements (X), periodic system, and periodic table, where S and R stand for structure and relation upon X, respectively.

would exist.[11] Moreover, contrary to general information spread by chemistry textbooks, even for the most common allotropes, not all of their properties are oscillating. In this respect Mendeleev's insight went too far when claiming that the law was applicable to all properties.[12]

Part of the success and the reason for the popularization of the periodic system lies in the use Mendeleev made of it for estimating properties of simple substances and compounds. Perhaps a better description of the prediction process would be relying not on the law but rather on the system,[13] which would avoid the problems caused by a lack of periodicity for certain properties. What is important and worth studying is the periodic *system*—its structure and the different functions (not necessarily periodic) that can be found between the system and a desired property.

[11] It is very unlikely that the range of $f(Z)$, for property f (say density), perfectly coincides with that of g (Z), for property g (say thermal conductivity); which is the requirement for unicity of the law. On the other hand, as the law refers to simple substances and each element can be represented by several allotropes, if all allotropes are regarded for all elements, the number of possible periodic laws is given by $\prod a_i$, with a_i being the number of allotropic forms for element i. Just by considering five allotropes for C, five for P, three for O, three for Se, seven for B, four for Sb, and five for Fe, for example, the number of periodic laws is 31,500.

[12] Mendeleev stated "not only in the forms of the compounds that we observe a regular dependency when the elements are arranged according to the magnitude of the atomic weights, but also in their other chemical and physical properties" (Jensen 2005, 45).

[13] Which was actually as Mendeleev derived algorithms for property estimations, i.e. not focusing on the "periodic law" but on the relations of classes and on the internal ordering of classes. See the translation into English of the original papers by Mendeleev in Jensen (2005).

From Similarities to the Periodic System

Mendeleev was interested in the mathematics underlying the periodic law, stressing that periods of elements cannot be treated as periods of continuous functions[14] but require a modification of continuous mathematics to cope with their discrete nature (Jensen 2005, 170; Jensen 2005, 221). Mendeleev wrote: "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" (Jensen 2005, 221). He adds, "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" (Jensen 2005, 221). Indeed, such an abstraction is still absent, despite the different approaches from group theory, information theory, and statistics (King & Rouvray 2006). However, a different approach, based on classification and relations among classes was suggested in 2000 by Villaveces, who wrote: "It seems that the set of chemical substances is a topological space wherein relationships such as belonging to a class, neighbourhood or hierarchy of classes, etc. are more important than differential relationships"[15] (Villaveces 2000, 22). And he added: "This seems to be the mathematical structure underlying the periodic table and which would explain that predictions were possible when considering the whole set of chemical elements along with their equivalence classes" (Villaveces 2000, 22). This hypothetical structure of the periodic system is what we call *Villaveces' conjecture* and it has been the driving force of the similarity studies in which we have been involved and which are here analyzed along with other approaches.

Every similarity study looks for a classification of a set X of elements. The question that arises is whether it is possible to know the maximum number of classifications that may result given the number of elements in X. In other words, how many classifications are possible? A first approach is counting all possible subsets of X (power set of X); this is given by 2^n, with n the number of elements in X. Thus, for 118 elements, about 10^{35} subsets are possible. But in this counting there are subsets that may share elements, such as {Ga, Tc, Fr} and {Tc, Fr, Sb}. If one wants to avoid overlapping subsets and wants the union of subsets to build up the whole set, one is interested in counting the partitions[16] of X; which is given by the Bell numbers that grow faster than 2^n. A further refinement of this counting results when one has a rough idea of the number of classes of a particular size one is interested in—for example, the

[14] "neither the trigonometrical functions [...], nor the pendulum oscillations [...], nor the cubical curves [...], can [...] represent periods of chemical elements" (Jensen 2005, 170).
[15] Translated from Spanish by the author.
[16] For example, a partition of {Ga, Tc, Fr, Sb} is {{Ga, Tc}, {Fr, Sb}}. This corresponds to a crisp classification, where each element only belongs to a single class. However, there are fuzzy classifications where each element belongs to more than one class. See for example Rayner-Canham's classifications in this volume.

number of classes of four elements ($k = 4$) in a set of 10 elements. This is given by the Stirling numbers of the second kind $S(n,k)$ (Comtet 1974). If we assume that the number of classes of chemical elements is about the number of columns in the conventional medium-long form table (Scerri 2007) plus the lanthanoids and actinoids, the possible number of classifications is $S(118, 20) \approx 10^{135}$, but if one is just interested in metals and non-metals, then $S(118, 2) \approx 10^{35}$ and if semimetals are included $S(118, 3) \approx 10^{55}$. This gives an account of the colossal number of classifications of chemical elements that may result. Thus, if the periodic system were a random structure, each classification of chemical elements based on different properties would likely lead to a different classification. However, classifications of chemical elements show, again and again, that even if the properties are varied, the results change very little, which indicates a kind of underlying and invariable structure for the periodic system. In this chapter, we analyze seven similarity studies of chemical elements.

For similarity studies three kinds of input are needed: things to classify, properties characterizing them, and a mechanism to assess (dis)similarity. In formal terms, what is needed is a set of elements, their properties, and a (dis)similarity function. For chemical elements, the first question is the number of elements to analyze, which depends on the sort and number of properties characterizing them, for elements with little information are normally discarded.

Schummer (1998) has noted that properties characterizing materials are classified according to the context in which the material is embedded. Hence, there are (1) mechanical forces leading to *mechanical properties* like elasticity; (2) thermodynamic conditions like temperature associated with *thermodynamic properties* like melting point; (3) electromagnetic fields related to *electromagnetic properties* like specific magnetic susceptibility; (4) contexts of other chemical substances leading to *chemical properties* like the capacity for oxidation or the solubility in a certain liquid; (5) contexts of biological organisms associated to *biological properties* like antibiotic effects; and (6) contexts of ecological systems related to *ecological properties* like ozone depletion potential. Properties of type (1)–(3) are called *physical properties* and are characterized by "excluding the chemical factor" that is by working with inert container materials and atmospheres (Schummer 1998).

In the current chapter we discuss seven similarity studies of chemical elements, whose main features are shown in Table 4.1. The relationship of these approaches, besides similarity of chemical elements, is their phenomenological perspective; that is, mainly using experimental properties of bulk substances. There are some other non-phenomenological approaches based on theoretical descriptions of isotopes, atoms, and their electronic densities (Robert & Carbó-Dorca 1998, 2000, Khramov et al. 2006). All approaches of Table 4.1, except Leal et al (2012), characterize chemical substances by physical properties, while Leal et al (2012) is only based on chemical properties. Further we consider the most salient features of these two groups of approaches.

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TABLE 4.1 Phenomenological similarity studies of the periodic system

AUTHOR(S) (PUBLICATION YEAR)	ZHOU ET AL. (2000)	SNEATH (2000)	KARAKASIDIS & GEORGIOU (2004)	RESTREPO ET AL. (2004)	RESTREPO ET AL. (2006A)	CHEN (2010)	LEAL ET AL. (2012)
Elements/ Atomic Numbers Z	H-Sn/Z=1-50	H-La, Hf-Bi/Z=1-57, 72-83	H-Nd, Sm-Dy, Y-Lu, Hf-Po, Rn, Ra-Ac/Z=1-60, 62-66, 70-71, 72-84, 86, 88-89	H-La, Hf-Rn/ Z=1-57, 72-86	H-La, Hf-Rn/ Z=1-57, 72-86	H-Xe/Z=1-54	H, Li-F, Na-Cl, K-At, Ra-Es/Z=1, 3-9, 11-17, 19-85, 88-99
Number of Elements	50	69	83	72	72	54	94
Number of Properties	7	54	2	31	128	10	4,700
Kinds of Properties	Physical	Physical and chemical	Physical	Physical and chemical	Physical and chemical	Physical and chemical	Chemical
Properties of Elements (simple substances)	X	X	X	X	X	X	
Properties of Compounds		X		X	X	X	X
(Dis)similarity Function	Fuzzy similarity	Gower's coefficient	Fuzzy similarity	Hamming, Euclidean, Gower and Cosine functions	Hamming, Euclidean, Gower and Cosine functions	Kohonen network	Symmetric difference

NOTES: Dedicated to Professor José L. Villaveces.

Approaches from Physical Properties

These six works are characterized by not stating the simple substances used.[17] The properties used vary in number, from 2 to 128, and in kind. In Karakasidis & Georgiou (2004) the only two properties used are first ionization potential and atomic number; while Chen used atomic mass, minimum oxidation state, atomic radius, electronegativity, state of matter, melting point, boiling point, heat of atomization, and ionization potential. But in Sneath and Restrepo chemical properties are added to the study. Sneath[18] used binary compounds of O, S, F, Cl, Br, and I; plus methyl-, ethyl-, and phenyl-compounds and complexes with donor oxygen, sulfur and nitrogen groups; and Restrepo used properties from geochemical origin.[19] In the majority of these studies atomic number and atomic weight are disregarded to assess to which extent the classification of chemical elements depends on these properties of great historical importance. The results indicate that the classifications are, in general, not affected by these properties.

Similarity results are depicted in Figure 4.3 and show a mixture of vertical (columns in the periodic table) and horizontal (rows) similarities but especially notorious are the horizontal similarities of Karakasidis & Georgiou (2004), which coincide with the periods of the table. This result is mainly given by the use of the first ionization potential to characterize the elements (the other property used was the atomic number, which monotonically increases throughout the structure of the table), a property that oscillates with the periods and it is in fact one of the properties used in the textbooks to show periodicity. Several of the other works include this property but its effect is combined with the effects of the other properties leading to the patchwork of vertical and horizontal similarities of the other tables in Figure 4.3.

Vertical similarities of elements close to the noble gases are in general invariant to the properties and substances selected for the different studies. In contrast, similarities of transition metals are more sensitive to properties and substances.[20] Supporting this, Sneath discusses the high degree of uncertainty in the classification of some transition elements like Cr, Tl, Pb, Pd and Co. In Zhou et al. (2000) Fe, Co, Ni, Ru, Rh and Pd show up as a class of similar elements, which are part of the so-called platinum metals with well reported chemical similarities (Greenwood & Earnshaw 2002).

[17] For example, which allotrope was chosen: α-rhombohedral- or β-rhombohedral-boron?

[18] Peter H. A. Sneath (1923–2011) was a leading biologist with a strong interest in chemistry; he conducted the work analyzed here (which is a fundamental piece for all subsequent similarity studies of the chemical elements) in 2000. He, along with Robert R. Sokal (1926–2012), was a pioneer of numerical taxonomy.

[19] These properties come from the work by Railsback (2003), which is further analyzed in his chapter in the current volume.

[20] This was already noted by Mendeleev: "The large periods [...] beginning with the alkali metals, which give the most powerful alkalies, end with the halogens, which correspond to the most powerful acids, and contain intermediate elements with less distinctly marked chemical properties" (Jensen 2005, 266).

Some other similarities are found, such as *diagonal relationships*, in other words, the similarity in chemical properties between an element and that to the lower right of it in medium-long periodic table—as in the similarity between Be and Al (Fig. 4.3). It is also found in all studies that H is not similar to any other element; Sc, Y, and La show up as a similarity class in all cases, except for Zhou et al. (2000), who did not consider La, and for Karakasidis & Georgiou (2004) who used properties mapping periods. There is evidence of the *singularity principle*, the principle that the chemistry of the second-period elements is often different to the later members of their respective groups (Rayner-Canham 2000), as exemplified by B, C, N, O, and F, which are in most of the cases not similar to the elements of their groups (columns).

A question treated in Sneath (2000) and Restrepo et al. (2006a) was about the *minimum number of properties needed to characterize the elements*. Sneath ran a principal component analysis study to reduce the 54-dimension space of properties to a new space of components resulting from linear combinations of the 54 properties used. The components attaining a high percentage of the variance of the original properties are regarded as the minimum number of properties needed to characterize the elements. He found that the 10 first most relevant combinations (principal components) accounted for about 80% of the total variance, indicating that at least 10 dimensions are needed to represent the elements with the kind of properties used. A principal component analysis study was also carried out in Restrepo et al. (2006a) and it was found that about 90% of the variance was attained by the first 31 principal components, which shows, as Sneath has already discovered, the difficulty in finding few components gathering most of the information of the chemical elements. This keeps raising the question of the minimum number of properties to describe chemical elements.

Sneath also clustered properties and found that most of them hold more than 98% resemblance, where chemical and physical properties are strikingly very similar. Not so similar properties are the first ionization energy and the boiling point, which makes one consider the discriminatory power of the properties and their mutual relationships. Results by Karakasidis & Georgiou (2004) indicate that part of the atypical character of the first ionization energy is depicting horizontal similarities, while the other properties show other trends. In any case, a detailed study of the distribution of all properties is needed to explore their similarities.

Besides the aforementioned results, Restrepo et al.'s work of 2004 introduced a novel approach to similarity: *chemotopology*, which takes the classifications to build up topological basis that are further used to explore similarities of different subsets of elements. These similarities are analyzed through different topological properties: closures, interiors, exteriors, derived sets, and boundaries (Restrepo et al. 2006b). In general, the *interior* of a set *A*, in terms of similarity, contains those elements that are more similar to the elements of *A* and may be regarded as representatives of *A*. The *exterior* of *A* gathers those elements that are different from elements in *A*. The *closure* of *A* contains the

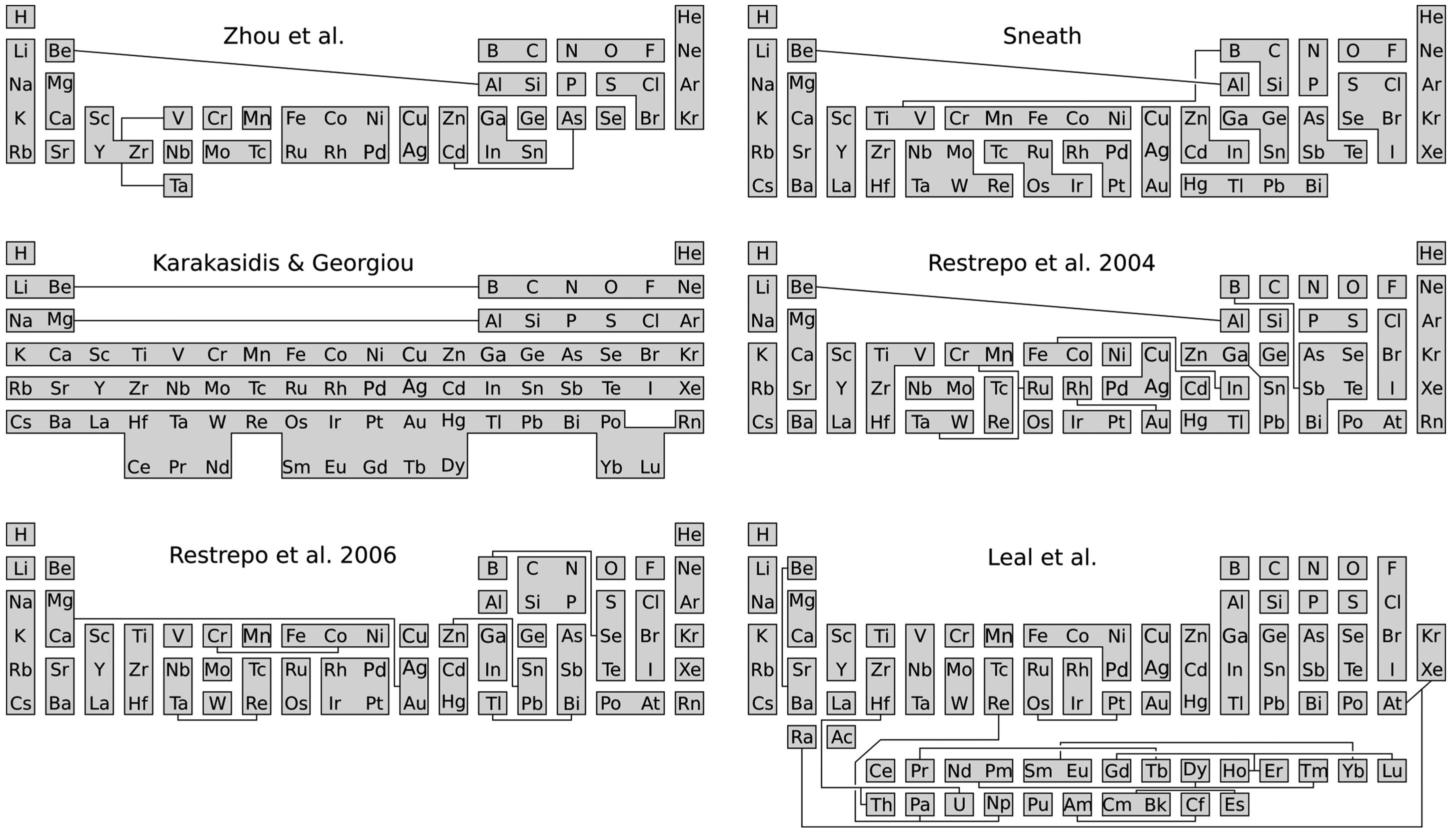

FIGURE 4.3 Classification results of the phenomenological similarity studies, where boxes indicate similarity classes.

elements that are similar to the elements of *A*; they do not have to be only similar to elements of *A* (as interior points are) but can hold resemblances with elements which are not included in *A*. The *derived set* of *A* gathers those elements that are similar to elements in *A*, not because of their own similarity, but because of the similarity of their neighbors. The *boundary* of *A* is given by those elements that are similar to the elements of *A* and also to the elements that are different to the elements of *A*. A review of chemotopology and its applications is found in Restrepo & Mesa (2011).

Chemotopology, applied to classification results of Restrepo et al. (2004, 2006a) shows that alkali metals, alkaline earth metals, {Sc, Y, La}, halogens, and noble gases are classes of elements whose interiors and closures are the same sets; for example, the interior and closure of {Sc, Y, La} is {Sc, Y, La}, which indicates that there is no other element similar to the elements of each class, a result strengthened by the finding of empty boundaries for those classes. The derived set shows (Restrepo et al. 2004) that every alkali metal is at least similar to another alkali metal; the same behavior is found for {Sc, Y, La}. But, in the same study, alkaline earth metals, halogens, and noble gases do not follow this similarity pattern, for Ba, F, and He turn out to be not part of the derived set of their respective groups.

Different topological properties, resulting from non-local and non-vertical similarities on the table, were found for most vertical classes (groups) of transition metals. Thus, for example, it is observed in Restrepo et al. 2004 that to the interior of {Fe, Ru, Os} only belongs Os, that to its closure belong, besides {Fe, Ru, Os}, Co, In, Ta, and W; that its boundary is made by the elements of the interior, except Os, indicating the lower resemblance of Os to Fe and Ru and the non-vertical similarities of Fe and Ru.

In Chen (2010) three main classes (metals, semimetals, and non-metals) are found, however without clear criteria for their selection and for the assignment of each element to each class.[21] Besides similarities found in previous works, two new classes were found: {Nb, Mo, Tc} and {Li, Mg}, {Li, Mg} being a case of diagonal relationship. A novelty introduced in Chen (2010) is the estimation of the classification of some few elements: Cs, Au, Hg, Pb, and Rn.[22]

Approach from Chemical Properties

A fundamental piece of information normally overlooked in chemistry textbooks is that Mendeleev's studies on chemical elements rested mainly on oxides, hydroxides, hydrides, and halides, whose resemblances were employed

[21] It is presumed that the classification was based on the nearness of the neurons of the Kohonen network containing elements (characterized by two numbers representing two dimensions); however, sometimes the horizontal nearness is given more importance than the vertical one.
[22] Unfortunately, the author did not mention the particular results for all these elements, but expressed that they were placed "in excellent locations"; it is only mentioned that Rn was placed in the same neuron as Xe.

to come up with similarities on chemical elements.[23] Mendeleev indicated the need to look at compounds rather than to properties of chemical elements, e.g. he claimed that "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" (Jensen 2005, 263). And Mendeleev adds, "The elements, which are most chemically analogous, are characterized by the fact of their giving compounds of similar form RX_n" (Jensen 2005, 264).

In contrast to the popular neglect of compounds and the overemphasis of simple substances and their physical properties for studies on the periodic system, some authors have highlighted the important role of compounds and have mentioned the related problem of quantifying qualitative parts of chemistry for similarity studies (Schwarz 2007). The questions that arise are what can be done by having information of compounds and what kind of information is needed? Following Mendeleev, it is found that valences are important properties for chemical elements, which are obtained by stoichiometric decomposition of compounds in chemical analysis (Schwarz 2004).

Thus, considering historical aspects of the periodic system, especially its reliance on chemical compounds, valences, and stoichiometries of compounds, rather than on properties of isolated elements (simple substances); we ran a novel study based only on compounds. The study (Leal et al. 2012) is influenced by Schummer's (1998) idea that chemistry is rooted on the relational character of substances (Bernal & Daza 2010), which combined with concepts from category theory (Bernal et al. 2015) and social network analysis (Restrepo 2017) leads to the idea that a chemical substance (not necessarily an element) is not only characterized by properties measured upon the isolated substance, but, most important, by the other substances with which the substance in question is related, for example by chemical reactivity.

Schummer (1998) leads to the claim that (1) two substances belong to the same substance class if they are chemically similar and (2) they are similar if each of them react under the same conditions to form product substances of a common substance class. As (2) is difficult to meet, for it is not easy to find information about chemical reactions under the same reaction conditions, Leal et al. (2012) relaxed (1) and (2) as: (1´) two chemical elements belong to the same class if they are chemically similar and (2´) two chemical elements are chemically similar if each of them forms binary compounds of the same class. Hence, the general concept of chemical reaction is simplified to the study of reaction products, namely compounds (binary compounds) through

23 Mendeleev thought that chemical elements were characterized by their interaction with others (as noted in Gordin's chapter of this book); it is an idea with philosophical basis. Mendeleev wrote: "Alone, you are simply nature's slave. Your individual is only zoological, animal, and all your humanness and all that you revere, all of this is from others, with others, and not for you alone, not personal but general."

the inspection of their formulas, where no attention is paid to the kind of reactions and the conditions leading to the binary compounds.

At this point, two chemical elements A and B are similar if they form binary compounds of the sort AC and BC, C being another chemical element. Hence, for example Na and K are similar as they form with O substances that later on react with water in a similar fashion. There are cases however, where the diversity of combinations is important for the discussion of similarity. For example, B, F, and Cl form binary compounds with H but it would be too crude to claim that B, F, and Cl are similar because of that fact. If the diversity of combinations is included, one finds that F and Cl are more similar to each other than to B, for B and H form by far more compounds (boranes) than F and Cl with H.

Leal et al. (2012) considered two chemical elements A and B as similar if they form binary compounds A_wC_x and B_yC_z, C being another chemical element, with similar values of w and y, on the one hand and of x and z on the other. The more combinations with different chemical elements and with similar stoichiometry, the more similar two chemical elements are. Leal et al. (2012) used 4,700 binary compounds accounting for 94 chemical elements for which at least one binary compound has been reported in the literature.[24] It is noteworthy that, so far, there is no other similarity study accounting for more elements than those considered in this study, which, for the first time, include actinoids.[25] Lanthanoids are only considered in Leal et al. (2012) and in Karakasidis & Georgiou (2004), but in the latter case with very little properties.

By exploring the formulae of the binary compounds, a neighborhood for each element *A* was defined gathering those elements with which *A* appears together in the formula along with information about the stoichiometry of the combination. Then the similarity among elements was assessed by contrasting their neighborhoods through their symmetric difference, which accounts for the differences between couples of neighborhoods.[26] These similarities led to the classification shown in Figure 4.3, where it is seen, again, that several groups of elements such as alkali, alkaline earth metals and halogens form similarity classes.

In Sneath (2000), Restrepo et al. (2004, 2006a), and Leal et al. (2012) the technical approach to similarity was through hierarchical cluster analysis (Everitt et al. 2011), which combines similarity functions and grouping methodologies to come up with a classification that is depicted as a *dendrogram*. A dendrogram is a hierarchy of classes, and there are different methods for selecting the most salient classes of the dendrogram (Everitt et al. 2011). In the

24 Restrepo (2017) explains how the procedure leads to a network and how the search for similarities corresponds to the reduction of the network by equivalences, using elements of social network analysis.

25 A more complete study of binary compounds is currently carried out by our research group accounting for more than 15,000 compounds.

26 In similarity studies it is customary to quantify distances among objects as the inverse of their similarity. Hence, distance values d may be transformed into similarities s by $s = 1\text{-}d$, with d in [0, 1] (Deza & Deza 2006).

aforementioned works a compromise between the number of classes and their populations was sought so that highly populated classes are found. Such an approach was discussed in Uribe et al. (2005) and looks for classes of up to *n* elements. In Leal et al. (2012) *n* was set up to 4, therefore groups with five elements like alkali and alkaline earth metals were split, for example, {Li, Na} and {K, Rb, Cs}, and {Be, Sr, Ba} and {Mg, Ca}.

Similarities were found to be stronger for alkali metals than for alkaline earth metals; the dendrogram (Leal et al. 2012) shows that {Li, Na} and {K, Rb, Cs} are merged, while {Be, Sr, Ba} and {Mg, Ca} are not merged into a class of five elements but into the class merging {Be, Sr, Ba}, {Cd, Zn, Hg}, and {Mg, Ca}—indicating resemblance among alkaline earth metals but also of those metals with the above-mentioned transition metals. V and Zn groups are other examples of columns of the periodic table showing up as similarity classes.

There are some fragments of groups of the periodic table such as {Al, Ga, In, Tl}[27], {Ge, Sn, Pb}, {Sc, Y}, {Mo, W}, {Rh, Ir}, and {Cu, Ag} that form similarity classes. The presence of fragments rather than of complete groups indicates that not every element in a column of the periodic table combines in a similar fashion as the other elements of the column; that is the case of H, B, C, N, O, Cr, Ti, Mn, and Au (to name but a few), in their respective groups. In fact, there are 18 elements (single-classes) whose chemistry is totally different from that of members of their columns. Some of these single classes are instances of the singularity principle, such as B, C, N, and O; these have appeared in our previous similarity works (Restrepo et al. 2004, 2006a).

Zr and Hf turned out to be similar to Th and U, which are actinoids. This coincides with recent results on similarities of actinoids with 6th-row transition metals (Liu et al. 2017). Another example is the resemblance between Tc and Re and Pa and Np.

The well-known strong similarity among lanthanoids, which contrast with the reported relaxed similarity among actinoids, was observed by (see Liu et al. 2017). An interesting dissimilar actinoid is Pu, whose singularity has been reported by Schwarz (Liu et al. 2017).

Scerri (2007) has pointed out the discussion about the element at the beginning of the third row of the transition elements, which in some tables is La and in others Lu. Schwarz & Rich (2010) have asserted that Lu cannot be considered an *f*-block element (lanthanoid), for it does not fill *f* orbitals (as they are already filled), and has suggested that Lu should be regarded as a *d* element (transition metal). According to our results, La appears between two clusters, one of 11 lanthanoids and another of transition metals, namely {Y, Sc}. Lu is part of the clusters of 11 lanthanoids and the small four-element cluster containing it is {Er, Ho, Lu, Gd}. These results show that Lu is more similar to lanthanoids than to transition metals, while La shares similarities with lantha-

[27] If the dendrogram (Leal et al. 2012) is explored, it is found that {Al, Ga, In, Tl} is similar to Au and to {Cu, Ag}, rather than to B.

noids and with transition metals; therefore La must be the element located at the beginning of the third row of transition metals.

Scerri (2007) has also discussed the elements at the beginning of the fourth row of the transition elements, being Ac in some tables and Lr in others. Unfortunately no relevant data was available for Lr, therefore it is not possible to discuss its resemblance to other elements. Ac is found in a single class, which in turn is similar to a class of elements with a very small number of binary compounds—Ra, Kr, Xe and At.

Applying the chemotopological approach shows that the closure of each one of the following sets *X* turned out to be exactly the same sets *X*: halogens, alkali metals, alkaline earth metals, lanthanoids, V group, Cr group, VIII group (old IUPAC numbering), Cu group, Zn group, B group, C group, pnictogens, and chalcogens, as well as {B, C, N, O}, among others. This indicates that none of these classes has similarity with any other element outside of the respective class.

It is noteworthy that the classes {Fe, Co, Ni, Pd}, {Ru, Os, Pt} and {Rh, Ir} comprise the group VIII.[28] This reminds us that the similarity in the chemistry of these "platinum metals" was what led Mendeleev to group them together (Mendeleev 1889), as noted in his claim that "Only among these metals are compounds of the type RO_4 or R_2O_8 formed (which is why they are designated as the eighth group)" (Jensen 2005, 49). Our results show that it is valid to group them together, for they combine in a similar fashion (similar stoichiometry) with similar elements and constitute a set of elements with similar properties as those of the neighboring groups of the noble gases. That is, the interior and closure of platinum metals are the same elements; the boundary is empty and, interestingly, the derived set is the same set (leaving aside Pt), which shows that it is the least similar element to the "platinum metals."

Again, as in the previous works, the topological properties of the groups close to the noble gases show that their vertical similarities are the rule, that is, there are no similarities with side elements. Aside from the interesting result of the platinum metals, the topological properties of other transition metals are striking because they now turn out to be elements similar to their neighbors—that is,there are no longer similarities of, for example, Fe, Co, and In or Zn with Ga, Sn, and Pb (Restrepo et al. 2004).

Conclusions and Outlook

We think similarity studies of the chemical elements should avoid cases like this one: suppose only density and melting point are employed for the study, suppose the density for graphite and for α-rhombohedral boron are at hand as well as the melting point for diamond and for β-tetragonal boron. If the simi-

[28] In the old IUPAC group numbering or VIIIB in the CAS numbering and the VIII group of Mendeleev's periodic table (Mendeleev 1889).

larity study is carried out, it would produce conclusions biased toward the kind of simple substances selected. Why are all the allotropes of C and B not selected? If they were selected, how should we treat, in mathematical terms, all those property values of a single basic substance? Is it right to characterize elements with a mixture of properties of different simple substances?

The same questions apply to compounds. Are we sure we are using properties of the same compounds? None of the studies discussed have made this point clear and it is very likely that they have mixed properties of different simple substances and compounds associated with the same chemical element (basic substance). Presumably all studies have retrieved substance properties from literature and databases where the statement about the clear identification of the simple substances is not normally made. Hence, before classifying elements and selecting properties for that task, *a clear statement about the kind of simple substances used for the classification is needed*.

How is it possible that the "mixture" of properties of allotropes and compounds of recent studies leads to similar classifications as those found in early 19th-century periodic systems? Is it an indication of a current compensation of errors serendipitously matching the right historical results? Or is it showing that the periodic system since its origins has mixed up properties of simple substances to come up with a general periodic system? We are tempted to suggest that the latter is the case: that the periodic system is a general depiction of ordering and similarity of chemical elements accounting for a large and diverse set of properties of different realizations of elements and compounds.[29]

We discussed the error of assigning properties of simple substances to the elements in the periodic table. It was mentioned that this can only be done if the boxes for elements in the table can be expanded into the different simple substances of the elements. This multidimensionality of each box could be shown with dynamic periodic tables in the Internet, which would be linked and fed by authoritative repositories of chemical information. Such a periodic table could also include a module for data analysis bringing up-to-date knowledge on the chemical elements based on experimental facts gathered in the repositories.[30]

Even if the current chapter is mainly dedicated to similarity approaches to the periodic system, we have shown that *it is a mistake to regard the system as a structure where only similarities are important*. By going back to the first publication by Mendeleev on the subject, we have found that order and similarity are the two key concepts for the system and they have been so since its discovery. Therefore, we agree with Schwarz's (2007) when claim that similarity is not enough to build up a periodic table, but we do not agree with his statement that

[29] By reading Mendeleev's papers on the periodic system and how he came up with it, the diversity of factual chemical knowledge that was included to devise relationships among elements is clear. The invitation is to devise mathematical algorithms able to cope with large amounts of chemical information to build up a more general periodic table avoiding biases related to properties and substances.

[30] This is an idea Eugenio J. Llanos has extensively discussed with this author.

the periodic table is needed to know the similarities of the elements. We have shown that similarity studies give a nice account of the resemblances among elements, in fact better than that depicted by periodic tables, for periodic tables cannot show all similarities (e.g. similarities among transition metals and actinoids) in just a depiction. This is a technical restriction resulting from the bi-dimensional character of most periodic tables, which combined with the ordering of elements make it impossible to show all similarities at once.[31] We then suggested that *if similarities are the aim, a better representation of bi-dimensional periodic tables is a dendrogram* or a structure of similarity classes depicting levels of similarity as the similarity landscape reported in Restrepo (2017).

Contrary to Mendeleev's claim, not all properties of chemical elements, as simple substances, are periodic (i.e., oscillating regarding elements ordered by atomic number). Hence, if periodicity was key to deriving the periodic system, how can it be explained that all the discussed similarity studies produce, in general, classes of elements that match to a high degree with the 19th-century periodic system? It seems that the oscillating character of the properties and in general the sort of distribution of property values is not required to come up with the periodic system. But then, what? Villaveces' conjecture sheds light on a possible answer: *it is the topological structure of the space of properties of simple substances and compounds, which when mapped onto basic substances, show the structure we know as periodic system of chemical elements*.

Regarding the minimum number of independent properties needed to characterize chemical elements, principal component analysis, as attempted by Sneath (2000) and Restrepo et al. (2006a), may give an answer. Schwarz (2007) claims that for about 100 elements described by 100 properties, between 5 and 10 principal properties (components) would be needed. This attending to $F \approx P^{1/n}$, with $n = 2\text{-}3$, where F is the number of components and P the number of properties. In fact, Sneath's (2000) work showed that 10 components are needed, while Restrepo et al. (2006a) needed fewer than 31. This is still an open question requiring, besides statistical analysis of the properties, a clear definition of what the intention of the classification is, which results in appropriate properties being selected for the classification.

The similarity results we have reported show that vertical similarities (columns in the periodic table) of elements close to the noble gases are in general invariant to the properties and substances selected for the different studies. In contrast, similarities of transition metals are more sensitive to properties and substances. This broad distinction of the similarity, ergo topological relationships, of chemical elements make us ponder, again, the properties needed to describe the elements. Perhaps attention needs to be focused on the transition metals, since finding properties able to characterize them will presumably not affect the similarities of groups around the noble gases. It is well-known, for

[31] The best depiction, if any, of these relationships constitutes an interesting optimisation problem. Note that the reference to the "best" is in mathematical terms, rather than in aesthetic ones.

example, how the similarities of transition metals change using only relational properties of elements into binary compounds (Leal et al. 2012) where a large amount of vertical relations are found, which contrasts with several horizontal similarity relations found in the other studies.

Scerri has posed the question whether classes of chemical elements constitute actual natural kinds. The results here discussed suggest that a positive answer can be given at least for alkali metals {Li, Na, K, Rb, Cs},[32] *pseudo*-alkali earth metals {Mg, Ca, Sr, Ba},[33] halogens {F, Cl, Br, I}, and noble gases {He, Ne, Ar, Kr, Xe, Rn}. Another promising set—at least in chemical terms—is made by platinum metals.

From a mathematical point of view, the stability of classes around noble gases and the relative lack of stability of transition metals is striking if one bears in mind the large number of classification possibilities given by the Stirling numbers of the second kind. Even if Pd is sometimes similar to Rh and Pt, some others to Ag and Cu, and still others to Ni, Co, and Fe; it has not shown up in the class {Pd, He, Gd, H, F}, or any other class that would suspiciously draw the attention of a chemist for its lack of chemical sense. What this shows, we claim, is that there is a chemical background underlying the similarity of the chemical elements and that *the classification of chemical elements is not a random result*.

In pedagogical terms the results from Leal et al. (2012) show that most of the similarity structure of the periodic system can be recovered by using only chemical properties, which contribute to the discussion on how to teach chemistry, whether from a microscopic and atomic level or from a macroscopic level of bulk substances (Nelson 2002). The work of Leal et al. (2012) favors the latter and it would be interesting to include this kind of approach in general chemistry courses by pointing out representative series of chemical reactions.

The results are mostly invariant to the inclusion or not of *atomic number and atomic weight*, which leads us to conclude that these properties, apart from their historical importance, *are not important for the similarity structure of the periodic system*. However, there is no doubt that their importance lays on the ordering structure of the system; the question that arises is whether only those properties are of importance for the ordering or whether there are others yielding the same structure.

The periodicity of the periodic system—those particular points in the ordering of elements where the order is "twisted" to bring closer similar elements—is not treated further.[34] Similarity studies do not bring complete information about that, for they disregard the order component of the system. However, the studies do indicate the elements that are similar, which, once ordering is regarded, become the indicators for the twisting. Hence, Schwarz's (2007)

32 Further information on other elements like Fr is needed.
33 We call them *pseudo*, for Be and Ra are not included.
34 The study by Karakasidis & Georgiou (2004) shows that classes correspond to periods, but this study depends strongly on the first ionization energy and also lacks the ordering structure of the system.

question on the amount of periodicity encoded by similarity approaches is fully answered once the similarity classes are endowed with order relationships.[35]

Schwarz (2007) raised the question of the explanation of the similarities of the chemical elements. Similarity approaches bring classifications and now it is the turn of theoreticians to bring explanations. But this also raises the philosophical question of what an explanation *is*. Is an explanation of the periodic system the framing of some physical properties of chemical elements into the realm of quantum chemistry? Or is this just a change of language and of scientific tradition (discipline)? Sneath's results show that almost all properties are very similar, including chemical and physical ones, but only ionization energy and the boiling point differ. Why this happens requires further study and may contribute to the discussion of the reducibility of chemistry to physics (Hettema 2013). Are chemical properties actually condensed in physical properties of the elements? Or could it be taken the other way round—that the physical properties can be obtained by exploring chemical properties?[36]

Chen (2010) has mentioned that there is no information about the relationships between classes. This was also noted by Mendeleev, who claimed that this is where the importance of the periodic system lies and where research on the system must go (Jensen 2005, 59). Surprisingly, this is still something to be carried out; perhaps there is a super-structure for the periodic system where the objects of study are no longer elements but classes and now the similarities and ordering are for classes instead of for elements.

Only one similarity study has gone beyond the characterization of the similarities and its mathematics. This is Chen's (2010) approach, in which prediction of classifications of elements was done. Besides improving the methodological approaches to similarity and working on the selection of properties characterizing simple substances, similarity approaches should follow Chen's steps and venture in the realm of estimations. For example, a classification of chemical elements based on pure chemical relationships à la Leal et al. (2012) combined with Chen's (2010) ideas of training a network to predict classifications of elements is an interesting line of work to pursue. Moreover, classifications can be used to develop models of properties of elements and also of compounds.

Scerri (2007) has mentioned the resemblance between atom clusters of elements and chemical elements. It would be interesting to include properties of these simple substances as contributing to the description of elements as basic substances. Another dimension on properties to be explored is their values

[35] Schwarz (2007) has shown how the twisting points on the order can be predicted by quantum chemical approaches for the bonded atoms, not for isolated ones, which makes the approach of Leal et al. (2012) closer to Schwarz's.

[36] This position is not so strange, because a lot of the early motivation to quantum concepts came from chemistry, especially from the periodic system (Scerri 2007). But most importantly, as many of the quantum chemical calculations, if not all, somehow seek to bring insight on results of wet-lab chemistry.

under different conditions, for example, electrical conductivity is affected by density, which is affected by temperature and pressure (Hensel et al. 2015). If properties under different conditions are included, what would similarities look like? Likewise, Schwarz (2011) and Rayner-Canham (2011) have suggested using Pourbaix diagrams to run chemotopological studies. This is something to be carried out for further exploration of this chemical account of chemical properties.

If the structure of the periodic system is finally formalized as an entanglement of ordering and similarity, as suggested by Villaveces' conjecture, approaches such as those derived by Klein to estimate properties of substances based on their ordering relations could be applied to the chemical elements (Panda et al. 2013).

The studies here reported have shed light on the similarity structure of the periodic system, which have shown that Villaveces' conjecture points in the right direction; but the same conjecture states that hierarchy of classes is important for the structure of the system. Thus, further research in that direction is needed to finally accept or reject the conjecture as a whole.

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