The Place of Zinc, Cadmium, and Mercury in the Periodic Table

William B. Jensen
Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172; *jensenwb@email.uc.edu*

One of the few facts that I can remember from my undergraduate inorganic course was my instructor's insistence that zinc, cadmium, and mercury should be classified as main-block elements rather than as transition-block or d-block elements. Though I have always assumed that the evidence for this statement was unambiguous, I have also noticed the appearance over the last decade of an increasing number of general chemistry texts, inorganic texts, and advanced inorganic monographs that either explicitly or implicitly contradict this assignment. The inorganic textbook by Cotton and Wilkinson, which has served as the American standard for nearly 40 years, has always been firm in its treatment of the members of the Zn group as main-block elements, whereas the text by Holleman and Wiberg, which has served as the German standard in this field for nearly a century, has always classified them as outer-transition metals *(1, 2).* Likewise, the recent monograph by Massey on the main-block elements treats them as members of the main block, whereas the recent monograph by Jones on the d- and f-block elements treats them as transition metals *(3, 4).* A further examination of advanced monographs on coordination chemistry and organometallic chemistry also revealed the same inconsistency, with roughly a 50–50 split between those texts that included the Zn group among the transition metals versus those that did not *(5, 6).*

In contrast to these explicit claims, many general chemistry and lower-level inorganic texts are ambiguous in their treatment of these elements, often classifying them as transition metals in one part of the text and as main-block elements in another *(7, 8).* Much of this schizophrenic behavior is attributable to the use of a periodic table similar to that given Figure 1, which is designed to introduce students to the names used for the various subdivisions of the table. I have found a table of this type in virtually every recent general chemistry text that I have examined, as well as in about a quarter of the more recent introductory inorganic texts. In all cases, the Zn group was incorrectly labeled as being a member of the d block or transition block. Those introductory inorganic texts that presented some sort of systematic survey of descriptive chemistry usually contradicted this assignment in their later discussions of the chemistry of these elements. On the other hand, the surveys of descriptive chemistry found in most of the general chemistry texts were so superficial that the existence of this inconsistency seldom became explicit.

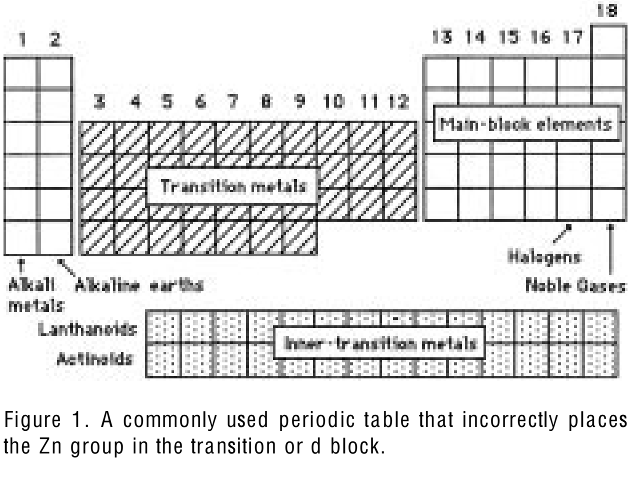


Figure 1. A commonly used periodic table that incorrectly places the Zn group in the transition or d block.

In light of these trends, I thought it might be of interest to summarize the evidence relating to the proper placement of the Zn group within the periodic table. This evidence can be subdivided into three categories based on its relevance to answering each of the following three questions:

- Where does the transition block end?
- Where does the d block end?
- Where does the Zn group fit into the main block?

As we will see, past opinions on this issue have generally been a function of the particular form of the periodic table advocated by the author in question, and for this reason it is also of interest to review some of the various schemes that have been proposed for graphically representing the placement of the Zn group within the table itself.

What Is a Transition Element?

During the last quarter of the 19th century, the term "Übergangsmetalle" or "transitional metal" was generally used to describe the metal triads of Fe-Co-Ni, Ru-Rh-Pd, and Os-Ir-Pt found in group VIII of the periodic table. Prior to the discovery of the noble gases, the maximum oxidation states of the known elements were found to undergo a cyclic variation from one to seven (Newland's law of octaves). Each short period of the table corresponded to one such cycle (e.g., Na to Cl), whereas each long period corresponded to two such cycles (e.g., K to Mn and Cu to Br). These latter cycles were separated by a triad of metals (e.g., Fe-Co-Ni) whose properties corresponded to a gradual transition between those of the last member of the first cycle (e.g., Mn) and those of the first member of the second cycle (e.g., Cu)—hence the name "transitional" or "transition" metal. With the discovery of the noble gases, it was further suggested that they also be classified as transitional elements, since they, like the noble metals, also bridged the gap between one valence cycle, Li–F, and the next, Na–Cl *(9–11).*

The first use of the term "transition" in its modern electronic sense appears to be due to the British chemist C. R. Bury, who first used the term in his 1921 paper on the electronic structure of atoms and the periodic table *(12).* As early as 1916, G. N. Lewis had suggested that the unique properties of the elements in the center of the longer (i.e., 18-element) periods might be due to the presence of "variable" kernels or cores in their atoms, though he did not elaborate on his suggestion *(13).* Using Lewis' hint as a starting point, Bury postulated that the outermost or *n* shell of a noble gas atom (other than He) always contained eight electrons, but once that shell became part of the atomic core for the atoms of the succeeding period, it could, beginning with period 4, expand its electron occupancy from 8 to 18 in the case of the $n - 1$ shell, or from 18 to 32 in the case of the $n - 2$ shell. Bury referred to these as the "8–18 transition series" and the "18–32 transition series", respectively, and used them to rationalize the electronic structures of both our current d-block and f-block elements. Bury's particular use of the term "transition" was presumably intended to indicate that these elements were undergoing a transition in the occupancy of their underlying $n - 1$ or $n - 2$ shells from 8 or 18 electrons at the beginning of the series to 18 or 32 electrons at the end of the series.

The eventual adoption of Bury's terminology by chemists is probably due to G. N. Lewis, who summarized Bury's conclusions in his 1923 monograph on *Valence and the Structure of Atoms and Molecules*, where he explicitly refers to the elements of Bury's series as "transition elements" *(14).* Similar suggestions concerning shell-filling sequences were made simultaneously by Niels Bohr, based largely on spectroscopic rather than chemical evidence *(15).* However, to the best of my knowledge, Bohr never used the term "transition element" in his writings *(16).*

Though the work of Bury and Bohr was soon incorporated into textbook discussions of the electronic structure of the atom, most texts remained conservative in their coverage of the periodic table, and it was not until the end of the Second World War that the older identification of the group VIII metal triads with the term "transition metal" was completely displaced by the newer electronic usage *(17).* As we will see, it is not an accident that this change also coincided with a widespread switch from the older "short" 8-column version of the periodic table (Figure 2) to the so-called "long" or 18-column version of the table (Figure 3). By the early 1940s, the terms "transition" and "inner transition" had also largely replaced Bury's original numerical modifiers, and the term "representative element" had become a common synonym for the members of the main block *(18, 19).*

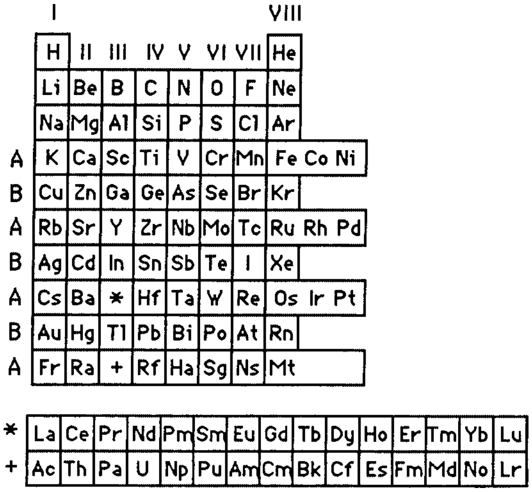


Figure 2. An updated version of the short or 8-column block form of the periodic table showing the original meaning of the A and B subgroups or series.

Where Does the Transition Block End?

In his famous review article of 1871, Mendeleev hesitated between classifying Cu, Ag, and Au with the alkali metals in group I or with the transition metals in group VIII, thereby converting them into transitional-metal tetrads (Table 1, line 1). In the end, he listed them in both locations, but enclosed them in parentheses in order to indicate the tentative nature of their assignments *(20).* Group assignment in Mendeleev's table was based on maximum valence or oxidation state and the existence of Cu(II) and Au(III) compounds definitely precluded the assignment of these elements to group I. Yet, if they were excluded from group I, a fundamental asymmetry appeared in the short form of periodic table. Groups II–VII all bifurcated after period 3 into what Lothar Meyer later called A and B "Untergruppen" or subgroups. If the metals of the copper group were not forced into group I, then it would fail to show a similar bifurcation. Mendeleev was at least honest enough to indicate his indecision but, in the case of his successors, Platonic symmetry soon triumphed over the facts of chemistry. Thus, in

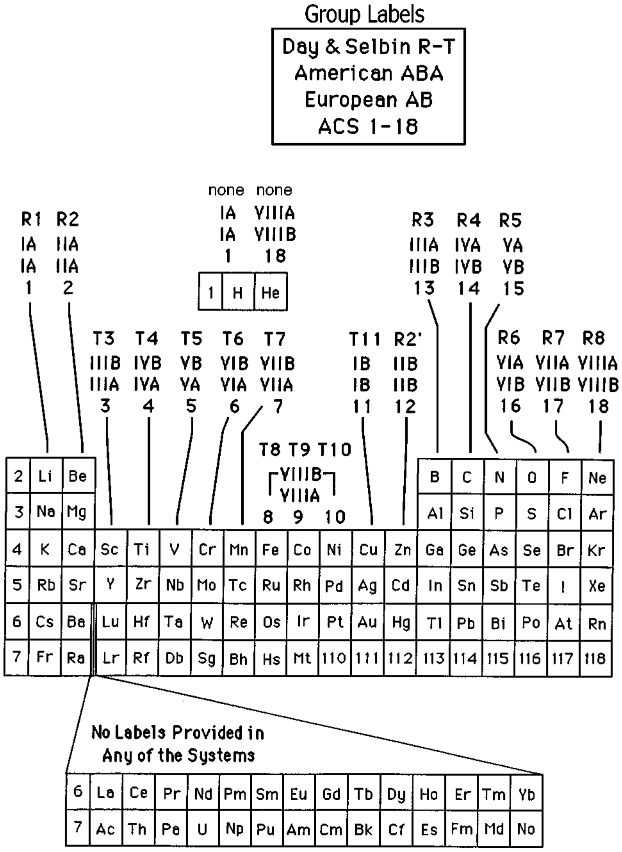


Figure 3. An updated version of the 18-column block form of the periodic table showing various labeling systems for the groups.

most pre-electronic periodic tables, the transition elements began at Fe, Ru, and Os and ended at Ni, Pd, and Pt, rather than at Cu, Ag, and Au (Table 1, line 2).

In his book *(14),* G. N. Lewis suggested that the transition elements could be chemically differentiated from the main-block elements not only by characteristic differences in their overall patterns of observed oxidation states, but also by their ability, in at least some of these states, to form colored, paramagnetic ions (Table 2). To Lewis' original list, we can also add the characteristic absence of stereoactive lone pairs on the central atom in their lower oxidation-state compounds *(21).* Of these four characteristic properties, Bury focused almost exclusively on oxidation-state patterns as a criterion for identifying which elements qualified as transition metals. All active valence electrons (ε) were assumed to be in the outermost n shell. When an element exhibited an oxidation state less than the number of electrons (ν) added since the preceding noble gas, this indicated that the excess electrons were no longer acting as valence electrons but had gone into the $n - 1$ or $n - 2$ shells instead. Thus the existence of one or more oxidations states for which $\varepsilon < \nu$ was taken as evidence that the atom in question was a transition element.

Based on the oxidation states known at the time, Bury found that the first transition series began at Ti and ended at Cu, that the second transition series began at Ru and ended at Pd, and that the third transition series began at Os and ended at Au (Table 1, line 3). As can be seen, Bury's criterion is highly dependent on the state of our knowledge of the known oxidation states of the elements. As our knowledge of the latter increases, so will the number of transition elements. If one updates Bury's assignments using a modern inorganic text, his criterion would classify all elements from the Sc group through the Cu group as transition metals (Table 1, line 5).

Table 1. Various Interpretations of the Term "Transition" Metal

Date	Source	Row 4	Row 5	Row 6
1871	Mendeleev	Fe–Cu	Ru–Ag	Os–Au
1880–1945	Short table	Fe–Ni	Ru–Pd	Os–Pt
1921	Bury	Ti–Cu	Ru–Pd	Os–Au
1922	Bohr	Sc–Ni	Y–Pd	Lu–Pt
Updated	Bury	Sc–Cu	Y–Ag	Lu–Au

Table 2. Lewis' Empirical Criteria for Differentiating between Transition and Main-Block Elements

Transition Element	Main-Block Element
Variable oxidation states often separated by one unit	Constant oxidation state or states separated by two units
Often form colored ions	Ions usually colorless
Often form paramagnetic ions	Ions usually diamagnetic
Absence of stereoactive lone pairs on central atom	Lone pairs on central atom often stereoactive

Using similarities in the arc spectra of the elements as a way of characterizing the nature of the differentiating electron added to create a given atom from its predecessor, Bohr concluded that all three transition series (though, as we saw, he never used this term) began with the Sc group and ended at the Ni group. The spectra of Cu and Zn were clearly analogous to those of the alkali metals and alkaline earth metals, respectively *(22).* By the 1950s, most inorganic textbooks had adopted Bohr's classification criterion rather than that of Bury, even though they continued to use Bury's terminology *(18, 19).* When stated in terms of the s, p, d, f orbital notation later introduced by Hund, this criterion defines an outer-transition element as a simple substance containing atoms having an incomplete $(n - 1)$d subshell *(23, 24).* Given the $[\mathrm{NG}](n - 1)\mathrm{d}^{10}\mathrm{s}^1$ and the $[\mathrm{NG}](n - 1)\mathrm{d}^{10}\mathrm{s}^2$ configurations of the Cu and Zn groups (where [NG] stands for a noble gas or pseudo-noble gas core), neither qualify by this definition as transition elements (Table 1, line 4).

It is of interest to note the conflict between the chemical and spectroscopic definitions of a transition element. On the basis of the chemical criteria given by Lewis and Bury, the elements of the Cu group qualify as transition metals, whereas as on the basis of the spectroscopic definition given by Bohr and Hund, they are main-block elements. On the basis of either definition, the metals of the Zn group are unambiguously identified as main-block elements.

What Is a d-Block Element?

Given that most chemists now use the terms "transition element" and "d-block element" interchangeably, the reader might well wonder why this question deserves a separate section *(25).* However, there are some authors who claim that these two terms are not synonymous. Thus W. C. Fernelius, in a 1986 review of labelling problems and the periodic table, insisted that, although the members of the Zn group were not transition elements, they were nevertheless d-block elements. He further stated that this latter concept had a "definite and consistent meaning", though he failed to indicate just what that meaning was *(26).* A survey of the three dozen or so inorganic texts in my office also failed to turn up an unambiguous definition.

One possibility is to define a d-block element as an element whose differentiating electron occupies an $(n - 1)$d orbital. A second possibility, following that given by Daintith, is to define it as any element having a $[\mathrm{NG}](n - 1)\mathrm{d}^x\mathrm{s}^z$ configuration, where x can vary from 1–10 and z can vary from 0–2 *(27).* The first definition would preclude the Zn group, for which the differentiating electron occupies an ns orbital, whereas the second definition would include the Zn group, as well as those transition elements having irregular configurations (e.g., Pd). But while this last definition does reproduce the d block as it is shown in Figure 1, it appears to have been invented after the fact to rationalize the frequent inclusion of the Zn group among the transition metals, and it is highly questionable whether it has either chemical or spectroscopic significance.

Chemistry is based on a differentiation between valence electrons and core electrons, and it is the former that are of most importance in defining the chemistry of a given element and in determining its assignment to a given group of the periodic table. As we have seen, spectroscopic characterization of the valence electrons in these elements shows that, in the case of the neutral atoms, the significant break occurs between the Ni group and the Cu group, though this fails to coincide with a significant break in chemical properties. *I, on the other hand, would argue that the chemically significant indicator is not whether an atom has a filled versus a partly filled (n – 1)d subshell, but whether the (n – 1)d electrons from this subshell can function as valence versus core electrons.* In other words, we can define a d-block element as any element that uses either (n – 1)d electrons or empty (n – 1)d orbitals in its bonding. This definition automatically precludes elements in which the (n – 1)d electrons have ceased to function as valence electrons and have instead become a part of the atomic core.

Bury and Lewis considered the (n – 1)d subshell to always be a part of the atomic core. It merely functioned as a reservoir of electrons that could be easily transferred to the outermost or true valence shell. By contrast, the above definition considers the (n – 1)d subshell to be a part of the valence shell as long as there is evidence for the involvement of (n – 1)d electrons or orbitals in chemical bonding.

In lower oxidation-state species, that portion of the (n – 1)d valence-electron density not involved in bond formation is stored “internally” and consequently is generally not stereoactive. As noted earlier, this is in sharp contrast to the main-block elements in which that portion of the valence-electron density not involved in bond formation is generally stored—with the exception of the so-called inert pair effect—in the form of stereoactive lone pairs. Hence, when species containing a main-block atom act as electron-density donors or Lewis bases, the structure of the isolated base undergoes only minor perturbations upon neutralization. For example, in the case of neutralization of ammonia by a proton, the arrangement of electrons pairs around the N atom remains essentially tetrahedral:

$$H^+ + {:}NH_3 \rightarrow NH_4^+ \tag{1}$$

On the other hand, when a transition-metal complex acts as a Lewis base, it undergoes substantial structural rearrangement as a result of the stereochemical activation of part of the original nonbonding valence-electron density *(28).* Thus, in the case of the neutralization of the tetracarbonylcobalt anion by a proton, the arrangement of the electron density around the Co atom changes from tetrahedral to trigonal bipyramidal:

$$H^+ + Co(CO)_4^- \rightarrow HCo(CO)_4 \tag{2}$$

Table 3. A Comparison of the Properties of the Cu Group with Those of the Zn Group

Atom	Valence Electrons	Core Configuration	Known Oxidation States[a]	Colored or Paramagnetic Ions
Cu	$3d^{10}4s^1$	[Ar]	I, II, III, IV	Yes
Ag	$4d^{10}5s^1$	[Kr]	I, II, III, V	Yes
Au	$5d^{10}6s^1$	[Xe, $4f^{14}$]	(I^-),[b] I, III, V	Yes
Zn	$4s^2$	[Ar, $3d^{10}$]	II	No
Cd	$5s^2$	[Kr, $4d^{10}$]	II	No
Hg	$6s^2$	[Xe, $4f^{14}$, $5d^{10}$]	II	No

[a] Excludes oxidation states, such as Hg(I), which involve homonuclear metal–metal bonding and for which the oxidation number no longer reflects the number of valence electrons used in bonding.

[b] Thought to be present in the compound CsAu.

Table 4. A Comparison of the Properties of Be and Mg versus Those of Zn and versus Those of Ca

Property	Be	Mg	Zn	Ca
Valence configuration	$2s^2$	$3s^2$	$4s^2$	$4s^2$
Core configuration	[He]	[Ne]	[Ar, $3d^{10}$]	[Ar]
Oxidation state	II	II	II	II
Electronegativity[a]	0.99	0.9	0.99	0.79
Atomic radius/pm	113.3	160	133.2	197.3
Ionic radius/pm	34	78	83	106
Coordination number	4	6	4–6	6–8
Flame test	colorless	colorless	colorless[b]	red
Complex formation (hard ligands)	strong	strong	strong	moderate
Complex formation (soft ligands)	moderate	weak	moderate	weak
Qualitative analysis[c]	aluminum group	alkaline earth group	aluminum group	alkaline earth group
Formation of organometallics	good	good	good	poor
Hydroxide	amphoteric	basic	amphoteric	basic

[a] Modified Martynov–Batsanov scale. Values are approximately two-thirds of those on the Pauling scale.

[b] Sometimes reported as bluish–green streaks in the outer flame.

[c] Based on ref 57.

Where Does the d-Block End?

All of the elements from the Sc group through the Cu group exhibit one or more oxidation states in which the element in question meets the above conditions and thus qualify as d-block elements. The members of the Zn group, however, do not. This is best seen by comparing the properties of the Cu group with those of the Zn group (Table 3). With the exception of their M(I) oxidation states, all of the members of the Cu group form high-oxidation-state compounds that require use of one or more $(n-1)$d electrons, thus indicating that, in spite of the filled $(n-1)d^{10}$ subshells in the configurations of their neutral atoms, this subshell can still serve as a source of valence-electron density *(29).* Even in the case of the M(I) oxidation state, there is now evidence that the filled $(n-1)d^{10}$ subshells are involved in weak metal-metal bonding. This appears to be due to a mutual polarization of the filled subshells and is most pronounced in species containing low-lying excited states capable of mixing with the ground state. Evidence for these homonuclear d^{10}–d^{10} interactions is particularly strong for the members of the Cu group and has been reviewed by Jansen *(30)* and more recently by Pyykö *(31).*

In sharp contrast, the members of the Zn group contribute only two valence electrons to the bonding in their known compounds. In no case is there any convincing evidence that either $(n-1)$d electrons or empty $(n-1)$d orbitals are involved in their bonding interactions, thus suggesting that, in contrast to the Cu group, the $(n-1)d^{10}$ subshell is now part of the atomic core, just as it is for the case of those p-block elements that follow the Zn group in the periodic table *(32, 56).* This inference has also been confirmed by theoretical calculations. At the end of their molecular orbital study of the changing role of the $(n-1)$d orbitals in ZnS, FeS, and CrS, Hinchliffe and Dobson concluded that *(33)*:

> Whereas the bonding in CrS involves mainly the partly filled 3d orbitals, and in FeS a combination of 3d and 4s, in ZnS the "valence orbitals" on Zn are 4s and the 3d electrons behave as "core" electrons.

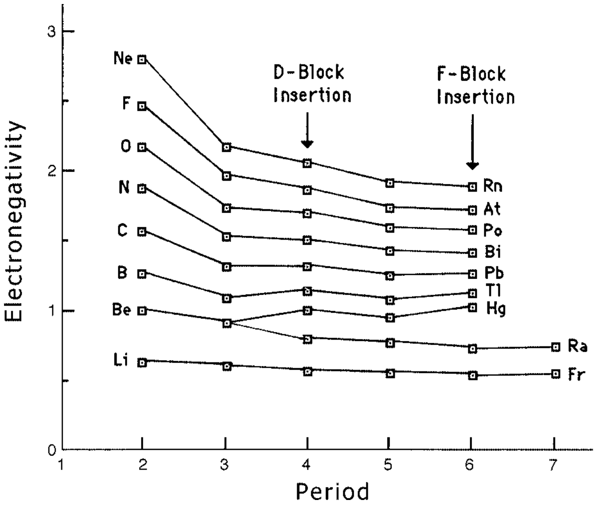


Figure 4. A plot of group electronegativity trends for the main block elements (modified Martynov–Batsanov scale) showing the bifurcation at Mg. If one follows the Ca–Ra branch at Mg, the trends parallel those of the alkali metals in group I. If, instead, one follows the Zn–Hg branch at Mg, the trends parallel those shown in groups III–VIII. This change in pattern is due to the insertion of the d and f blocks and the resulting increase in Z^* accounts for the enhanced electronegativities of the Zn–Hg branch over those of the Ca–Ra branch and for the similarity between their chemistry and that of Mg and Be.

Where Does the Zn Group Fit into the Main Block?

As we have seen, from a spectroscopic point of view, the members of the Zn group are analogous to the alkaline earth metals or group II elements. From a chemical point of view, Zn and Cd most resemble Be and Mg, not only in terms of their atomic radii, ionic radii, and electronegativities (Table 4), but also in terms of the structures of their binary compounds and in their ability to form complex ions with a wide variety of oxygen and nitrogen donor ligands (including complex hydrates and amines). Indeed, prior to the introduction of electronic periodic tables, the similarity between Be and Mg and Zn and Cd was often considered to be greater than the similarity between Be and Mg and the rest of the alkaline earth metals (Ca–Ra). Many inorganic texts written before the Second World War placed their discussion of the chemistry of Be and Mg in the chapter dealing with the Zn subgroup rather than in the chapter dealing with the Ca subgroup, and the same is true of many older periodic tables, including those originally proposed by Mendeleev *(34, 35).* Even as late as 1950, N. V. Sidgwick, in his classic two-volume survey of *The Chemical Elements and Their Compounds*, felt that it was necessary to justify his departure from this scheme in the case of Mg *(36)*:

> The gap between magnesium and the succeeding elements is sufficient to make it desirable to treat the magnesium compounds separately, but in the general discussion we may include it along with the alkaline earths metals proper, the elements from calcium to radium.... There has been much argument as to whether magnesium has the properties of a member of group IIA (alkaline earth metals) or IIB (zinc, cadmium, mercury); in fact of course it has resemblances to both. It is found in nature rather with the A elements than with the B. In its chemistry it shows analogies to both subgroups; in its power of complex formation it stands between the two, and seems to come nearer to B than A, but this is a natural result of its small size....

As suggested by Sidgwick's final comment, these similarities are easily understood as a consequence of having inserted the d block between the Ca and Zn subgroups. This results in an enhancement of the effective nuclear charges (Z^*) for Zn and Cd over those of Ca–Ra and leads to values for their radii and electronegativities that are much closer to the values found for Be and Mg than are those of the Ca subgroup. In the case of Hg, the combination of both the d-block and f-block insertions, as well as significant relativistic effects, results in properties that are virtually unique, though

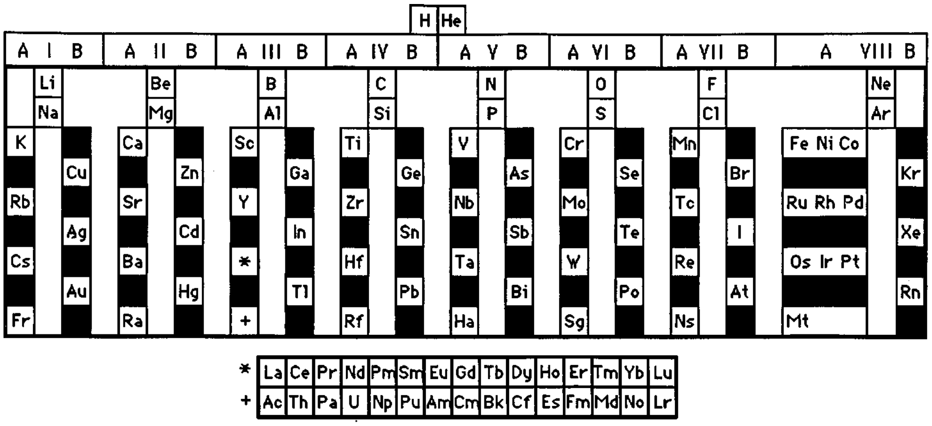


Figure 5. An updated Venable–Sears modification of the 8-column short table given in Figure 2, emphasizing the bifurcation of each group into A and B branches or subgroups.

this element still retains the formal similarity of having only two outer *n*s-type valence electrons *(37).*

In general, if one plots a given property for the members of group II, the group trend will parallel that shown by the alkali metals in group I if, after Mg, one follows the Ca–Ra subgroup or branch, but will parallel the pattern shown by groups III–VIII if one follows the Zn–Hg subgroup or branch. This is illustrated in Figure 4 for group trends in electronegativity. In summary, both the chemical and spectroscopic evidence clearly place the Zn group in group II of the main-block elements and lead to the irresistible conclusion that, following Be and Mg, there is a fundamental bifurcation of this group into a Ca–Ra branch and a Zn–Hg branch.

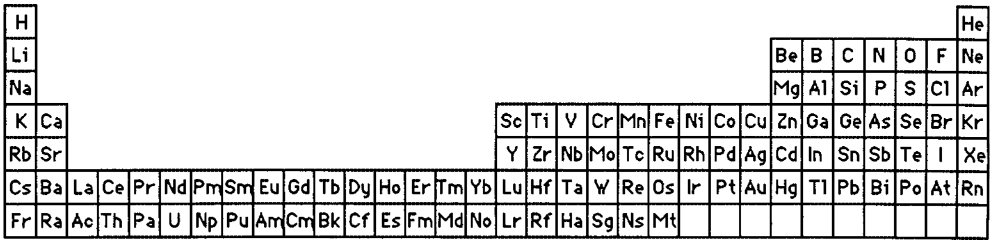
Representing Affiliation by Position

Given the above conclusion, how can we indicate this bifurcation of group II on a periodic table? As long as chemists preferred to use the short 8-column form of the table, this was not a problem, since, beginning with period 4, all eight groups automatically bifurcated into an A and B branch or subgroup. This is best shown in the version of the short table (Figure 5) proposed by Venable in 1895 and again by Sears in 1924 *(38, 39).* The pairs of elements found in periods 2 and 3 and located at the head of each group were known as the “typical elements”, and many short tables also made some attempt to indicate whether these pairs most resembled their corresponding A or B subgroups, usually by preferentially aligning them over one branch or the other *(40).*

It was only with the increasing preference for the longer 18- and 32-column tables that the placement of Zn group or, more accurately, the placement of Be and Mg became a problem. These expanded tables destroyed the alignment of most of the subgroups by spatially separating the transition elements from the main-block elements. While this consequence is considered a great improvement, it simultaneously separated the main-block Ca and Zn subgroups as well and raised the question of whether Be and Mg should be aligned with the Ca–Ra branch or with the Zn–Hg branch.

This problem is well illustrated by a debate that occurred between Alfred Werner and Richard Abegg. In April of 1905, Werner proposed a 32-column periodic table in which he followed Mendeleev in placing Be and Mg above the Zn subgroup rather than above the Ca subgroup (Figure 6; ref *41, 42*). Abegg, who was a strong advocate of the short table, wrote a rejoinder in which, among other things, he objected to this placement *(43, 44).* His only contrary argument was that, if he plotted the change in properties down the Be–Ra alternative, he obtained regular trends, whereas, if he plotted them down the Be–Hg alternative, he obtained irregularities at both Zn and Hg. However, as we have already seen, this difference is a consequence of the d- and f-block insertions and the fact that the group trends for the Be–Ra choice parallel those of group I whereas those for the Be–Hg choice parallel the trends for groups III–VIII.

This exact same debate was repeated nearly 20 years later when Fritz Paneth published a paper in 1923 on new ways of formulating the periodic table *(45).* In his proposed 18-



H																															He
Li																									Be	B	C	N	O	F	Ne
Na																									Mg	Al	Si	P	S	Cl	Ar
K	Ca															Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr															Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	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
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Ha	Sg	Ns	Mt										

Figure 6. An updated version of Werner’s 32-column block-table of 1905 showing his placement of Be and Mg in the Zn group.

column table (Figure 3), he placed Be and Mg above the Ca subgroup rather than above the Zn subgroup. This elicited a response the next year from Paul Pfeiffer, who presented detailed chemical arguments, similar to those given above, for why these two elements should be aligned with the Zn subgroup instead *(46).* Paneth's only substantive counter-argument was that the members of Zn subgroup had a filled $(n-1)d^{10}$ subshell in their configurations that was absent in the case of both Be and Mg and in the members of the Ca subgroup *(47).* But again, as we have already seen, these d electrons function as core electrons rather than as valence electrons. Just as the presence of filled $(n-1)d^{10}$ subshells in the cores of the elements following the Zn group in no way disqualifies them from being classified as p-block elements, so their presence in the cores of the Zn-group elements in no way disqualifies them from being classified as s-block elements.

There is virtually no chance that the short 8-column form of the periodic table will ever regain its former popularity. However, there is at least one form of the 32-column table that allows one to maintain the spatial affiliations of the old subgroups while simultaneously separating the transition metals from both the main-block elements and from the lanthanoids and actinoids. This is the famous step-pyramid table first proposed by Thomas Bailey in 1882 and again by Julius Thomsen in 1895 *(48, 49).* This table saw extensive textbook usage in the period 1925–1945, largely as a result of its popularization by Niels Bohr *(22).* Group affiliation in this table is indicated either by vertical alignment or by means of diagonal tie lines, thus allowing one to indicate simultaneously multiple relationships *(50).* As can be seen in the updated version given in Figure 7, Mg is simultaneously connected to both the Ca and Zn subgroups by means of solid diagonal lines, thus indicating, in keeping with the facts summarized earlier by Sidgwick, equal rather than preferential affiliation, and thus perfectly resolving our conflict.

In my opinion, the step-pyramid form of the periodic table is indisputably superior to the common 18-column block table used in virtually all of our textbooks, especially in the case of advanced inorganic courses in which these subtler chemical relationships become important. In the case of introductory classes, however, I have encountered a certain resistance on the part of students to this form of the table. Much of this is, of course, due to the fact that they have already become familiar with the 18-column block table in their high school chemistry courses and do not want to switch

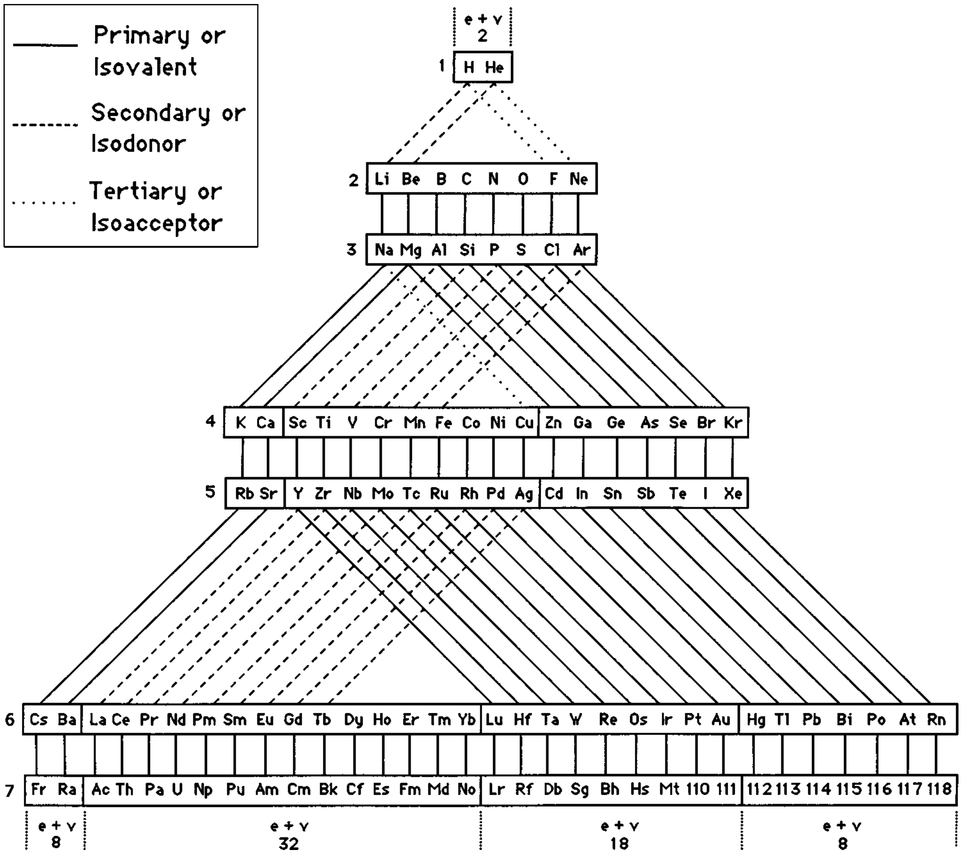
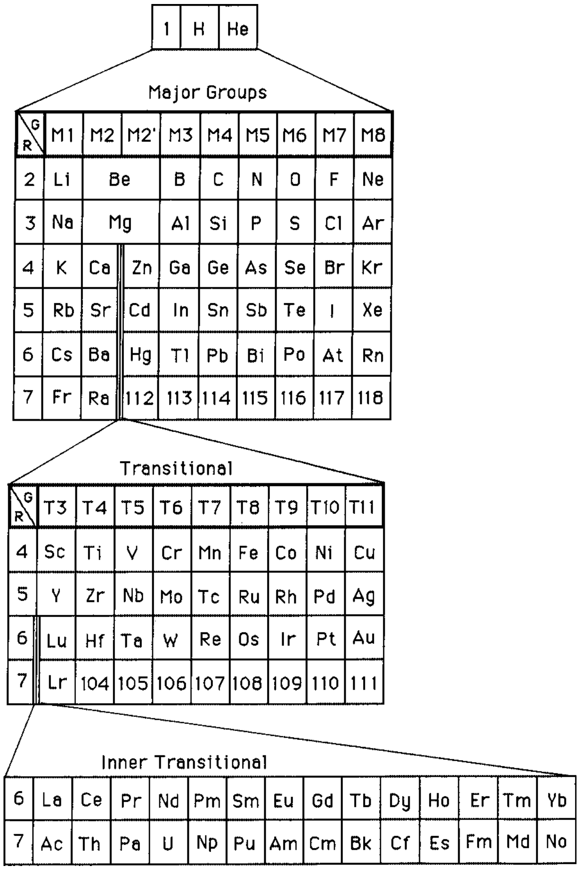


Figure 7. A modernized step-pyramid table showing the bifurcation of Group II following Mg. Numbers to the left of the rows represent the periods. The "e + v" numbers indicate the total number of valence electrons (e) and valence vacancies (v) per electronic block.

gears. But they also seem to be bothered by the use of diagonal as well as vertical alignments and by the increasing separation between the s-block and p-block elements as one moves from the top to the bottom of the table. Since the descriptive chemistry of the introductory course is largely restricted to these two blocks of elements, the students tend to view the d- and f-block insertions as unnecessary distractions.

An elegant solution to these problems was proposed by R. T. Sanderson more than 30 years ago *(51, 52).* Just as we shorten the full 32-column periodic table into an 18-column table by pulling out the f-block elements and attaching them as an appendix at the bottom of the table, so Sanderson did the same for the d-block, thus generating what might properly be called a "double-appendix" table. A slightly revised form of this table created from the step-pyramid table in Figure 7 is shown in Figure 8. As can be seen, this table correctly shows the termination of the d block at the Cu group, the termination of the f block at the Yb group rather than at the Lu group *(53),* and the placement of both the Ca and Zn subgroups together in group II of the main block.

Even more important from a pedagogical standpoint, Sanderson's table has decomposed the periodic table into three rectangular subtables—one for the main-block or sp-block elements, one for the transition or d-block elements, and one for the lanthanoid–actinoid or f-block elements. Each subtable has its own internal consistency and can be selectively emphasized at different stages of the curriculum—the main-block subtable in introductory courses, the transition-block subtable in intermediate inorganic courses, and the f-block subtable in advanced inorganic courses.



1	H	He

Major Groups

G R	M1	M2	M2'	M3	M4	M5	M6	M7	M8
2	Li	Be		B	C	N	O	F	Ne
3	Na	Mg		Al	Si	P	S	Cl	Ar
4	K	Ca	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	112	113	114	115	116	117	118

Transitional

G R	T3	T4	T5	T6	T7	T8	T9	T10	T11
4	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
5	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
6	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au
7	Lr	104	105	106	107	108	109	110	111

Inner Transitional

6	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
7	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Figure 8. An updated version of Sanderson's double-appendix table showing the proper location of the Zn group and the proper termination of both the d block and the f block. Sanderson did not provide group labels for the f-block elements

Despite its extraordinary advantages, Sanderson's double appendix table has seen virtually no use beyond his own writings *(54).* It is unclear whether this is due to resistance on the part of authors and publishers, who fear that any departure from the norm will diminish the sale of their textbooks, or to the fact that the use of the periodic table to correlate the facts of descriptive chemistry is so superficial in most textbooks that the very real limitations of the 18-column block table never become apparent.

Representing Affiliation with Labels

Affiliation can, of course, be indicated by group labels as well as by spatial alignment. In the original European AB labelling system (Figure 3, third row of labels), the Zn subgroup was labeled IIB and the Ca subgroup was labeled IIA. The A and B modifiers were intended to indicate that the Ca subgroup belonged to the first valence cycle of the long periods and the Zn subgroup to the second valence cycle, respectively. However, to students and chemists who are unfamiliar with the logic behind this scheme, it appears that the Zn group is being incorrectly classified with the succeeding p-block elements, all of which also carry the B modifier. In the American ABA system (Figure 3, second row of labels), the calcium and zinc subgroups are again labeled IIA and IIB, respectively, but the modifiers now refer to main-block (A) versus transition-block (B) elements instead and thus incorrectly classify the Zn group with the transition metals. Hence neither of the traditional modifier systems is satisfactory.

A much better scheme was suggested by Sanderson and is shown in Figure 8. This scheme uses an MT modifier system to indicate whether a given group of elements belongs to the main block or major groups (M) or to the transition block (T). In Sanderson's system the Ca and Zn subgroups are labeled M2 and M2', respectively, thus clearly indicating the fundamental bifurcation of group 2. Examination of the textbook by Day and Selbin (who use R for representative element and label the Ca and Zn subgroups R2 and R2' instead) shows that modifier systems of this type can be used on the standard 18-column block table (Figure 3, top row of labels) to correctly indicate the placement of the Zn group even in the absence of the spatial alignment provided by the alternative tables discussed in the previous section *(55).*

Unhappily, the recent decision of IUPAC to substitute enumerator labels in place of descriptive labels would appear to rule out Sanderson's solution. Their suggested 1–18 labels (Figure 3, fourth row of labels) provide only "finger count" information about the number of columns in the periodic table but tell us nothing about the chemistry or logic of the classification scheme. Although this decision may make computer indexing easier, it also tends to disguise some fundamental problems, such as the Be and Mg placement discussed above, and thus diminishes our understanding of chemistry.

Summary

Forcing the Zn group into the transition or d block, because the resulting periodic tables are thought to be more symmetric and easier for students to memorize, is in many ways the 20th century equivalent of the 19th century's decision to force the Cu group into group I along with the alkali metals. We all realize that, for the sake of our students, we often need to simplify the material we teach, but simplifying a theory or model by leaving out details is very different from falsifying the facts (however idiosyncratic) of chemical behavior.

Literature Cited

1. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; See the table of contents and Chapter 15.
2. *Holleman–Wiberg Inorganic Chemistry*, 34th ed.; Wiberg, N., Ed.; Academic Press: New York, 2001; Chapters 19, 23.
3. Massey, A. G. *Main Group Chemistry*, 2nd ed.; Wiley: New York, 2000; Chapters 2, 6.
4. Jones, C. *D- and F-Block Chemistry;* Royal Society of Chemistry: Cambridge, England, 2001.
5. Examples of advanced monographs that include the Zn group among the transition metals include: Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry;* Brooks/Cole: Monterey, CA, 1985. Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms;* Brooks/Cole: Monterey, CA, 1985.
6. Examples of advanced monographs that exclude the Zn group from the transition metals include: King, R. B. *Transition-Metal Organometallic Chemistry: An Introduction;* Academic Press: New York, 1969. Nicholls, D. *Complexes and First-Row Transition Elements;* Macmillan: London, 1974.
7. For a typical example from a general chemistry text, see Atkins, P. W. *General Chemistry;* Scientific American Books: New York, 1989, p 44, Figure 2.3. This incorrect classification of the members of the Zn group as d-block elements is also adopted within the text, see p 775.
8. For a typical example from an introductory inorganic text, see Rayner-Canham, G. *Descriptive Inorganic Chemistry;* Freeman: New York, 1996, p 20, Figure 2.3. This classification of the members of the Zn group as d-block elements contradicts their later treatment within the text, where they are correctly described as main-block elements, see p 454.
9. Caven, R. M.; Lander, G. D. *Systematic Inorganic Chemistry From the Standpoint of the Periodic Law;* Blackie & Son: London, 1907; pp 53–54.
10. Mellor, J. W. *Modern Inorganic Chemistry;* Longmans: London, 1927; p 993.
11. Partington, J. R. *A Text-Book of Inorganic Chemistry;* Macmillan: London, 1939; pp 412–415, 955.
12. Bury, C. R. *J. Am. Chem. Soc.* 1921*, 43,* 1602–1609.
13. Lewis, G. N. *J. Am. Chem. Soc.* 1916*, 38,* 762–785.
14. Lewis, G. N. *Valence and the Structure of Atoms and Molecules;* Chemical Catalog Co.: New York, 1923; pp 63–64.
15. Bohr, N. *Nature* 1921, *107,* 104–107.
16. This statement is based on a survey of the papers and lectures reprinted in *Niels Bohr: Collected Works–The Periodic System (1920–1923);* Nielsen, J. R., Ed.; North-Holland Publishing: Amsterdam, 1977; Vol. 4.
17. Compare, for example, the use of the term transition element in the 1907 edition of ref *9* with that given in the postwar edition of 1945. See, Caven, R. M.; Lander, G. D.; Crawford, A. B. *Systematic Inorganic Chemistry from the Standpoint of the Periodic Law*, 6th ed.; Blackie & Son: London, 1945; p 64. This switch occurred much earlier in this country than in Europe.
18. Moeller, T. *Inorganic Chemistry: An Advanced Textbook;* Wiley: New York, 1952; pp 102–103.
19. Gilreath, E. S. *Fundamental Concepts of Inorganic Chemistry;* McGraw-Hill: New York, 1958; p 130.
20. Mendeleev, D. *Ann. Chem. Pharm. (Supplement Band)* 1871, *8*, 133–229.
21. For a more detailed list of classical chemical and physical differences between the main block and the transition elements, see Yoe, J. H; Sarver, L. A. *Organic Analytical Reagents;* Wiley: New York, 1941; pp 119–121.
22. Bohr, N. *The Theory of Spectra and Atomic Constitution;* University Press: Cambridge, 1922; p 70.
23. Hund, F. *Linienspektren und periodisches System der Elemente;* Springer: Berlin, 1927; pp 52–54.
24. Day, M. C.; Selbin, J. *Theoretical Inorganic Chemistry*, 2nd ed.; Reinhold: New York, 1969; p 100.
25. Eggleton, G. Transitional Elements. In *Macmillan Encyclopedia of Chemistry;* Lagowski, J. J., Ed.; Macmillan Reference: New York, 1997; Vol. 4, pp 409–412. This recent article treats the terms "transitional" and "d block" as synonyms and classifies the Zn group among the transition elements.
26. Fernelius, W. C. *J. Chem. Educ.* 1986, *63,* 263–266. A similar distinction, without independent justification of the term d block, appears in the recent textbook: Housecroft, K.; Sharpe, A. G. *Inorganic Chemistry;* Pearson: Harlow, England, 2001; p 434.
27. Daintith, J. *Dictionary of Chemistry;* Barnes & Noble: New York, 1981; p 63.
28. Shriver, D. F. *Acc. Chem. Res.* 1970, *3,* 231–238.
29. For a recent update on the oxidation states of the Cu group, see Müller, B. G. *Angew. Chem., Int. Ed. Engl.* 1987, *26,* 1081–1097.
30. Jansen, M. *Angew. Chem., Int. Ed. Engl.* 1987, *26,* 1098–1110.
31. Pyykö, P. *Chem. Rev.* 1997, *97,* 597–636.
32. Neither Jansen or Pyykö give detailed evidence for d^{10}–d^{10} interactions in the compounds of the elements of the Zn group. The strongest evidence that Jansen could offer was to suggest that the distortions of the metallic structures of these elements from ideal hexagonal and cubic closest packing might be due to this effect. However, the members of the Cu group show no such distortions in their metallic structures, even though they are well documented for their compounds. In any case, we would expect such polarizations to decrease in importance, if not totally disappear, as the $(n - 1)d^{10}$ subshell becomes more corelike in its behavior. See also Balasubramanian, K. *Relativistic Effects in Chemistry;* Wiley: New York, 1997.
33. Hinchliffe A.; Dobson, J. C. *Theoret. Chim. Acta* 1975, *39,* 211–216.
34. See, for example, Mellor, J. W. *Modern Inorganic Chemistry;* Longmans: London, 1927; Chapter 8. Partington, J. R. *A*

Text-Book of Inorganic Chemistry; Macmillan: London, 1939; Chapter 42. Hopkins, B. S. *Chemistry of the Rarer Elements;* Heath: Boston, 1923, Chapter 5.

35. See, for example, the tables given in Mendeleev, D. *Ann. Chem. Pharm. (Supplement Band)*, 1871, *8*, 133–229. Werner, A. *Berichte* 1905, *38,* 914–921.
36. Sidgwick, N. V. *The Chemical Elements and their Compounds;* Clarendon Press: Oxford, England, 1950; pp 219, 222.
37. Norrby, L. J. *J. Chem. Educ.* 1991, *68,* 110–111.
38. Venable, F. P. *J. Am. Chem. Soc.* 1895, *17,* 75–84.
39. Sears, G. W. *J. Chem. Educ.* 1924, *1,* 173–177.
40. For example tables, see Sears, G. W. *J. Chem. Educ.* 1924, *1,* 173–177. Letts, E. A. *Some Fundamental Problems in Chemistry Old and New;* Constable: London, 1914; p 54.
41. Werner, A. *Berichte* 1905, *38,* 914–921.
42. Werner, A. *Berichte* 1905, *38,* 2022–2027.
43. Abegg, R. *Berichte* 1905, *38,* 1386–1388.
44. Abegg, R. *Berichte* 1905, *38,* 2330–2334.
45. Paneth, F. *Angew. Chem.* 1923, *36,* 407–410.
46. Pfeiffer, P. *Angew. Chem.* 1924, *37,* 41.
47. Paneth, F. *Angew. Chem.* 1924, *37,* 421–422.
48. Bailey, T. *Phil. Mag.* 1882, *13* (5), 26–37.
49. Thomsen, J. *Z. Anorg. Chem.* 1895, *9,* 190–193.
50. Jensen, W. B. *Educ. Chem.* 1996, *32,* 122–123.
51. Sanderson, R. T. *J. Chem. Educ.* 1964, *41,* 187–189.
52. Sanderson, R. T. *Inorganic Chemistry;* Reinhold: New York, 1967; pp 14–16.
53. Jensen, W. B. *J. Chem. Educ.* 1982, *59,* 634–636.
54. For an exception, see Pode, J. *The Periodic Table;* Halsted: New York, 1970; p 21.
55. See table in Day M. C.; Selbin, J. *Theoretical Inorganic Chemistry*, 2nd ed.; Reinhold: New York, 1969; p 84.
56. There has also been an unsubstantiated claim that it is possible to electrochemically generate a Hg(cyclam)$^{3+}$ cation in acetonitrile at −78 °C with a lifetime of about 5 seconds. For details see Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.
57. Noyes, A. A.; Bray, W. C. *A System of Qualitative Analysis for the Rare Elements;* Macmillan: New York, 1927; p 8.