

## CLASSIFICATION, SYMMETRY AND THE PERIODIC TABLE

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**Abstract**—The scientific use of qualitative, descriptive class concepts versus quantitative, causal mathematical relations is first examined, both with respect to their relative importance in the fields of chemistry, physics, and biology, and with respect to the potential relevance of symmetry considerations. The graphical representation of class concepts by means of sorting maps is then introduced and illustrated with examples from the field of chemistry. When atomic number is used as one of the map coordinates, a special class of map is produced that exhibits symmetry features in the form of an approximate periodicity. This, in turn, leads both to enhanced predictive abilities for the maps in question and to chemistry's most powerful example of the use of class concepts—the periodic table. The paper concludes with a detailed analysis of the current status of the periodic table in chemistry as exemplified by the step—pyramid form of the table and with a brief commentary on the abuse of symmetry considerations in the construction and interpretation of periodic tables in general.

### EXPLANATION AND CLASSIFICATION: STAMP COLLECTING RECONSIDERED

The archetypical model of the scientific method usually portrayed in books on the philosophy of science is based on the science of physics and has, since the time of Newton, pivoted around the use of fundamental theories to deduce explicit mathematical relationships between quantifiably measurable properties. In other words, it has centered around making explicit relationships of the general form:

$$u = f(x, y, z \dots), \quad (1)$$

where  $u$ ,  $x$ ,  $y$  and  $z$  are properties with assignable numerical values[1-2]. Even in the absence of a fundamental theory relating the properties in question, it is possible, if a sufficiently broad range of values have been experimentally determined for the properties, to mimic this process by empirically fitting the values to some functional form—a technique that forms the basis of great deal of applied engineering. The use of such empirical relationships is generally one of interpolation since attempts to extrapolate them beyond the original range of experimental values are fraught with danger. In addition, because of the absence of a theoretical rationale for the functional form in question, such relationships are considered to be lacking scientific “explanation”.

Symmetry can enter into (1) in two contexts. The first of these might be called *physical symmetry* and is the type of symmetry normally discussed in books on the subject[3-7]. Thus certain numerical values of  $u$  may periodically reappear as  $x$ ,  $y$ ,  $z$ , are varied, or the value of  $u$  may be invariant to certain permutations of  $x$ ,  $y$ ,  $z \dots$  or to changes in their signs, etc. The second kind of symmetry might be called *logical symmetry* and was first explicitly pointed out by Rosen[5], who called it the “symmetry of analogy” and defined it as “. . . the invariance of a relation or statement under changes of the elements involved in it.” In other words, it is based on the observation that the same functional form can frequently be applied to a wide range of different physical systems. A good example would be the concept of a generalized work function in thermodynamics as the product of a generalized force and a generalized coordinate[8] or, as a more extreme example, the concept of a generalized systems theory for describing open systems whose laws would be invariant to the specific elements of the system, be it a reactor in a chemical plant, a living cell, an organ, an organism, a society, or an entire planetary ecosystem[9]. A variety of these analogies, commonly encountered in elementary physics, have been discussed in an interesting book by Shive and Weber[10]. The value of such analogies in stimulating research, as well as their dangers, are self-evident and will be touched on later.

A great deal of chemistry has been successfully treated in terms of the physics—engineering

model described by (1). So much so, that it is not uncommon in books on the philosophy of science to find chemistry contemptuously dismissed as a branch of applied physics with little or nothing new to teach us about the nature of the scientific method or the world. However, a closer examination of a typical chemistry text quickly raises doubts about this facile judgement. For, in addition to the quantitative, dynamic, causal concepts so typical of physics, one also encounters a large number of qualitative, static, descriptive, classificatory concepts more reminiscent of biology. Indeed, the use of such *class concepts* in chemistry is pervasive, as indicated by the partial list in Table 1, and reflects not only the nature of the subject matter but the nature of what is considered to be acceptable "chemical explanation".

Unlike the causal relationships typified by expression (1), the problem of predicting class behavior can seldom be given an explicit functional form. In the simplest possible case, the class behavior will correlate with certain ranges of a quantifiable property  $x$  of the species in question:

$$\begin{aligned}\text{Class } A &= f(\text{range } A \text{ of } x) \\ \text{Class } B &= f(\text{range } B \text{ of } x), \text{ etc.}\end{aligned}\quad (2)$$

That is, instead of the simple one to one mapping characteristic of the relation (1), we have a many to one mapping. However, since recourse to the use of class concepts in the first place is frequently a reflection of the complexity of the phenomenon being described, the most common case is usually a good deal more complicated:

$$\text{Class } A = f(\text{range } A \text{ of } x, \text{ range } A \text{ of } y, \text{ range } A \text{ of } z \dots), \quad (3)$$

where, although a species may have a value of  $x$  lying within the required range for class  $A$ , it will still not correlate with that class unless it simultaneously possesses values of  $y$  and  $z$  also falling within the required ranges. Moreover, the components of relations (2) and (3) may vary widely in their precision. Classes may correspond to easily recognizable either/or situations, such as whether a series of solids are of structure type I, structure type II, etc or whether binary liquid pairs are miscible or nonmiscible in all proportions at the temperature in question, or they may correspond to some ill-defined but widely used distinction, such as whether the species in question are metallic or nonmetallic. Likewise, the properties correlating with the class behavior may range from those with assignable numerical values, such as electronegativity, radius, partial charge, or a NMR shift, to more vague concepts, such as the ability to undergo a certain type of reaction.

As suggested above, the most commonly accepted reason for the use of class concepts instead of mathematically explicit functional relationships is that the phenomena in question are too complex to treat rigorously using currently available theories and mathematical concepts. This, in turn, carries the implication that sciences making heavy use of class concepts, such as chemistry and biology, are somehow immature and still await a complete reduction of their subject matter to the rigor and precision of theoretical physics. The most extreme expression of this point of view has been attributed to Rutherford, who is reputed to have dismissed any activity not coming up to the standards of physics as stamp collecting rather than science. Though there is certainly an element of truth in this, there is also a more subtle and fundamental reason for the use of class concepts in chemistry.

The average introductory textbook frequently defines chemistry as the science of matter and the changes it undergoes, a not particularly enlightening statement since it applies with equal

Table 1. Examples of chemical class concepts

|          |                    |            |
|----------|--------------------|------------|
| element  | base               | rare earth |
| compound | salt               | chalcogen  |
| solution | oxidant            | halogen    |
| mixture  | reductant          | ketone     |
| metallic | electrophile       | ester      |
| ionic    | nucleophile        | ether      |
| covalent | hard and soft ions | aldehyde   |
| acid     | alkali metal       | alcohol    |

force to physics and even to biology. Indeed, all science deals with matter in some fashion and what is really of interest is what aspect of matter has been singled out for detailed study by the particular science. Thus physics may be naively defined as the study of the general properties of matter and biology as the study of matter when organized in living systems, but what of chemistry? The answer was provided nearly 90 years ago by Wilhelm Ostwald[11], who suggested that chemistry was the study of matter when organized from the standpoint of specific substances. In Ostwald's opinion the first and most fundamental law of chemistry lies in the observation that the multitude of material bodies around us can be classified not only in terms of size, shape, and function but in terms of substances, that is, the observation that aluminum, as defined by a certain set of specific properties, is recognizable as aluminum, be it in the form of an automobile door or a spoon. Thus on a simple Comtean hierarchy, chemistry is the first science to deal in detail with a particular organizational aspect of matter, the first science to have species, the first science to have a natural history as well as a natural philosophy component, and consequently the first science to make pervasive use of class concepts.

What is being suggested here is that class concepts play such an important roll in chemistry and biology, not because of some immaturity in these sciences, but because they have an added classificatory dimension that is largely missing in physics. In other words, stamp collecting is part of their job. Though biologists are certainly interested in understanding life in terms of the fundamental laws of physics, they are also interested in aspects of living systems for which such reductionism is of limited value, such as establishing the range of present and past living organisms, the appearance of new species via evolution, the correlation of organism size with metabolism or geographical distribution, the relative rates of limb and organ growth during development, etc. Likewise, while chemists are certainly interested in understanding chemical reactivity and structures in terms of quantum mechanics and thermodynamics, they are also interested in discovering new chemical species and in establishing simple correlations between known classes of species. Indeed these tasks are frequently more relevant to the direct solution of chemical problems. Thus the knowledge that a species is an ester, coupled with a knowledge of how substituent effects can modify ester-like behavior, may be infinitely more useful in a practical synthesis problem than a detailed quantum mechanical calculation or at least in retrospectively understanding the experimental behavior[12].

This parallelism with biology has also been noted by some historians of chemistry, who have emphasized that the 18th century chemical revolution was in many ways more Linnean than Newtonian in character[13–17], and more recently by some writers on the philosophy of science like D. W. Theobald, who has pointed out yet another interesting parallel[18]:

Theories are rarely highly controlled by observation in chemistry, since theories are, as I have explained, generally rationalizing constructions covering vast arrays of experimental data, rather than precise mathematical formulations vulnerable to a single quantitative misfortune. . . . In chemistry we are often setting out to understand what has actually occurred rather than deliberately contriving to fulfil predictions. We are, so it has been said, telling 'likely stories' rather than hazarding and testing prophecies. As we shall see, it is this difference of temporal emphasis which aligns chemistry with biology as much as with physics.

Theobald goes on to point out that this heavy use of retrodictive rationalization is closely related to the use of class concepts in both sciences as these are required to organize the factual arrays in the first place. Thus chemistry occupies a curious position in our naive Comtean hierarchy. It is bracketed on both sides by less ambiguous examples of the use of certain scientific tactics. The use of causal mathematical reductionism is better illustrated by the practice of physics, whereas the use of class concepts and retrodictive rationalization of broad factual patterns is better illustrated by the practice of biology. This may in part account for the deluge of books, both scholarly and popular, on the philosophical implications of modern physics and biology, while chemistry remains devoid of any such appeal and chemists rather philistine in their philosophical outlook[19–23].

This rather lengthy philosophical digression aside, the question arises as to what role, if any, symmetry can play in predicting and correlating the class concepts summarized by relation (3). That logical symmetry or analogy plays a role is self-evident as this is the essence of classification. The establishment of the class *alkali metals* automatically implies the existence

of member-invariant class statements, such as M is an air and moisture sensitive metal forming chlorides of the type MCl and sulfides of the type  $M_2S$ . But what of the role of physical symmetry?

#### SORTING MAPS AND CLASSIFICATION

Answering this question requires some way of making relation (3) more explicit, and this may be done by means of an empirical procedure known as a sorting map. To construct a sorting map one requires a set of species whose class assignments are already known (e.g. structure type, miscible–nonmiscible, reactive–nonreactive, etc.) and for which numerical values of the properties thought to determine or correlate with this class behavior are also known (e.g. electronegativity, radius, charge, etc.). Using these properties as the coordinates, the species are then plotted, a different point symbol being used for each class, and the resulting map is then examined to determine whether the properties in question have produced a significant sorting or separation of the classes. If so, the properties are considered to play a significant role in determining the class behavior and best-guess class boundaries are added to the map. These allow for interpolative prediction of class behavior for species other than those used to construct the original map provided that values for each of the property coordinates are known. Though this procedure can in principle be applied to  $n$  simultaneous properties, limitations of spatial visualization normally limit it to two or three. Some typical two-dimensional sorting maps of chemical interest are shown in Figs. 1–4.

The coordinates of the maps in Figs. 1–4 were intuitively selected based on the qualitative bonding concepts used by virtually every chemistry text to verbally rationalize the behavior in question. However, such knowledge is not a necessary prerequisite as computer programs, like the SIMCA method of Wold and coworkers[24], have been developed to systematize the search for relevant property coordinates. Here again a set of species with known class assignments (called a *learning set*) as well as a set of potentially relevant properties is required. The computer then systematically explores the usefulness of different property pairs (using one property per coordinate as well as combinations of properties) as sorting coordinates and mathematically assesses the degree of sorting obtained in each case in order to arrive at the optimal set. This set of coordinates can then be applied to interpolatively predict the class behavior of other species (called the *test set*). Wold *et al.* characterize SIMCA as method for analyzing chemical data in terms of *similarity and analogy* and point out that it is really an example of the more general subject of *pattern recognition* in chemistry.

Though sorting maps allow us to better visualize and systematize the use of class concepts, the maps in Figs. 1–4 do not appear to display any overt symmetry properties. Is this a function of our choice of coordinates or is physical symmetry simply irrelevant to the problem at hand?

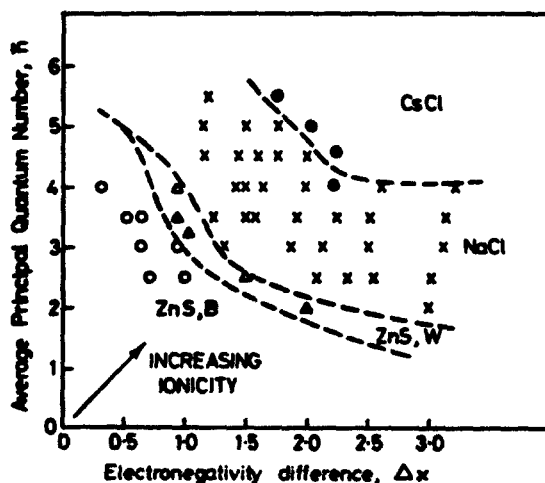


Fig. 1. Structure sorting map for binary AB octet species. Modified from [81].

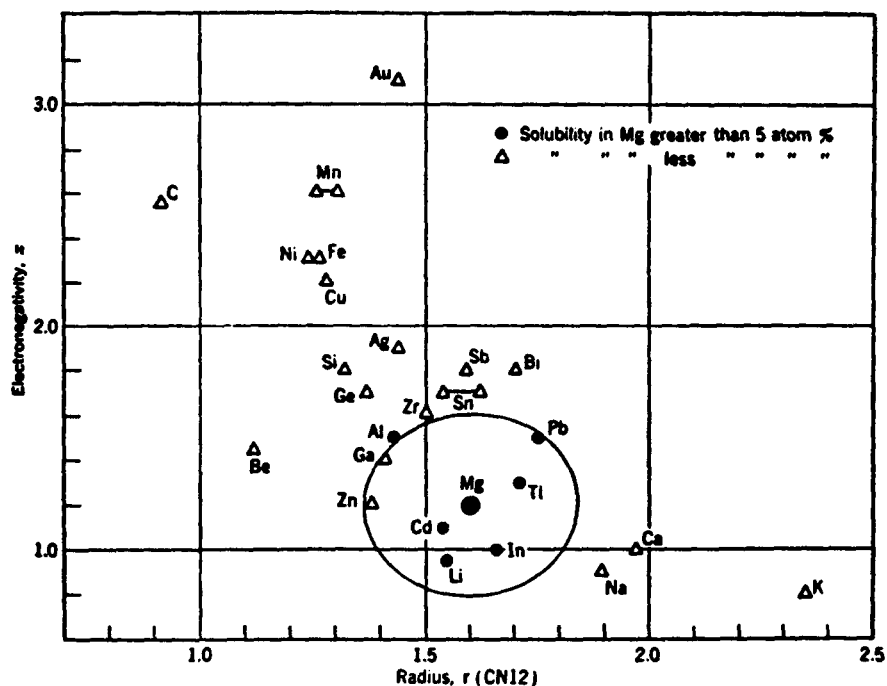


Fig. 2. Solubility sorting map for binary magnesium alloys[82].

The answer lies in the assertion of J. C. Phillips, who has pioneered the application of sorting maps to problems of solid state structures, that the sorting map procedure is in essence a form of "Mendeleevian analysis", i.e. it is identical in spirit to the procedure used by Mendeleev in deducing what is perhaps chemistry's most powerful example of the use of class concepts—the periodic table, and that, in fact, the periodic table itself is really a sorting map[25].

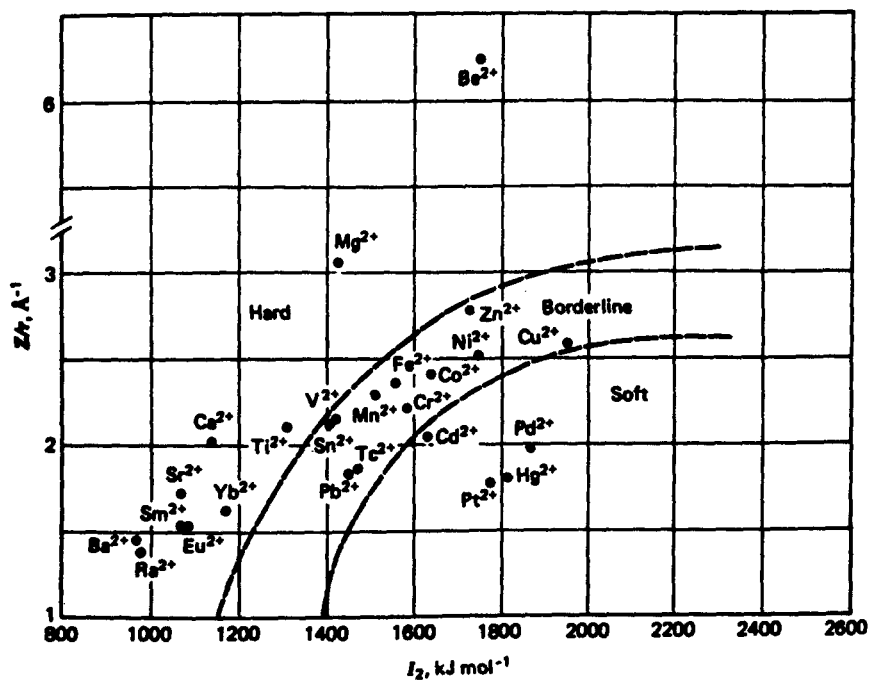


Fig. 3. Sorting map for hard and soft divalent cations. Coordinates are charge to radius ratio and second ionization potential[83].

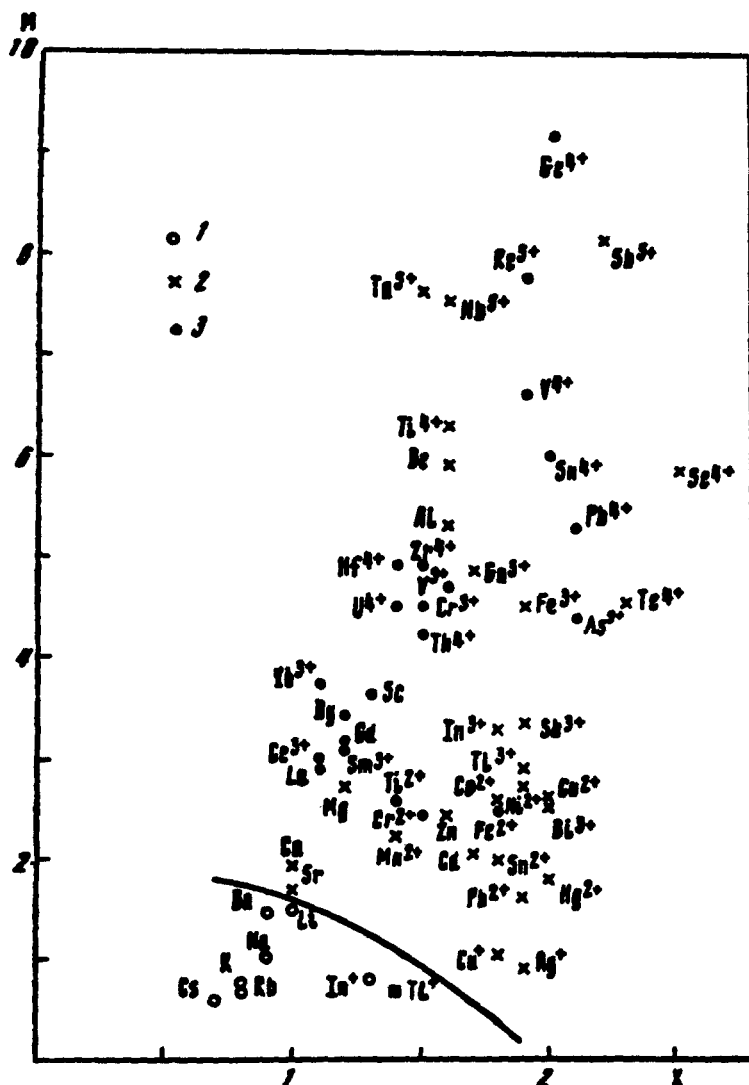


Fig. 4. Sorting map for  $\text{TiCl-MCl}$  binary phase diagrams. Coordinates are charge to size ratio for  $\text{M}^{n+}$  and its electronegativity[84]. Type 1 points indicate eutectic formation, Type 2 indicate compound formation, and Type 3 indicate systems not yet investigated.

#### SYMMETRY AND CLASSIFICATION: THE PERIODIC TABLE

The simplest way to test Phillips' assertion is to plot the atomic number of an element versus the maximum number of available valence electrons per atom (i.e. maximum oxidation state) as shown in Fig. 5. Though seldom thought of in this context, this map, as Mazurs has emphasized[26], is really a type of periodic table and corresponds to a modernized version of the table (Fig. 6) proposed by Mendeleev in his 1889 Faraday Lecture based on a plot of the element's atomic weight versus its maximum oxygen valence[27–28]. As will be seen shortly, more commonly encountered versions of the periodic table may be viewed as symmetry related transformations of this more fundamental form, a step which Mendeleev appears to have taken implicitly in arriving at his original table. However, in the case of the second major originator of the periodic table, Lothar Meyer, this use of a two-dimensional property–property map as a preliminary step appears explicitly in the form of his famous atomic volume–atomic weight plot (Fig. 7)[29]. Indeed, it was not long before chemists realized that virtually any measurable property of an element, or even of the element's compounds, could be used in conjunction with the atomic weight to produce a periodicity map. Some 19th century chemists, like Thomas Carnelly, virtually based their entire careers on the production and study of these maps, and

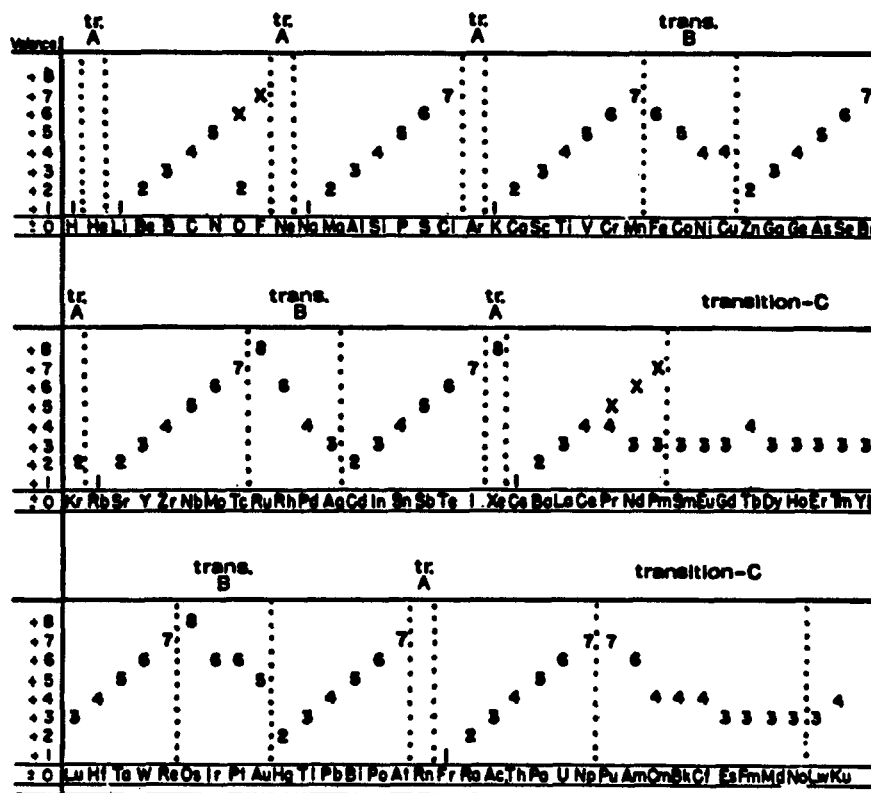


Fig. 5. Plot of maximum oxidation state versus atomic number. Except for the O and F points (see text) this is identical to a plot of the maximum number of valence electrons versus atomic number. This plot is actually continuous and has been broken into three sections solely for reasons of size.

interest in them managed to persist well into the third decade of this century[30]. Some typical examples (modernized by replacing atomic weight by atomic number) are shown in Figs. 8 and 9.

Comparison of the maps in Figs. 1–4 (Type I) with those in Figs. 5–9 (Type II) shows some significant differences. Whereas Type I maps fail to show any recognizable symmetry features and tend to clump members of the same class into the same spatial region, Type II maps show approximate symmetry in the form of an approximate periodicity and tend to place members of the same class not in the same spatial region but rather in symmetry related regions. This, in turn, leads to a significant difference in the predictive abilities of the two types of map. As noted earlier, Type I maps can be used to interpolatively predict a species' class behavior given a knowledge of the values of its sorting map coordinate properties. The reverse process of predicting the values of the coordinate properties from a knowledge of the species' class is much less useful as it can only yield a range of values, though some use of this has been made in establishing upper and lower bounds for solubility parameters[31]. Nothing can, of course, be inferred about whether or not a given class is missing any as yet to be discovered members.

The characteristic patterns arising from the symmetry features of Type II maps, however, radically alter this situation. By restricting a species to a relatively narrow portion of the map's pattern they allow not only interpolative prediction of class behavior from a knowledge of the coordinate properties, but the reverse process, as well as the interpolative prediction of missing class members and their accompanying coordinate properties. This is well illustrated by Mendeleev's famous prediction of the existence and properties of eka-silicon (germanium), eka-boron (scandium), and eka-aluminum (gallium) and by the use of the periodic table to predict both the values of as yet undetermined atomic weights and to modify incorrectly reported values[32–36]. On the other hand, extrapolative use of Type II maps has historically proved as perilous as the extrapolative use of Type I maps, as evidenced both by the difficulties of 19th century chemists in accommodating the rare earth elements and by their failure to anticipate

| Symbols and Atomic Weights |     | The Composition of the Saline Oxides |                  |
|----------------------------|-----|--------------------------------------|------------------|
| B                          | A   | $R_2O_n$                             |                  |
|                            | [6] | [7]                                  |                  |
| H                          | 1   | 1                                    | —                |
| Li                         | 7   | 1†                                   | —                |
| Be                         | 9   | —                                    | 2                |
| B                          | 11  | —                                    | 3                |
| C                          | 12  | —                                    | — 4              |
| N                          | 14  | 1                                    | — 3° — 5°        |
| O                          | 16  |                                      |                  |
| F                          | 19  |                                      |                  |
| Na                         | 23  | 1†                                   | —                |
| Mg                         | 24  | —                                    | 2†               |
| Al                         | 27  | —                                    | 3                |
| Si                         | 28  | —                                    | — 3 4            |
| P                          | 31  | 1                                    | — 3° 4° 5°       |
| S                          | 32  | —                                    | — 3 — 4° 5° 6°   |
| Cl                         | 35½ | 1                                    | — 3 — 5° — 7°    |
| K                          | 39  | 1†                                   | —                |
| Ca                         | 40  | —                                    | 2†               |
| Sc                         | 44  | —                                    | — 3†             |
| Ti                         | 48  | —                                    | — 3 4            |
| V                          | 51  | —                                    | — 3 3 4 5        |
| Cr                         | 52  | —                                    | — 3 3 — 6°       |
| Mn                         | 55  | —                                    | — 2† 3 4 — 6° 7° |
| Fe                         | 56  | —                                    | — 2† 3 — 6°      |
| Co                         | 58½ | —                                    | — 2† 3 4         |
| Ni                         | 59  | —                                    | — 2† 3           |
| Cu                         | 63  | 1†                                   | — 2†             |
| Zn                         | 65  | —                                    | — 2†             |
| Ga                         | 70  | —                                    | — 3              |
| Ge                         | 72  | —                                    | — 2 — 4          |
| As                         | 75  | —                                    | — 3 — 5°         |
| Se                         | 79  | —                                    | — 4 — 6°         |
| Br                         | 80  | 1                                    | — — 5° — 7°      |
| Rb                         | 85  | 1†                                   | —                |
| Sr                         | 87  | —                                    | — 2†             |
| Y                          | 89  | —                                    | — 3†             |
| Zr                         | 90  | —                                    | — — 4            |
| Nb                         | 94  | —                                    | — 3 — 5°         |
| Mo                         | 96  | —                                    | — 3 3 4 — 6°     |
| ~~~~~(1)~~~~~              |     |                                      |                  |
| Ru                         | 101 | —                                    | — 3 3 4 — 6 — 8  |
| Rh                         | 104 | —                                    | — 3 3 4 — 6      |
| Pd                         | 106 | 1†                                   | — 2 — 4          |
| Ag                         | 108 | 1†                                   | —                |
| Cd                         | 112 | —                                    | — 2†             |
| In                         | 113 | —                                    | — 3 3            |
| Sn                         | 118 | —                                    | — 2 — 4          |
| Sb                         | 120 | —                                    | — 3 4 5          |
| Te                         | 125 | —                                    | — — 4 — 6°       |
| I                          | 127 | 1                                    | — 3 — 5° — 7°    |
| Cs                         | 133 | 1†                                   | —                |
| Ba                         | 137 | —                                    | — 2†             |
| La                         | 139 | —                                    | — 3†             |
| Ce                         | 140 | —                                    | — 3 4            |
| Pr                         | 142 | —                                    | — 3 — 5          |
| ~~~~~(14)~~~~~             |     |                                      |                  |
| Yb                         | 173 | —                                    | — 3              |
| ~~~~~(1)~~~~~              |     |                                      |                  |
| Ta                         | 182 | —                                    | — — 5            |
| W                          | 184 | —                                    | — — 4 — 6        |
| ~~~~~(1)~~~~~              |     |                                      |                  |
| Os                         | 191 | —                                    | — 3 4 — 6 — 8    |
| Ir                         | 193 | —                                    | — 3 4 — 6        |
| Pt                         | 196 | —                                    | — 2 — 4          |
| Au                         | 198 | 1                                    | — 3              |
| Hg                         | 200 | 1†                                   | — 2†             |
| Tl                         | 204 | 1†                                   | — 3              |
| Pb                         | 206 | —                                    | — 2† — 4         |
| Bi                         | 208 | —                                    | — 3 — 5          |
| ~~~~~(5)~~~~~              |     |                                      |                  |
| Th                         | 232 | —                                    | — — 4            |
| ~~~~~(1)~~~~~              |     |                                      |                  |
| U                          | 240 | —                                    | — — 4 — 6        |

Fig. 6. Mendeleev's plot of oxygen valence versus atomic weight. Excerpted from a larger table in [28].



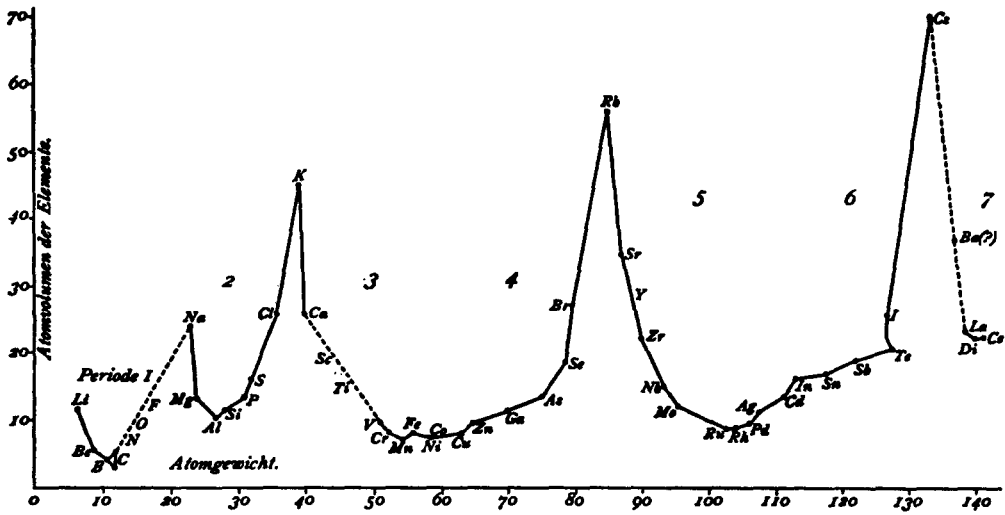
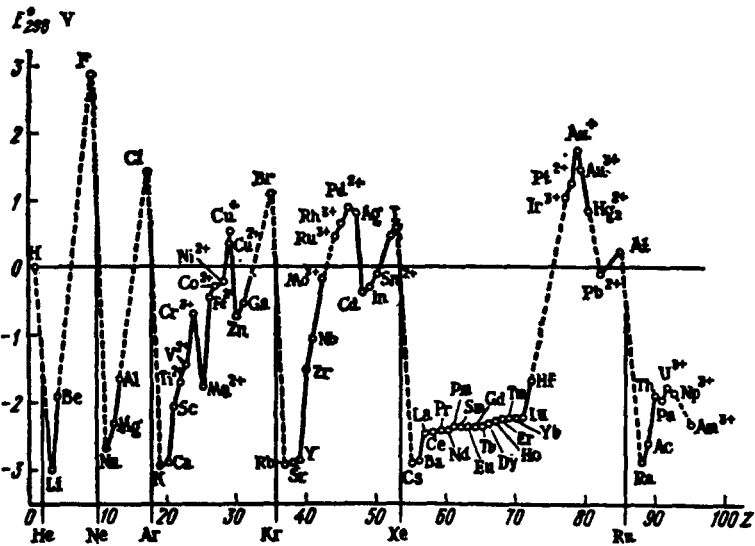
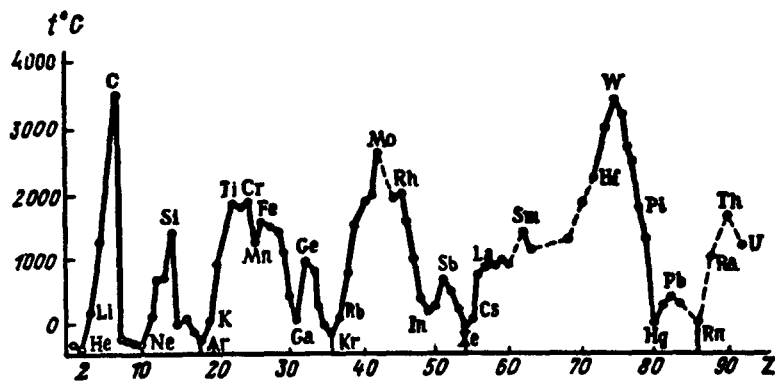


Fig. 7. L. Meyer's atomic volume–atomic weight periodicity map[73].

Fig. 8. Various property–atomic number periodicity maps for the elements in their standard states[85]. *Top*: melting points. *Bottom*: standard electrode potentials.

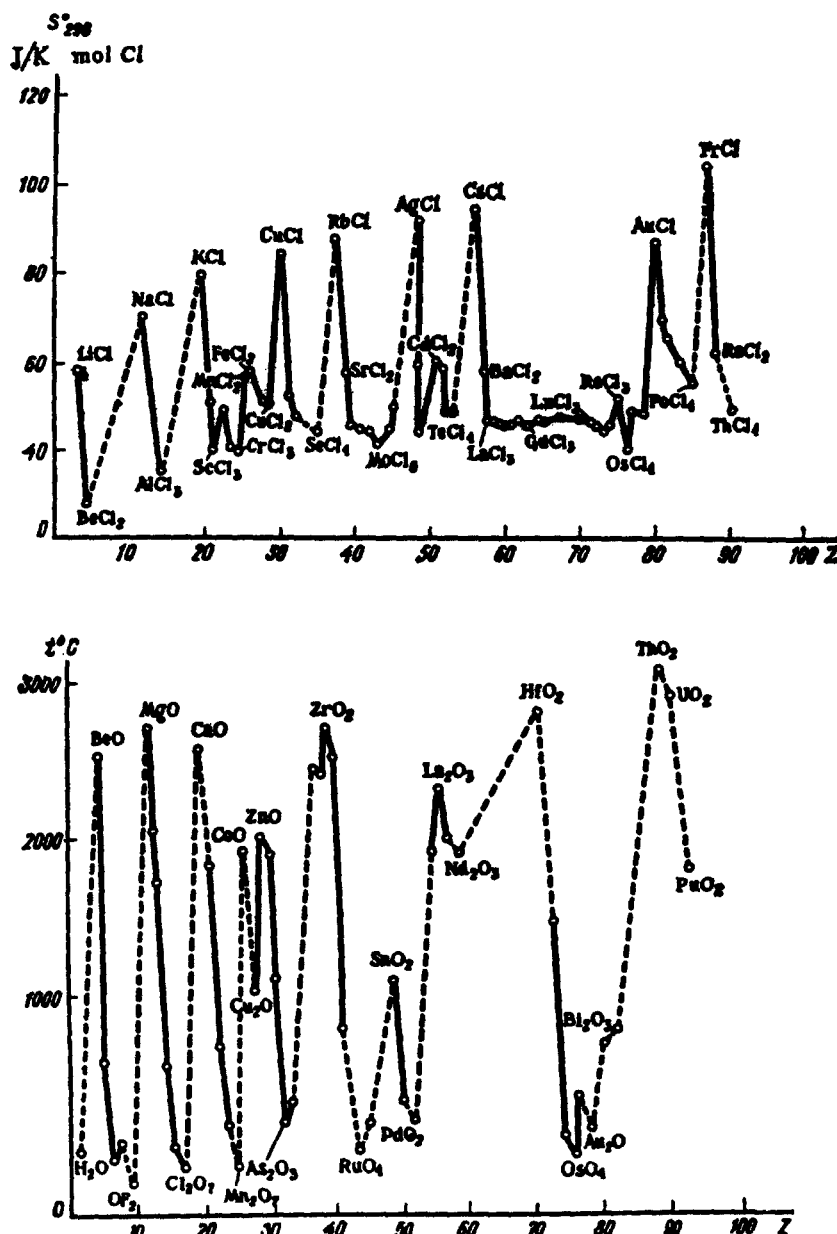


Fig. 9. Various property-atomic number periodicity maps for binary compounds[85]. *Top*: entropies of formation for chlorides. *Bottom*: Melting points of oxides.

the discovery of the noble gases[37]. Indeed, in a recent article on the subject, Karpenko estimates that about 200 "spurious" or nonexistent elements have been reported in the chemical literature since the end of the 18th century, and that the lion's share of them have been associated with attempts to extrapolate sections of the periodic table[38].

Another important aspect of Type II, versus Type I, maps lies in the 19th century chemist's conviction that any significant classification of the elements had to be based on a *natural system* of some sort, that is, it should arise naturally or spontaneously from a study of the elements' properties rather than being based on some *artificial* or arbitrarily selected criterion or theoretical preconception[17,39]. The fact that all Type II periodicity maps lead to essentially the same result and that in principle the classes spontaneously appear on the maps as elements in symmetry related positions, rather than being imposed beforehand, both suggest that the resulting classification is really a natural one. On the other hand, the assertion that the classes can be recognized solely on the basis of symmetry is probably overly ambitious as the symmetry in question is often only very approximate. In actual fact many natural classes of elements, such

as the halogens, the alkali metals, and the alkaline earths, had been recognized by chemists long before the work of either Mendeleev or Meyer, thus substantially simplifying the problem of recognizing class relations on the maps. Inspection of textbooks from around the period 1865–1870 shows that the most common properties used for this purpose were valence and metallic character[40–41]. Though actual maps weren't used because of the lack of a quantitative metallicity scale, it is possible to generate a modern map that essentially reproduces these classifications by using the Herzfeld refractivity–volume ratio as the metallicity coordinate[42]. It would, of course, be historically inaccurate to imply that the development of the periodic table was motivated solely by an empirical search for a natural classification of the elements. Belief in the inherent simplicity and unity of matter, sparked by Prout's hypothesis, and a certain perverse fascination with purely numerical relationships between atomic weights, sparked by Doebereiner's triads, also played a role[32,39]. However, it is interesting that, retrospectively at least, Mendeleev emphasized only the natural classification aspect and even went so far as to deny that the periodic table implied anything about the structure of atoms or the unity of matter[17].

As noted earlier, most common periodic tables are not based directly on the property–atomic number(weight) maps themselves, but on a transformation of these maps whereby the symmetry related members of each class are brought together in a single region of the map. In addition, this transformation is both generalized and qualitative, i.e. it attempts to simultaneously represent the form of as many kinds of property–atomic number maps as possible. However, since not all of these maps display periodicity to the same degree, it is possible to prioritize them by ranking the properties relative to their importance in determining class behavior, with properties like maximum oxidation state and electronic configuration near the top of the list and properties like specific conductivity near the bottom; this, in turn, giving rise to the concept of primary, secondary, and tertiary analogies between elements (see below). The game of constructing a periodic table then becomes one of finding a transformation that will make explicit as many of these analogies as possible. This transformation may range from a simple doubling over of the map on itself at each periodic repetition, to some elaborate three-dimensional extension, but whatever the device, the task has managed to exercise the ingenuity of chemists for more than a century now and has led to literally hundreds of different suggestions.

#### CHOOSING A MODERN PERIODIC TABLE

Numerous books[26,32–36,39,43–48] and reviews[49–50] have been devoted to describing these suggestions, the most thorough being that of Mazurs, who lists more than 700 tables proposed between 1869 and 1970[26]. Mazurs has also developed a detailed classification of these tables, though in selecting a suitable table for modern use only three of his criteria need to be considered:

- (1) three-dimensional (3D) versus two-dimensional (2D) tables,
- (2) short and medium length versus long tables,
- (3) chemical versus electronic configuration tables.

3D periodic tables, or—more properly—periodic models, have frequently been advanced based on the claim that they illustrate continuity more effectively than 2D or planar tables and are capable of making explicit a larger range of analogies because of the greater flexibility inherent in their 3D geometries. The forms most commonly proposed have been based on cylindrical or conical helices with occasional use of lemniscates and even spheres. Mazurs has also shown that most planar tables correspond to various 2D projections of these 3D models. In choosing a table, these 3D models have been ruled out as they are generally expensive to construct and impossible to effectively reproduce in books and on wall charts. In addition, their 3D shapes make it impossible to simultaneously view the entire table, often necessitating a fair amount of spatial manipulation in order to obtain even a general overview. Besides, the concept of continuity is understood by convention in the repeating periods of the planar tables and, as will be seen, it is possible to select a planar table capable of representing not only conventional primary *intra*-group analogies but more subtle secondary *inter*-group analogies as well.

Mazurs uses length to further divide periodic tables into three major categories:

- (1) *short tables* of 8 columns, with the *d*-block interleaved with the *s* and *p*-blocks and the *f*-block set to one side,
- (2) *medium tables* of 18 columns, with the *d*-block fully expanded, but the *f*-block still set to one side,
- (3) *long tables* of 32 columns, with both the *d* and *f*-blocks fully incorporated and expanded.

Short tables have virtually disappeared from use in the United States, where the currently popular form is a medium length block table (which is ironically, but incorrectly, called a long table). In choosing a table, only long 32 column tables have been considered. While there may have been valid reasons for setting the *f*-block elements to one side when their electronic configurations were poorly understood and it was thought that their only oxidation state was III (thus requiring that 30 elements be crammed into two squares of group III), this is no longer the case. The only result of this convention at present is to suggest to students that these elements are somehow dull and unimportant and so can be set to one side and ignored, which is regrettably just what happens in most introductory courses and not a few advanced inorganic courses as well. The only discernable advantage of the currently popular medium block table is that it allows one to make the printing larger. In short, it is time we get rid of what D. A. Johnson has aptly termed the periodic table's "antiquated footnote".

Chemical tables are based primarily on considerations of the elements' chemical and physical properties and especially on the values of their highest oxidation states. In other words, they give precedence to the periodicity displayed by the sorting maps in figures 5 and 6. These considerations are reflected in the common conventions for numbering the classes or groups (thus group VII reflects the VII oxidation state of Cl in  $\text{ClO}_4^-$  rather than the more common I-oxidation state of  $\text{Cl}^-$ ), and in the use of the A and B groups or series in the longer periods to link together elements with common maximum oxidation states but otherwise relatively distinct chemical and physical properties (e.g., Ca(II) and Zn(II)). Electron configuration tables, on the other hand, frequently dispense with family and group labels based on oxidation state, relying instead on the periodic repetition observed in both the nature (*s*, *p*, *d*, or *f*) and number of outer electrons for the isolated gas phase atoms.

Chemical tables have frequently been criticized because of the numerous exceptions to the maximum oxidation state labels. Thus F formally fails to attain the VII state of a group VII element in any of its compounds, and only Ru and Os ever attain the VIII state of group VIII. Even more serious, all of the members of group IB have maximum oxidation states greater than I (i.e., Cu(IV), Ag(III), and Au(V)[51–52]). Finally, as mentioned earlier, this approach has traditionally crammed all of the *f*-block elements into group IIIB, though many are known to exhibit higher oxidation states[53–54]. Ironically, most of these problems stem from a simple failure to update what are essentially late 19th century labels in light of recent chemical advances. As will be seen shortly, when this is done most of these problems disappear. On the other hand, it should be pointed out that similar objections can be raised concerning electronic configuration tables and labels based on idealized filling rules, as nearly 20% of the elements have ground state configurations that violate these rules. An even graver problem is He, which should be classed with the alkaline earth metals according to its electronic configuration rather than with the noble gases as indicated by its chemical and physical properties[55–56]. What all of this means is simply that the periodic table is a true natural classification based on the simultaneous consideration of as many property–atomic number maps as possible. Since none of these maps exhibits perfect periodicity, the result is the best "averaged" representation and one which is consequently imperfect with regard to any single property considered in isolation, be it maximum oxidation state or electronic configuration. In short, the table should combine the best features of both the traditional chemical table and the more recent electronic configuration tables.

Based on the above criteria—namely that the table should be a 32 column planar table that optimally combines the advantages and information content of both the traditional chemical table and the modern electronic configuration table—it was felt that the best choice, from among

the multitude described by Mazurs, was the modified step-pyramid table shown in Fig. 10. This form of the table was actually proposed as early as 1882 by Bayley[57], who, however, used vertical rather than horizontal periods (Fig. 11), and again, apparently quite independently, by the Danish thermochemist J. Thomsen[58] in 1895 (Fig. 12). Though used in a modified medium length 18 column form by a variety of chemists in the early part of the century (Summarized in [59]), it did not attain any real popularity until Bohr[60–61] revived Thomsen's original long form in the early 1920s in conjunction with his work on atomic spectra (Fig. 13). As a consequence the table is frequently referred to as the Thomsen–Bohr table, though it should perhaps be more accurately called the Bayley–Thomsen–Bohr table.

#### ADVANTAGES OF THE STEP-PYRAMID TABLE

In addition to its overall aesthetic appeal, resulting from its symmetric shape, the step-pyramid table has a number of distinct advantages over the currently popular medium length block table, both from the electronic configuration standpoint and from the standpoint of a traditional chemical table.

##### *Advantages as an electronic configuration table*

Though the columns of the step-pyramid table are not explicitly labeled with electronic configurations, these and other structure information for isolated gas phase atoms are implicit and relatively easy to extract. The uses and advantages from this point of view can be succinctly summarized as follows:

(1) The elements are explicitly classified by electronic type as *s*, *p*, *d* and *f*-block elements. These blocks are indicated on the table by thick dividing lines and by labels at the top and bottom of each block. Coloring each block and its connecting solid diagonals a different color brings these divisions into striking relief.

(2) Because the *f*-block elements have been fully inserted into the table in their natural order of appearance, the ideal electronic configurations of each kind of atom can easily be obtained simply by counting the squares from H to the element in question and inserting the appropriate type of electron per square as indicated by the block labels. The required quantum number *n* in each case is identical to the period number of the square in question.

Periods

1 H He

2 Li Be B C N O F Ne

3 Na Mg Al Si P S Cl Ar

4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe

6 Ce La Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

7 Fr Ra Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr Rf Hs Mt 106 107 108 109 110 111 112 113 114 115 116 117 118

Groups

I A II A III A IV A V A VI A VII A transition-C III B IV B V B VI B VII B trans. B II B III A IV A V A VI A VII A tr. B

ns np (n-1)d (n-2)f

Fig. 10. The modified Bayley–Thomsen–Bohr step-pyramid periodic table.

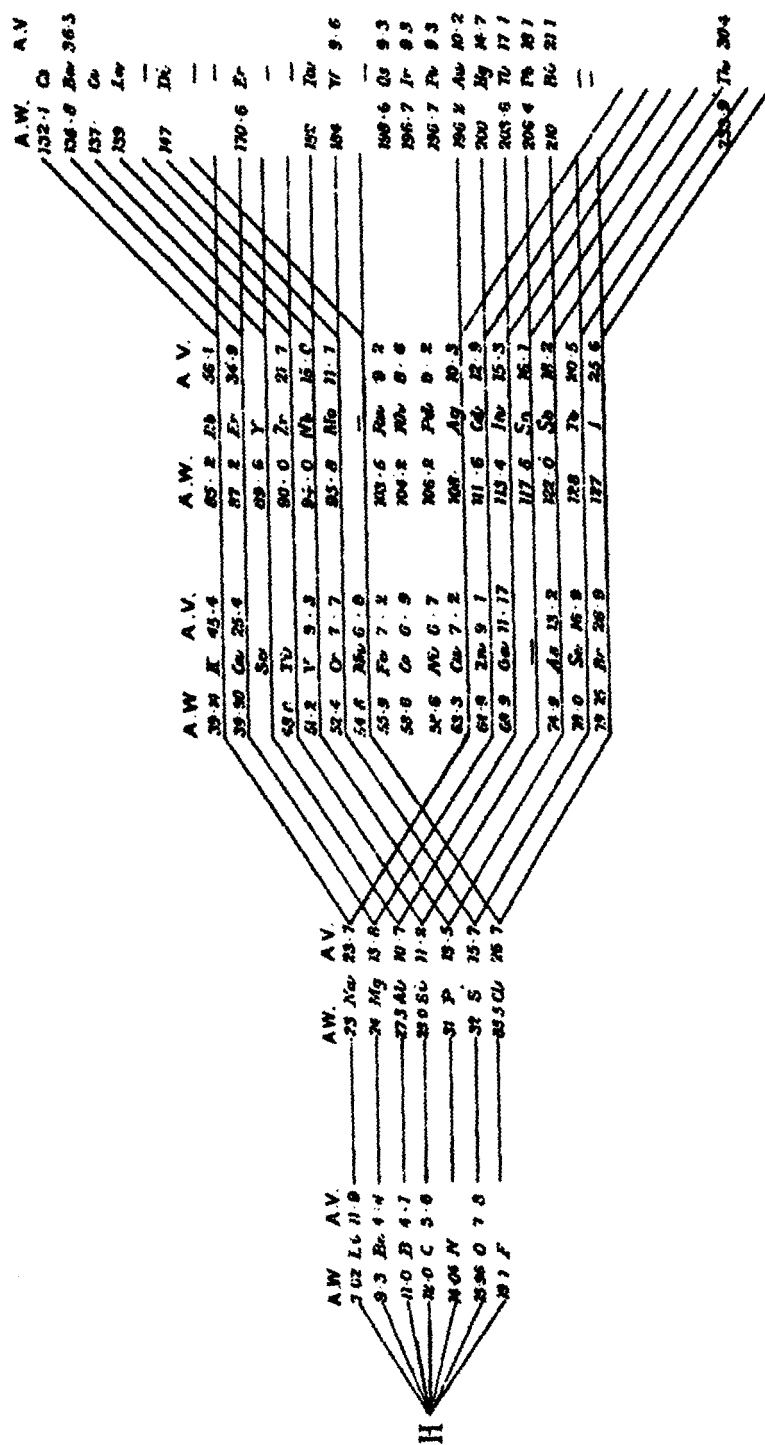


Fig. 11. Bayley's 1882 table[57].

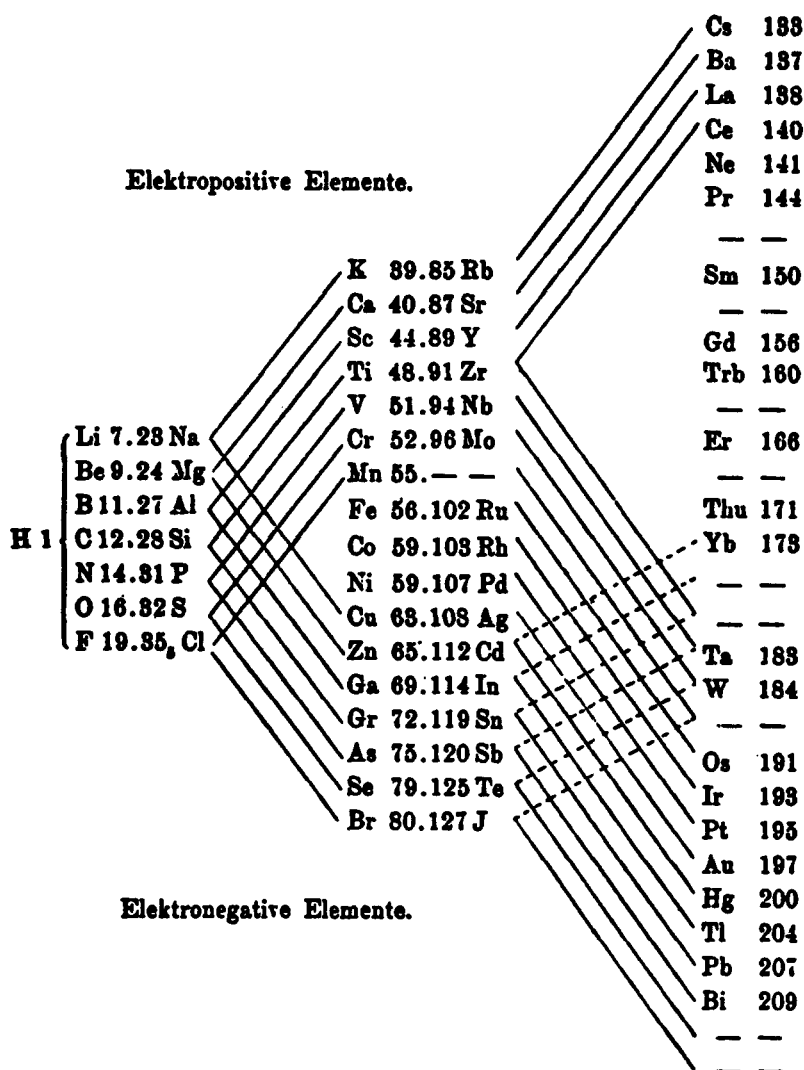


Fig. 12. Thomsen's 1895 table[58].

(3) The real spectroscopic ground state configuration of the isolated gas phase atom, when different from the ideal configuration, is obtained from the number of dots in the upper right hand corner of the element's square. In the case of *d*-block elements, these indicate the number of *ns* electrons in the ideal configuration that must be converted into  $(n - 1)d$  electrons in order to obtain the real configuration. In the case of the *f*-block elements, they indicate the number of  $(n - 2)f$  electrons that must be converted into  $(n - 1)d$  electrons.

(4) In contrast the currently popular block table, the step-pyramid table incorporates the recent conclusion that La and Ac should be classified as *f*-block elements with irregular configurations, whereas Lu and Lr should be classified as the first members of the *d*-block in periods 6 and 7[62].

(5) The table not only classifies elements into groups according to their outer electronic configurations, but further subdivides the elements within each group of the  $p$ ,  $d$  and  $f$ -blocks according to the electronic structures of their cores by placing each core type on a different step of the pyramid. Thus N, P, As, Sb, and Bi are all placed in group VA by virtue of their common outer  $ns^2np^3$  configurations. However, Bi, on the bottom step, has a [Noble Gas]( $n - 2$ ) $f^{14}(n - 1)d^{10}$  core, Sb and As, on the second step, have a [Noble Gas]( $n - 1$ ) $d^{10}$  core, and P and N, on the third step, have just a [Noble Gas] core. In the case of the  $p$ -block and the period 6  $d$ -block elements, especially, these core variations lead to variations in chemical behavior associated with the  $d$ -block and  $f$ -block (or so-called lanthanide) contractions. As a result, the

The diagram shows Bohr's 1922 periodic table, which is a step-like arrangement of elements. The elements are organized into columns and rows, with lines connecting them to show the periodicity. The elements are labeled with their atomic numbers and chemical symbols. The arrangement is as follows:

| Period | Group 1 | Group 2 | Group 3 | Group 4 | Group 5 | Group 6 | Group 7 | Group 8 | Group 9 | Group 10 | Group 11 | Group 12 | Group 13 | Group 14 | Group 15 | Group 16 | Group 17 | Group 18 |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1      | 1 H     |         |         |         |         |         |         |         |         |          |          |          |          |          |          |          |          |          |
| 2      | 2 He    |         |         |         |         |         |         |         |         |          |          |          |          |          |          |          |          |          |
| 3      | 3 Li    | 4 Be    | 5 B     | 6 C     | 7 N     | 8 O     | 9 F     | 10 Ne   |         |          |          |          |          |          |          |          |          |          |
| 4      | 11 Na   | 12 Mg   | 13 Al   | 14 Si   | 15 P    | 16 S    | 17 Cl   | 18 Ar   |         |          |          |          |          |          |          |          |          |          |
| 5      | 19 K    | 20 Ca   | 21 Sc   | 22 Ti   | 23 V    | 24 Cr   | 25 Mn   | 26 Fe   | 27 Co   | 28 Ni    | 29 Cu    | 30 Zn    | 31 Ga    | 32 Ge    | 33 As    | 34 Se    | 35 Br    | 36 Kr    |
| 6      | 37 Rb   | 38 Sr   | 39 Y    | 40 Zr   | 41 Nb   | 42 Mo   | 43 Tc   | 44 Ru   | 45 Rh   | 46 Pd    | 47 Ag    | 48 Cd    | 49 In    | 50 Sn    | 51 Sb    | 52 Te    | 53 I     | 54 Xe    |
| 7      | 55 Cs   | 56 Ba   | 57 La   | 58 Ce   | 59 Pr   | 60 Nd   | 61 Pm   | 62 Sm   | 63 Eu   | 64 Gd    | 65 Tb    | 66 Dy    | 67 Ho    | 68 Er    | 69 Tm    | 70 Yb    | 71 Lu    | 72 Hf    |
| 8      | 73 Ta   | 74 W    | 75 Re   | 76 Os   | 77 Ir   | 78 Pt   | 79 Au   | 80 Hg   | 81 Tl   | 82 Pb    | 83 Bi    | 84 Po    | 85 At    | 86 Rn    |          |          |          |          |
| 9      | 87 Fr   | 88 Ra   | 89 Ac   | 90 Th   | 91 Pa   | 92 U    |         |         |         |          |          |          |          |          |          |          |          |          |

Fig. 13. Bohr's 1922 table[60].

lower member of a step tends to resemble the upper member of the step below more closely than it resembles the other member of the same step (e.g., Al resembles Ga more than it resembles B, Zr resembles Hf more than it resembles Ti, etc.). Thus the steps group elements more by similarity of total electronic configuration than by similarity of chemical properties.

#### Advantages as a chemical table

Following traditional chemical tables, the step-pyramid table uses both maximum oxidation state group numbers and A–B group modifiers. Its advantages over other chemical tables lie in its extension of the group concept to the *f*-block, resulting in an additional C series of groups to parallel the traditional A–B series; its use of an updated set of oxidation labels that eliminate most the exceptions found in the current system; and, most importantly, in its geometric ability to explicitly indicate not only primary intra-group analogies, but the secondary inter-group analogies that gave rise to the A–B modifiers in the first place, as well as certain tertiary analogies.

The original intent of the A–B group modifiers was to distinguish between elements in the long periods of the table having similar maximum oxidation states but otherwise relatively distinct chemical and physical properties (e.g. Mn and Br in period 3). As such, the order in which these labels were applied was to a certain extent arbitrary, at least as far as the 19th century chemist was concerned. With the advent of electronic configurations, however, it became apparent that this duplication resulted from two elements having the same total number of valence electrons, but otherwise distinct arrangements or configurations of these valence electrons (i.e.  $ns^2(n-1)d^5$  versus  $ns^2np^5$ ). In light of this knowledge, there is little doubt that the American A–B convention, which associates A with those elements deriving their valence electrons solely from the outermost *n* shell and B with those elements capable of (but not necessarily) also employing electrons from the *n* – 1 shell, is superior to the European convention, which retains the arbitrary nature of the original 19th century scheme. In other words, the American convention maximizes the correspondence between the chemical and electron configuration tables, whereas the European convention doesn't. A similar logic lies behind num-



bering the periods 1–7 rather than 0–6 as in some older tables. Relative to a chemical table this choice is arbitrary, whereas relative to a configuration table it isn't, since the first choice allows one to associate the period number with the primary quantum number  $n$  for the atoms of the period, whereas the second choice doesn't. Consequently the first choice maximizes the correspondence between the two types of tables. Because the step-pyramid table also attempts to assign group numbers to the  $f$ -block elements, the above reasoning requires the existence of a third "C series" of groups, where C indicates an element capable of (but not necessarily) also employing  $n - 2$  shell electrons as valence electrons.

The logic behind the revised oxidation-state labels is best seen by examining the maximum oxidation state–atomic number sorting map in Fig. 5. This shows a series of repeating cycles within which the maximum oxidation state progressively increases and numerically corresponds to the number of valence electrons lying outside the nearest noble gas or pseudo-noble gas core. These repeating cycles of progressive increase are, in turn, separated or bridged by shorter "transitional" series of elements within which the oxidation state variation is highly erratic and no longer shows a necessary correspondence with the number of "outer" electrons. Not all of the progressive cycles and transitional bridges are equivalent. In the A series the transitions occur with a single element (a noble gas) and the maximum oxidation state falls from a value of seven (e.g. Cl) to a value of one (e.g., K) as the cycle repeats. In the B series, on the other hand, the transitions occur more gradually, requiring four steps (e.g., Fe, Co, Ni, and Cu), and the maximum oxidation state falls from a value of seven (e.g., Mn) to a value of only two (e.g., Zn) as the cycle repeats. Finally, in the C series the transitions become even more gradual and erratic, requiring nine steps (e.g., Pu–No), and the maximum oxidation state falls from seven (e.g., Np) to a value of only three (Lr) and is not complete until the end of the  $f$ -block. Thus, although the proposed A–B–C series and transitions do not exactly parallel one another, they do form a systematic pattern of variation, the transitions becoming progressively longer (1, 4, and 9 elements respectively) and the minimum oxidation state at the end of each transition progressively greater (I, II, and III respectively).

Use of the terms transition or transitional elements in the above context actually corresponds to the historically correct usage, as these terms were originally applied solely to the group VIII triads (i.e., Fe–Co–Ni in period 4, Ru–Rh–Pd in group 5, and Os–Ir–Pt in period 6) rather than to  $d$ -block elements in general with incomplete  $d$  subshells[63]. As such, the terms were intended to suggest that these triads represented a gradual transition between the end of one cycle or period of increasing maximum oxidation states (e.g., K(I) to Mn(VII) in  $\text{MnO}_4^-$ ) and the beginning of another (e.g., Cu(I) to Br(VII) in  $\text{BrO}_4^-$ ). These elements were very similar in their atomic weights and chemical properties, exhibited variable oxidation states—reflecting their transitional natures, and frequently resisted attack by common reagents (hence the name noble metal for the heavier members). When the rare or noble gases were later discovered, it was suggested that they too were transition elements, as they also bridged the gap between successive cycles of increasing maximum oxidation states[64]. Indeed, they were considered to be more perfect examples of transitional species as the contrast between the elements at the end and beginning of successive periods (e.g., Cl(VII) and K(I)) was much sharper than that between elements at the beginning and end of successive series (e.g., Mn(VII) and Cu(I)), and the transition occurred in these cases in one step rather than three. Finally, the noble gases appeared to be chemically inert, and thus represented truly "noble" elements, in contrast to the known reactivity of the so-called noble metals. This view of the group VIII triads as imperfect "noble gases" was also used by later writers on the periodic table[65] and the observation that they should really be extended to transitional tetrads by incorporating Cu, Ag, and Au was first pointed out by Jorgensen[55–56]. Indeed, the knowledge of these elements' oxidation states was already sufficiently developed in Mendeleev's day to show the untenability of the group IB concept, and its inclusion in the periodic table is really an attempt to idealize the symmetry. Not only is I not the maximum oxidation state exhibited by these three elements, except for Ag(I), it is not even the most common oxidation state.

In terms of the modern electronic theory of atomic structure, the failure of these transitional or bridging elements to show any simple relation between maximum oxidation state and the number of electrons lying outside the nearest noble gas or pseudo-noble gas core, as well as the rapid fall in the maximum oxidation state from the value of seven observed just before the

transition to the value observed after its completion, can both be interpreted as indicating that the outer electrons in these elements are undergoing a rapid transition from the status of valence electrons to the status of core electrons and consequently exhibit a certain ambiguity in their behavior. Even in the case of the *f*-block elements, where this transition is much more leisurely and is not really complete before the end of the block, there is evidence of this process in the increased stability of Yb(II) and No(II) relative to the more common III + oxidation state[51].

Examination of the sorting map in Fig. 5 shows only five exceptions to the revised labeling scheme (O, F, Pr, Nd, and Pm). Since our true concern with group numbers is in identifying the maximum number of accessible valence electrons and we are only using maximum oxidation state as a convenient indicator of that number, the O and F exceptions are really only formalities of our conventions for assigning oxidation states and are due to the fact that these elements are two of the most electronegative in the table. There is little doubt that in solid state oxides and fluorides, despite the II- and I-oxidation states, all six valence electrons of oxygen and all seven of fluorine are implicated in bond formation (e.g., ZnO). On the other hand, if one were to extend the series to a maximum oxidation state of VIII rather than VII, as done in the past, the number of real exceptions would increase to eleven and there would be no A transition to parallel the B and C transitions. Finally, if one were to retain Cu, Ag, and Au as group IB and add analogous groups IC(Yb, No) and IIC(Tm, Md), as done by Mazurs[26], the exceptions would increase to 18. Thus the proposed scheme extends the oxidation state labels to the *f*-block while simultaneously removing most of the previous exceptions from the *s*, *p* and *d*-blocks. (For a discussion of alternative classifications of the *f*-block see [66–69].)

Use of the revised labeling scheme is not, of course, limited to the step-pyramid table, as it may be used in conjunction with any suitable long form 32 column table. Rather, as mentioned earlier, the particular advantage of the step-pyramid table over other 32 column tables lies in its ability to explicitly indicate not only primary intra-group analogies like other tables, but secondary inter-group analogies and tertiary analogies as well (Table 2). A primary analogy between two elements means that the elements in question have not only the same maximum number of outer valence electrons (defined as those lying outside the first noble gas or pseudo-noble gas core) but the same idealized arrangement or configuration for these electrons and, by implication, a closely related pattern of lower oxidation states as well. Such elements fall in the same *group* as distinguished by both the group number and modifier (e.g. IA, IIIB, VC, etc.). This relationship is indicated by placing the elements in the same column or by connecting offset columns by solid diagonal tie-lines. This is the only level of analogy explicitly indicated on most tables.

A secondary analogy between two elements means that the elements in question have the same maximum number of valence electrons but differing valence electron configurations. Consequently, although the elements exhibit certain similarities and analogies when in their maximum oxidation states, these do not necessarily extend to lower oxidation states. Such elements belong to the same *family*, as indicated by identical group numbers, but to different groups of that family, as indicated by different group modifiers (e.g., In family III: groups IIIA, IIIB, and IIIC). Thus the resulting secondary intra-family analogy is inter-group rather than intra-group in nature and is explicitly indicated on the table by connecting the elements in question with a dotted diagonal tie-line.

Although other forms of the table have continued to retain the A–B group modifiers, they do not explicitly indicate the inter-group analogies that gave rise to these labels in the first

Table 2. Levels of analogy in the step-pyramid table

| Order of Analogy | Nature of Analogy                           |  |                                | Type of Tie-Line |
|------------------|---|--|--------------------------------|------------------|
|                  | Same Idealized Outer Electron Configuration | Same Maximum No. of Valence Electrons <sup>†</sup> | Related Lower Oxidation States |                  |
| Primary          | Yes   | Yes  | Similar Pattern                | Solid            |
| Secondary        | No  | Yes  | Not Necessarily                | Dotted           |
| Tertiary         | No  | No   | At least One                   | Broken           |

<sup>†</sup>Defined as the number of electrons lying outside of the nearest noble gas or pseudo-noble gas core.

place. As a consequence the use of these secondary analogies has become almost a form of "lost knowledge" to most users of the table, leading to an inability to decide on the best A-B convention[70] and to IUPAC's regrettable decision to abandon these labels completely[71]. In contrast, the step-pyramid table, as Bayley noted nearly 100 years ago, allows one to construct a "kinship" chart for each family of elements that explicitly traces both the primary and secondary relations, with separate branches corresponding to each primary group, and kinks within each group corresponding to different core varieties[57]. These charts may either be extracted from the table as in Fig. 14 or traced directly on the table itself by coloring in the proper squares and diagonals (both solid and dotted).

It is important to emphasize that, with few exceptions, secondary inter-group analogies are only valid for maximum oxidation states. This is the only situation for which the oxidation number is an accurate reflection of the total number of active valence electrons. For lower oxidation states the number only reflects those valence electrons committed to heteronuclear bonding and other valence electrons may be present as stereoactive lone pairs or involved in

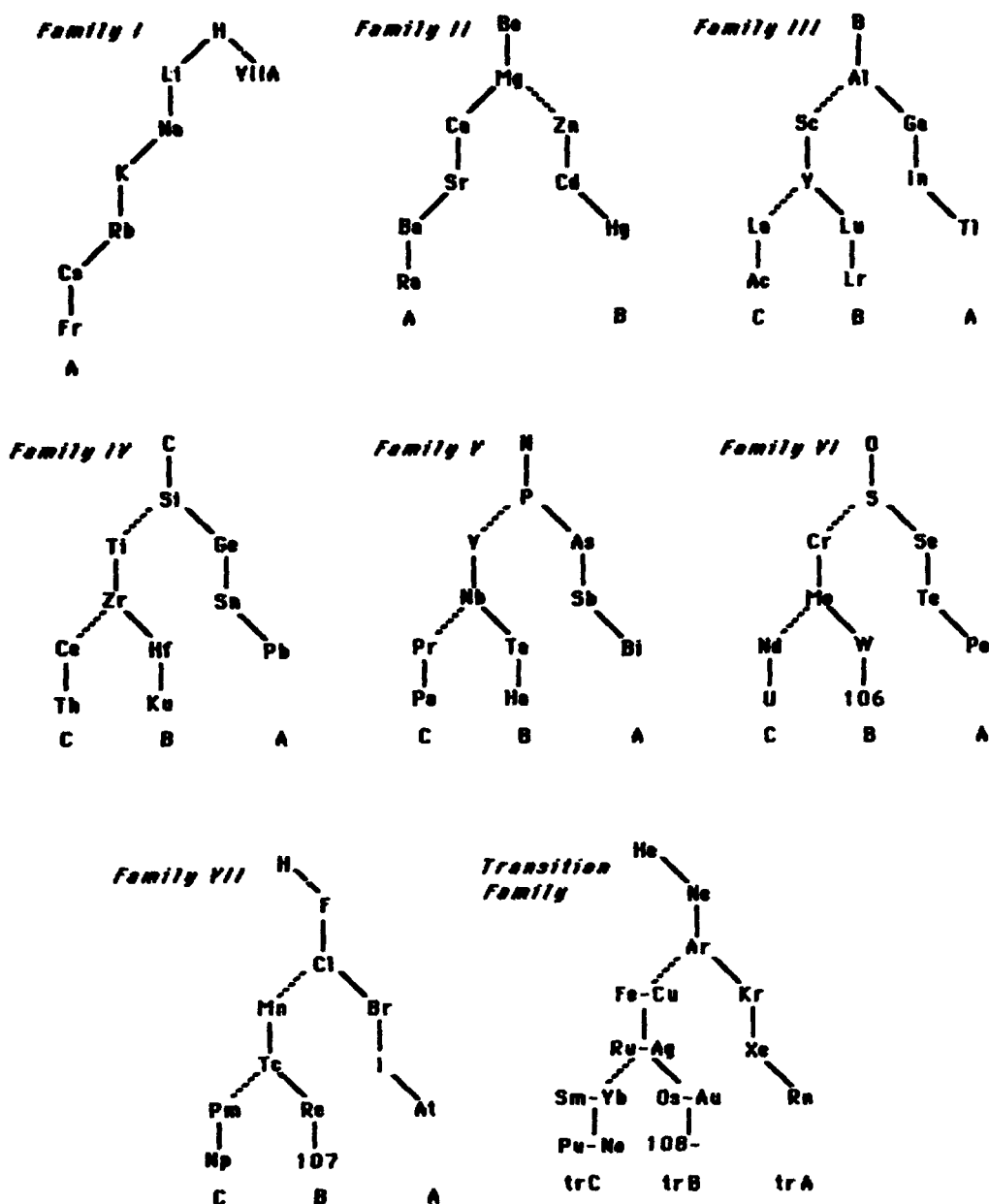


Fig. 14. Family kinship charts extracted from the step-pyramid table.

homonuclear catenation, thus leading to totally unrelated structures and reactivity patterns for the species being compared. Though, at first glance, it might seem absurd to compare Mn with Cl or Cr with S, similarities do exist for the highest oxidation states. Thus  $\text{Mn}_2\text{O}_7$  and  $\text{Cl}_2\text{O}_7$  have similar structures and permanganates ( $\text{MnO}_4^-$ ) and perchlorates ( $\text{ClO}_4^-$ ) are often isomorphous. Likewise,  $\text{CrO}_3$  and the chain form of  $\text{SO}_3$  have similar structures and chromates ( $\text{CrO}_4^{2-}$ ) and sulfates ( $\text{SO}_4^{2-}$ ) are isomorphous. It is also worth reminding oneself that large differences can occur within the same group—compare, for example, the properties of elemental  $\text{N}_2$  with those of Bi, or C with Pb, or even those of  $\text{CO}_2$  with  $\text{SiO}_2$ .

A tertiary analogy between two elements means that the elements in question exhibit certain similarities when at least one of the elements is in a lower oxidation state but that the elements have neither the same maximum number of valence electrons nor the same electronic configurations (e.g., Fe(III) and Al(III)). These are indicated by connecting the two elements with a broken diagonal tie-line. However, since this level of analogy is legion and highly erratic in its variation across the table, it is not for the most part explicitly indicated, though the table is capable of doing so. The sole exception is the analogy between H(I-) in its saline hydrides and the halogens X(I-) in their saline halides. This has been traditionally indicated either by floating H in space above the rest of the table or by simultaneously placing it at the heads of both groups IA and VIIA. The step-pyramid table, on the other hand, is able to indicate this analogy without removing H from the body of the table or duplicating its position.

It is also sometimes argued that H is placed above the table because it is totally unique in its properties. While it is true that H is unique relative to other IA elements, this is really a reflection of a systematic variation in the periodic table which shows that the elements in the first row of any new electronic block tend to show abnormalities relative to the elements in later rows of the same block, and that the degree of divergence decreases in the order  $s$ -block  $\gg p$ -block  $> d$ -block  $> f$ -block. Thus He, like H, is unique relative to other  $ns^2$  elements, a fact that places it among the noble gases rather than the alkaline earth metals (Note, however, that the definition of valence electron used in Table 2 lessens this problem by defining this number as 0 for the noble gases, thus placing helium's abnormality in its core structure). Likewise, C–F are quite distinct compared to other  $p$ -block elements, and the same is true to a lesser degree for Sc–Zn relative to the heavier  $d$ -block elements. In the  $f$ -block, on the other hand, the differences are less pronounced, though all of the oxidation state exceptions occur in the first row of the block. These systematic variations are frequently implicit in the organization of topics adopted by descriptive inorganic texts based on the periodic table (see, for example, the chapter headings in reference[51]). Note also that the traditional group IB analogy is really a tertiary rather than a primary analogy and that comparison of Cu(I), Ag(I), and Au(I) with the alkali metals is no more dictated by maximum oxidation states and electronic configurations than comparison with Tl(I) or Ga(I).

In summary then, the step-pyramid table does appear to be quite successful at accomplishing the goal outlined in the last section of optimally combining the best features of both the chemical and electronic configuration tables. This, however, raises the further question of whether or not these two types of tables are redundant. Jorgensen[55–56] has in fact explicitly raised this question and has concluded that this is not the case—a conclusion supported by the continued popularity of chemical tables. The structure of the table actually reflects idealized configurations and, despite attempts at half-subshell rationales, deduction of observed gas phase spectroscopic ground states from the table requires supplementary information such as the dots used in Fig. 10. Likewise, the relation between the spectroscopic table and chemical properties is not always straightforward, at least for the transitional elements.

Mendeleev was fond of making a distinction between simple bodies and elements. By the former he meant the elements in their bonded standard states and by the latter presumably the free atoms themselves. His point was that the explanation of the periodicity displayed by “simple body” sorting maps like those in Fig. 8 or by compound sorting maps like those in Fig. 9 lay ultimately in the properties of the true “real elements” rather than in those of the simple bodies and compounds “visually known to us” (see especially footnotes 11 and 17 of Chapter 15 of [28]). Today we are, of course, able to directly measure properties of the isolated gas phase atoms and construct corresponding property—atomic number maps like those in Fig. 15. The

assumption, however, that the maps in Fig. 15 “explain” those in Figs. 8 and 9, and consequently that the periodic table need only encode information about free atoms, is oversimplified. The structures of free atoms do not in fact persist in the structures of standard state simple bodies or compounds. Rather it is the valence electrons and cores that persist and which constitute our “true” elements. The value of free atom sorting maps is that free atoms are the simplest chemically interesting structures formed by our “true” elements and consequently their structures and periodicity are relatively easy to rationalize in terms of the properties of their constituent cores and valence electrons. These free atom maps can, in turn, be *correlated* with the more complex periodicity maps for standard state elements and compounds, though they do not really *explain* them in the sense outlined above. In short, we have available to us a class of periodicity maps that the 19th century chemist lacked and one that is simpler in its underlying structure (Fig. 16). However, the conclusion that the periodic table itself should reflect information about all three classes of maps remains intact and suggests that the American Chemical Society’s recent proposal to replace the oxidation state labels with a simple 1–18 numbering system will result in a loss of explicit information[71]. In addition, despite claims to the contrary, such a scheme would be awkward when used in conjunction with a 32 column table[72].

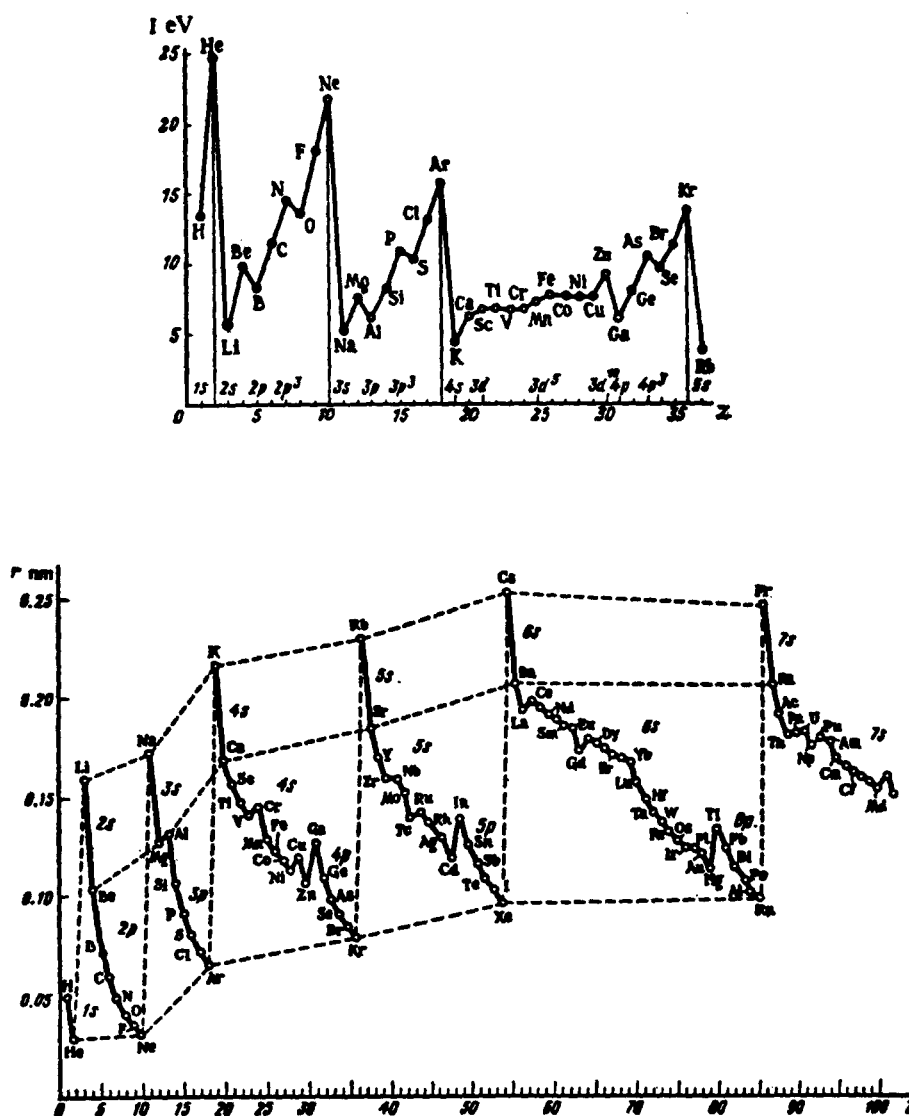


Fig. 15. Various property—atomic number periodicity maps for gas phase atoms[85]. Top: first ionization potential. Bottom: radius.

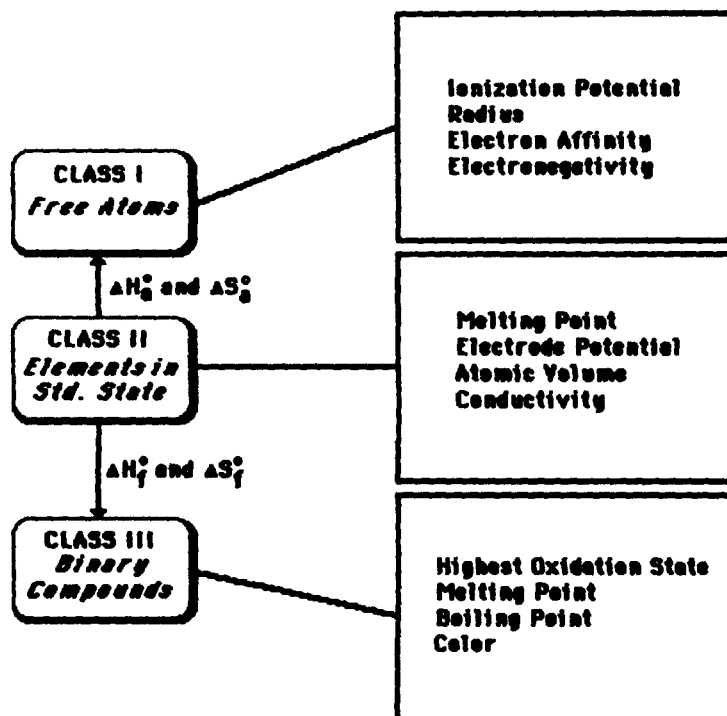


Fig. 16. The relationship between the three classes of property-atomic number periodicity maps. Maps can be constructed not only for the properties listed in each case but also for the connecting properties.

#### ABUSES OF SYMMETRY

In discussing the periodic table in the 1911 edition of his famous textbook, Nernst[73] commented that:

At first the establishment of the periodic system was regarded as a discovery of the highest importance, and far-reaching conclusions as to the unity of matter were expected from it; more recently a disparaging view has been taken of these noticeable, but unfruitful, regularities. One now often finds them underrated, which is intelligible enough, since this region, which especially needs scientific tact for its development, has become the playground of dilettante speculations, and has fallen into much discredit.

Anyone who has reviewed current papers dealing with this subject or who has been the recipient of unsolicited tables knows that there is still some truth to Nernst's complaint. Indeed, one is tempted to assert that, with the demise of alchemy, the construction of revolutionary new periodic tables has become the favorite expression of eccentricity in chemistry, almost on par with perpetual motion machines in physics and trisecting angles in mathematics. The temptation to read more into the shape of the table than is really there is almost overwhelming. Even someone as great as Werner was tempted[74]. Having postulated a missing element between H and He, he decided to perfect the symmetry of his table by guaranteeing that rows of differing length always occurred in pairs. Consequently he further postulated a row of three missing elements lying above the H-X-He row. Others have been luckier. Thus Bayley correctly postulated 31 elements (sans the noble gases) for period 6 (recall Fig. 11) though his reasoning appears obscure, leading van Spronsen to comment that Bayley apparently "designed his system on primarily aesthetic grounds", i.e. on the basis of symmetry[39]. Likewise, Thomsen (recall Fig. 12), applying Werner's logic to the other end of the table, suggested that Th and U were the only known members of a second 31 column period (again sans the noble gases), a proposition that is still the subject of speculation[75-77].†

†Reference [39] appears to have both miscounted the length of Bayley's table and to have overlooked Thomsen's comments on the placement of Th and U.

A far more common abuse, however, involves the symmetry of logic, i.e., the abuse of analogy. In terms of periodic tables, this most often takes the form of an unsupported micro-macro analogy, leading to the belief that one's favorite form of the periodic table is a literal macroscopic scale-up of the atom, the position of each box literally representing the physical position of the corresponding differentiating electron in the atom itself. The author has personally been treated to unsolicited examples of helical atoms and planar disk atoms, both complete with *s*, *p*, *d*, and *f* electrons in total disregard for the quantum mechanical interpretation of these concepts.

The psychologist Joseph Jastrow once wrote an essay entitled "The Natural History of Analogy" in which he laid the blame for virtually every human superstition and stupidity on man's predilection for this "primitive mode of logic"[78]. There is certainly little doubt that humans exhibit a strong attraction for symmetry in their conceptual schemes as well as their wallpaper designs, and that many features, for example, of Aristotle's (and certainly Plato's) thought stem from such considerations rather than from the results of direct observation and experiment. Nevertheless, it cannot be denied that analogy plays an important role in scientific creativity. Indeed, it has been studied in some depth by philosophers of science[79]. The real danger appears not to be analogy itself, but rather the analogy that is untested or, if one is a follower of Popper, the analogy that is untestable[80].

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