

The Periodic Law and Table

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Periodic Law, in chemistry, the generalization that many of the properties of the chemical elements are a periodic function of their atomic numbers. The law is best illustrated by plotting the value of the property in question for each element versus the element's atomic number. The most strongly periodic properties are those of the isolated gaseous atoms, such as the number of valence electrons, the atomic radius, the first ionization energy, and the electronegativity.

Many properties of simple substances and compounds also show a semi-periodicity, such as entropies and enthalpies of formation, entropies and enthalpies of atomization, and molar volumes. On the other hand, many other atomic and molecular properties, such as mass, electrical and thermal conductivities, characteristic X-ray frequency, and radioactive decay constants, show poor to negligible periodicity. In general, only those properties which show a high degree of correlation with both the number of valence electrons present in the atom and their shell number will display a significant degree of periodicity when plotted against atomic number.

Early Classifications of the Chemical Elements

The modern interpretation of a chemical element as an isolable, simple material substance, rather than as an abstract property or principle, is a product of the first chemical revolution (1770-1790), and is due primarily to the work of the French chemist, Antoine Lavoisier, and his collaborators. Lavoisier divided the known simple substances into the classes of "elements" proper or class generators, metals, nonmetals, and salifiable earths (figure 1). Elaborations of Lavoisier's original classification, based largely on a consideration of the acid-base properties and reducibility of the corresponding oxides, were made by Jöns Jakob Berzelius (1811), Louis-Jacques Thenard (1813), and Thomas Thomson (1817) in the early decades of the 19th century. These proposals remained the basis of textbook classifications well into the late 1850s.

Though the concept of atomic weight was introduced by John Dalton in the period 1803-1808, it was not until the work of Stanislao Cannizzaro in 1858 that it was finally possible to construct a self-consistent set

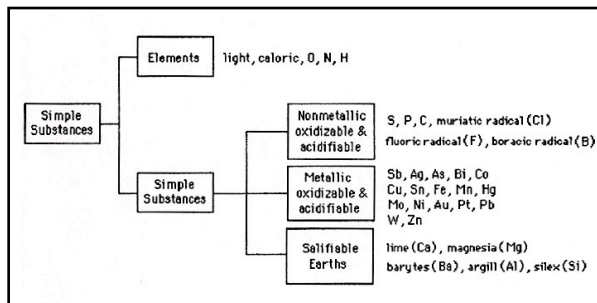


Figure 1. A modern diagrammatic summary of Antoine Lavoisier's classification of the elements, circa 1789.

of atomic weights that all chemists could agree upon. Closely allied with this event was the concomitant emergence of a second atomic property, known as valence, which served to characterize the combining capacity of an atom. Classical valence was essentially a way of summarizing the formulas of an element's compounds, in which the relative composition of a given compound, A_aB_b , was inversely related to the ratio of the classical valence values (ω_A and ω_B) of its component atoms by the equation:

$$a/b = \omega_B/\omega_A \quad [1]$$

To say that two different elements had the same valence was equivalent to saying that their possible chemical compounds with other elements all had analogous formulas. Thus boron (B), with a classical valence value of 3, forms the compounds BCl_3 and B_2O_3 with Cl (valence 1) and O (valence 2), respectively, and aluminum (Al), which also has a classical valence of 3, forms, as expected, the analogous compounds $AlCl_3$ and Al_2O_3 .

When coupled with the subsequent rise of chemical structure theory in the 1860s, the resolution of the atomic weight problem and the emergence of the valence concept form the substance of the second chemical revolution (1855-1875), which would, in its turn, give birth to both the periodic law and the periodic table.

In 1864 the British chemists, William Odling and Alexander Williamson, each independently suggested classifications (figure 2) of the chemical elements based on the valence values of their atoms, rather than on the

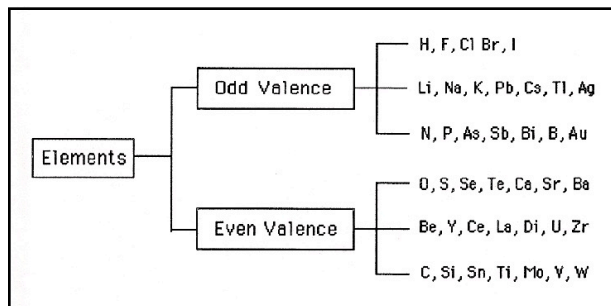


Figure 2. A modern diagrammatic summary of Alexander Williamson's valence classification of the chemical elements, circa 1864.

metallicity of the simple substances and the acid-base properties of their oxides, and similar valence classifications soon began appearing in the textbook literature (E. Frankland, 1866; A. Naquet, 1868; L. Cooley, 1869, etc.). By modern standards, these schemes had little problem in correctly grouping strongly electropositive main-block elements, such as the alkali metals and alkaline-earth metals, or strongly electronegative non-metals, such as the halogens, chalcogens, and pnictogens (Indeed, many of these natural groups were recognized by chemists long before the advent of the valence concept). However, classification of moderately electronegative main-block and transition-block elements proved more difficult, due in part to their variable valencies and, in some cases, to their poorly characterized chemistry.

Authors of these newer valence classifications frequently listed the elements within each valence group in order of increasing atomic weight. Others sought to establish numerical relationships between the atomic weights within each group, either by showing that the atomic weights of the middle members were the average of the atomic weights of the extremes (J. A. R. Newlands, 1863; W. Odling, 1864), or by showing that the differences between the atomic weights of successive members were multiples of one another (L. Meyer, 1864; G. Hinrichs, 1866).

The first of these approaches stems from observations made by the German chemist Johann W. Döbereiner in 1817 and 1829 on the equivalent weights of oxides and later directly applied to the atomic weights of the component elements instead. Attempts to discover other atomic weight averages or "triads" were later made by Leopold Gmelin (1827, 1843), Jean-Baptiste Dumas (1851), Michael Faraday (1852), Ernst Lenssen (1857), William Odling (1857), and Paul Kremers (1858), but the approach remained highly speculative and had no impact on either the textbook or research literature.

The second approach stems from the speculations of the British chemist William Prout in 1815 that the chemical elements were in fact polymers of a single primary matter or "Urstoff," variously called "protyle," "pantogen," etc. Prout had originally equated protyle with hydrogen, the lightest known element. When more accurate atomic weight determinations made this improbable, later workers equated it with half of a hydrogen atom and still later with a fourth.

These speculations were further fueled by the discovery of homologous series in the newly developing discipline of organic chemistry. Just as the successive members of an organic homologous series differed by a single CH_2 -unit, so the successive members of an atomic valence group were thought to differ by a fixed number of protyle or pantogen units. Early speculations of this nature are found in the work of Paul Kremers (1852), John Gladstone (1853), Josiah Parsons Cooke (1854), Jean Baptiste Dumas (1857, 1859), John Mercer (1858), and Max von Pettenkopfer (1858). As with the triad approach, the homolog approach remained highly speculative and had little or no impact on the textbook literature.

Discovery of the Periodic Law

An entirely new approach to the construction of valence tables was initiated in 1869 when the Russian chemist, Dmitri Mendeleev, announced his discovery that "the properties of the elements were a periodic function of their atomic weights." The resulting "periodic law" is best illustrated by plotting the property in question versus the corresponding atomic weights, a step first taken by the German chemist Lothar Meyer in 1870 (figure 3).

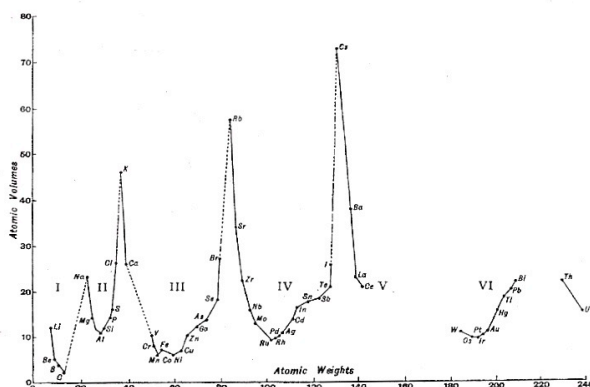


Figure 3. Lothar Meyer's periodicity curve of 1870 based on a plot of molar volumes (atomic volumes) of the simple substances versus their atomic weights (Oesper Collections).

periodic law and its implications for the construction of improved valence tables. Lothar Meyer, whose paper of 1870 was the first to comment and expand upon Mendeleev's work, claimed to have independently discovered the law as well, but freely acknowledged that Mendeleev had priority of publication. Even earlier, in 1864, the British chemist, John Alexander Reina Newlands, had discovered periodicity in the form of his "law of octaves" (so called because the properties of the elements repeated every eighth element, like the notes of the musical scale).

In constructing his periodic tables, Mendeleev took the bold step of assuming that apparent exceptions to his law were the result of one of three possible causes: 1) incorrect valence values, 2) incorrect atomic weight values, or 3) the presence of as yet undiscovered elements. Nor was he shy when it came to predicting what the true values should be. Many (but not all) of these predictions later proved to be correct. It was the success of these predictions, especially in the case of the three missing elements later discovered under the names of scandium, gallium and germanium, that played a key role in the acceptance of Mendeleev's work by the chemical community in the late 1870s and early 1880s. Newlands, on the other hand, had discovered his law of octaves using a small select set of only 24 elements (roughly corresponding to our current main-block elements). When he attempted to expand his classification to accommodate the remaining 38 elements known at the time, total chaos resulted.

Mendeleev, Meyer, and Newlands all eventually received recognition from their contemporaries for their roles in the discovery of the periodic law. Since 1889 at least three other scientists have also been suggested as possible codiscoverers, including the French geologist, Alexandre Emil Beguyer de Chancourtois; the British chemist, William Odling; and the Danish-American chemist, Gustavus Detlef Hinrichs. Close study of their papers, however, reveals that none of these candidates ever explicitly stated the periodic law and that their so-called periodic tables are really examples of advanced triad and homolog tables.

Electrification of the Periodic Law

In the period 1904-1924 chemistry underwent yet a third revolution based on the discovery and elucidation of the electrical composition and structure of the atom. This revolution impacted on the periodic law in three ways: 1) by replacing atomic weight with atomic number as the independent variable in the periodic law, 2) by replacing the empirical concept of valence with the number of outer or chemically active electrons in the atom, and 3) by redefining the concept of a chemical element

as a class of atomic nuclei having identical nuclear charges.

Already in the 19th century, several workers (J. A. R. Newlands, 1875; J. R. Rydberg, 1886, 1897) had suggested that the ordinal number of an element (the number defining its position in a list of atoms arranged in order of increasing atomic weight) should be used in place of the atomic weight as the independent variable in the periodic law. Using Ernest Rutherford's recently formulated nuclear model of the atom, a Dutch school teacher named Antonius van den Broek gave a physical interpretation to the ordinal number in 1911 by suggesting that it corresponded to the positive charge on the nucleus of the atom in question. This suggestion was experimentally confirmed two years later by Frederick Soddy, on the basis of the radioactive displacement laws, and by Henry Moseley, using X-ray spectroscopy.

Use of the ordinal number – now renamed the atomic number – eliminated several apparent exceptions to Mendeleev's original law involving the relative placement of the elements Ar and K, Co and Fe, and Te and I. Mendeleev had originally assumed that these difficulties were due to errors in the determination of the atomic weights in question. However, repeated redeterminations failed to eliminate these inversions. With the adoption of atomic number as the independent variable, the problem was resolved.

In 1904 the German chemist, Richard Abegg, equated the valence of an atom with the number of electrons in its outermost shell. Imperfect attempts to assign electronic structures to the atoms of each of the elements were made by Gilbert N. Lewis, Walther Kossel, Irving Langmuir, and Rudolf Ladenburg in the period 1916-1920. Our currently accepted structures were finally suggested independently by Niels Bohr and Charles R. Bury in 1921 and further refined to conform to the details of their spectroscopic configurations by Friederich Hund in 1925. As seen in figure 6, a plot of the total number of outer or "valence" electrons in an atom versus its atomic number is almost perfectly periodic, although the periodicity is complex. (The details of how

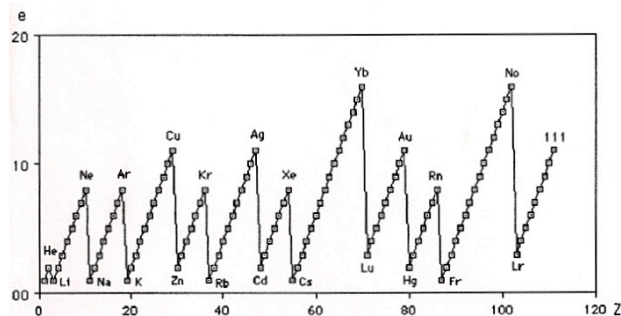


Figure 6. A modern periodicity plot of the number of valence electrons in an atom versus its atomic number.

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these valence electron counts are arrived at are outlined in the next section).

The phenomenon of radioactivity was first observed by Henri Becquerel in 1898 using the salts of uranium. In the years 1899-1909 more than a dozen new radioactive elements were reported by chemists and the problem of how to place all of them in the periodic table began to reach crisis proportions. This problem was resolved by Frederick Soddy in 1910 when he suggested that many of these so-called new radioelements were actually variations of a much smaller set of real elements, these variations having identical chemical properties but different radioactive properties and masses. In 1913 Soddy coined the term "isotope" to describe these variations and further defined them as atoms having identical nuclear charges but variable masses. The work of Francis W. Aston, also beginning in 1913, further confirmed the existence of isotopes in the case of non-radioactive elements using the technique of mass spectroscopy. With the advent of the isotope concept, the definition of a chemical element was transferred from that of a unique kind of atom, to that of a class of nuclei, all of which have identical nuclear charges.

Further developments of the electrical theory of matter soon made it possible to define and measure atomic properties other than valence, atomic weight, and atomic number. As shown in figure 7, such properties as atomic radius, atomic ionization energy, etc., show much more regular trends in periodicity than do the properties of the corresponding simple substances and their compounds (e.g., molar volumes, heats of formation, etc.) used by the 19th-century chemist to illustrate the periodic law

The Modern Periodic Table

A modern version of the periodic table, known as the step-pyramid table, is shown in figure 8. As with Mendeleev's horizontal table of 1871, the valence groups are arranged vertically (albeit with some diagonal offsets), and the periods run horizontally from left to right. Mendeleev's "short-form" table had attempted to force all of the elements into periods of equal length, either through the device of interleaving the main-block and transition-block elements, or by allowing for multiple occupancy of certain positions (e.g., by placing Fe, Co, Ni, and Cu together in group VIII of period 4). In sharp contrast, the periods in the "long-form" modern table are of variable length, so as to accurately reflect the spectroscopic details of the underlying electronic structures of the corresponding atoms, as first elucidated by Hund. As one moves from left to right across each period, one can envision the progressive buildup of the underlying electronic structures through the addition of ever more elec-

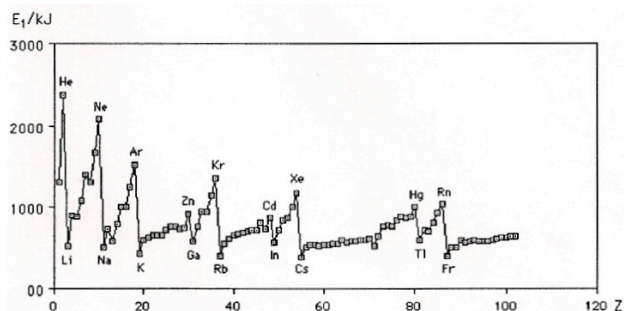


Figure 7. A modern periodicity plot of the first ionization energy of an atom versus its atomic number.

trons to the proper atomic shells and subshells of each successive atom.

Period 1 contains two elements (H-He), corresponding to the filling of the first electronic shell, which can hold a maximum of only two electrons. These electrons are referred to as s-electrons because they give rise to the so-called "sharp" lines found in the spectra of the atoms in question.

Periods 2 and 3 each contain eight elements (Li-Ne and Na-Ar), corresponding to the filling of the second and third electronic shells respectively, each of which can hold a maximum of eight electrons. The first two electrons (Li-Be and Na-Mg) in each shell are again s-electrons and the remaining six (B-Ne and Al-Ar) are known as p-electrons because they are responsible for the appearance of the so-called "principal" lines found in the spectra of the corresponding atoms.

Periods 4 and 5 each contain eighteen elements. Here the periodicity becomes more complex. The first two electrons are again s-electrons (K-Ca and Rb-Sr). At this point, however, the filling of the outermost shell is temporarily interrupted, and the next 10 electrons (Sc-Zn and Y-Cd) go into the underlying third and fourth shells, respectively. Although these shells were ostensibly filled at Ar and Kr, the subsequent increase in nuclear charge now allows for an expansion of their electron occupancies. These additional electrons are known as d-electrons because they give rise to the so-called "diffuse" lines found in the spectra of the atoms in question. Starting with Ga and In, the filling of the outermost shell is again resumed through the addition of the corresponding p-electrons (Ga-Kr and In-Xe).

Finally, periods 6 and 7 each contain 32 elements. Here again the underlying periodicity is further elaborated. As usual, the first two electrons go into the outer n-shell as s-electrons (Cs-Ba and Fr-Ra), the next 14 go into the underlying (n-2)-shell as f-electrons (La-Yb and Ac-No), the next 10 go into the underlying (n-1)-shell as d electrons (Lu-Hg and Lr-112), and the last six complete the filling of the outer n-shell as p-electrons (Tl-Rn and 113-118). The f-electrons are so named because

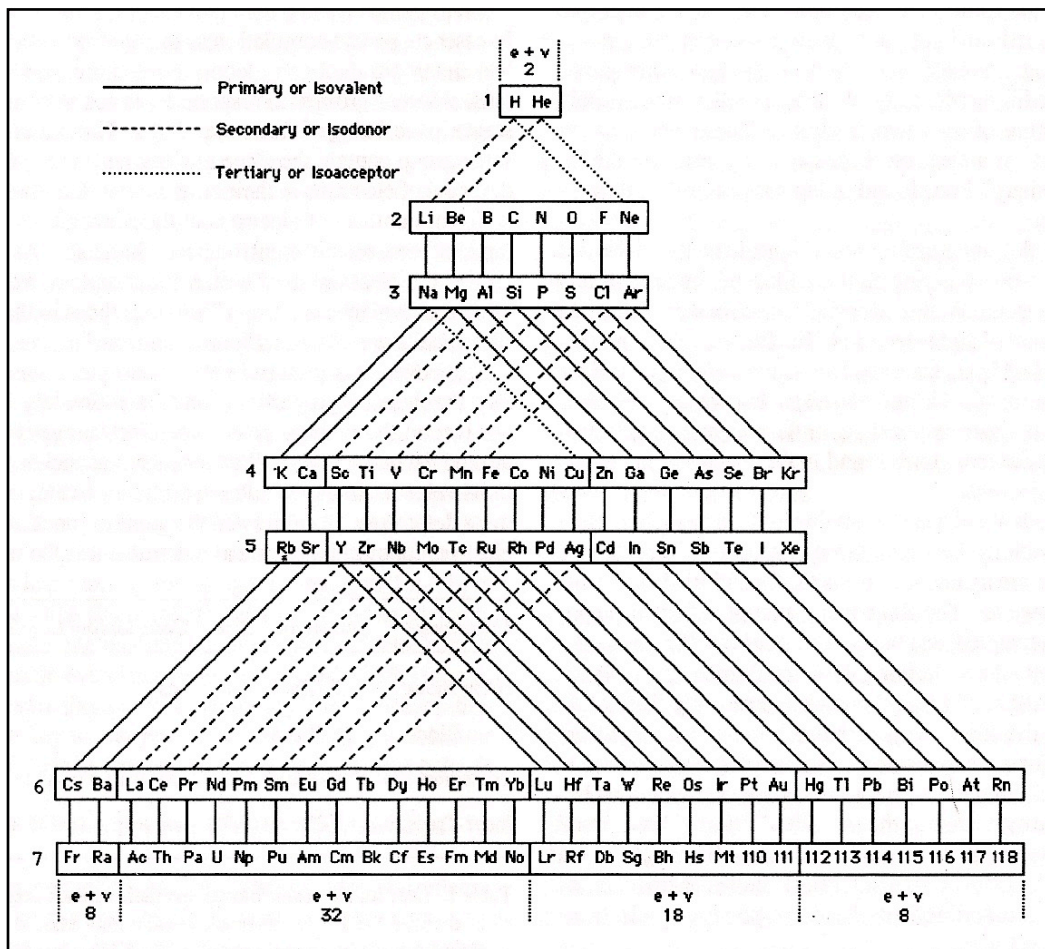


Figure 8. A modern “step-pyramid” version of the periodic table.

they are responsible for the appearance of the so-called “fundamental” lines in the spectra of the corresponding atoms.

The electronic filling sequence outlined above is actually idealized. In fact, about a third of the elements exhibit minor variations in their electronic structures or configurations involving interchanges of one or two of the s-, d- or f-electrons. However, these exceptions have little influence on the chemical behavior of the atoms in question.

Electronic Blocks and Valence Groups

In essence, period completion in the modern table parallels electronic-shell completion in the corresponding atoms, whereas groups correspond to atoms at equivalent stages in the filling of their outer shells. Thus atoms in the same group contain the same number and type (i.e., s, p, d, f, etc.) of electrons in their outer incomplete shells, but different numbers of electrons in their inner filled shells (and, of course, different nuclear charges). As noted above, the electrons in the outer, incomplete

shells are known as “valence electrons,” whereas those in the inner filled shells are known as “core electrons.”

However, this picture is still incomplete. In actual fact, the chemical properties of an atom ultimately depend not just on the number of valence electrons present but also on the number of unfilled levels or vacancies present in its valence shells. While the number of valence electrons determines the ability of the atom to function as an electron donor in its chemical reactions, it is the number of valence vacancies that determines its ability to function as an electron acceptor. It is rather the sum of an atom’s valence-electron count (e) and its valence-vacancy count (v) that determines both the size of its overall valence manifold (m) and its overall chemical behavior:

$$m = e + v \quad [3]$$

Note that the term “valence shells” rather than “valence shell” is used because the overall valence manifold may contain contributions not only from the outermost n-

Traditional	Systematic	m	Contributing Levels
H-He Block	S-Block	2	ns
Main Block	P-Block	8	ns + np
Transition Block	D-Block	18	ns + np + (n-1)d
Inner-Transition Block	F-Block	32	ns + np + (n-1)d + (n-2)f

Table 1. The four electronic blocks and their valence manifolds. Note that the S-, P-, D- F-block terminology should not be confused with the more common s-, p-, d-, f-block terminology which fails to take valence vacancies into account.

shell, but also from the underlying incomplete (n-1) and (n-2) shells.

From a modern electronic point of view, Mendeleev's short-form table erred in attempting to force elements having different-sized valence manifolds into the same group based solely on their valence-electron counts. Modern, long-form tables, on the other hand, first separate the elements into "electronic blocks" based on the size of their valence manifolds. Only then do they further divide them into individual valence groups based on their valence-electron counts. The resulting electronic blocks are shown in Table 1, along with a breakdown of each valence manifold in terms of its component shells and levels. Also included is a proposal for a set of more systematic names based on the nature of the levels added to the valence manifold of each successive block.

Despite their preference for the short-form table, Mendeleev and many other 19th-century chemists clearly recognized, on purely chemical grounds, the fundamental differences between the main-block and the transition-block elements and even proposed alternative, albeit less popular, tables in which these elements were spatially separated from one another. Full recognition of a separate F-block or inner-transition block, on the other hand, did not come until after the proposal of the "actinide hypothesis" by Glenn Seaborg in 1945. This postulated the existence of a row (Ac-No) of actinium-like (actinoid) elements in period 7 paralleling the rare-earth (La -Yb) or lanthanum-like (lanthanoid) elements found in period 6. Surprisingly, the recognition of a separate S-block for H and He came even later (Ramires-Torres, 1955; Huheey, 1972), even though this seemingly trivial observation holds the key to resolving the long-standing problem of where to place hydrogen and helium in the periodic table (see below).

Primary, Secondary, and Tertiary Relationships

In the step-pyramid table, atoms having identical valence-electron counts and identical valence-vacancy counts are said to exhibit a primary or isovalent relationship to one another. In the table, they are either aligned vertically with one another or are connected by means of a solid diagonal line. Elements of this type are both isodonors and isoacceptors. Consequently they tend to exhibit similar maximum and minimum oxidation states in their compounds. Thus both S and Se form higher oxides of the form XO_3 , in which both elements exhibit a maximum oxidation state of 6+, and both form binary chalcides salts (sulfides and selenides) in which they exhibit a minimum oxidation state of 2-.

Atoms having identical valence electron counts but different valence vacancy counts are said to exhibit a secondary or isodonor relationship to one another. In the step-pyramid table, they are connected by means of a broken diagonal line. Elements of this type are isodonors but not isoacceptors. Consequently, though they exhibit similar maximum oxidation states in their compounds, they display very different minimum oxidation states. Thus while Cl and Mn both form higher oxides of the form X_2O_7 , in which they exhibit a maximum oxidation state of 7+, the lowest oxidation state found for Cl is 1-, whereas that found for Mn is 3- (in $K_2[Mn(CO)_4]$).

Atoms having identical valence-vacancy counts but different valence-electron counts are said to exhibit a tertiary or isoacceptor relationship to one another. In the step-pyramid table, they are connected by means of a dotted diagonal line. Elements of this type are isoacceptors but not isodonors. Consequently, though they exhibit similar minimum oxidation states in their compounds, they display very different maximum oxidation states. Thus, while Cl and H both exhibit a minimum oxidation state of 1- in their chloride and hydride salts, in their corresponding oxides, Cl exhibits a maximum oxidation state of 7+, whereas H exhibits a maximum oxidation state of only 1+.

Note that primary relationships are always intra-block in nature, whereas secondary and tertiary relations are always interblock in nature.

Other Forms of the Periodic Table

The step-pyramid table has been used to illustrate the modern electronic version of the periodic law because it is the only table capable of simultaneously showing primary, secondary, and tertiary relationships. However, it is hardly the only acceptable version of the periodic table in existence. In a 1974 survey, the American chemist Edward Mazurs reviewed more than 750 different versions of the periodic table that have appeared in the

chemical literature since Mendeleev's original paper of 1869. Many of these tables are actually trivial variations of one another and each has both its positive and negative features. Among this multitude of choices, at least two are worthy of further mention.

The first of these tables does a superior job of emphasizing the fact that the elements fall into four distinct electronic blocks. It is shown in figure 9, and was first proposed by the American chemist, Robert Sanderson, in 1964. It is known as the "double-appendix" table because it is created from the full step-pyramid table by pulling down both the F-block and D-block elements as separate appendices and closing up the resulting gaps in the P-block. However, this is done at the cost of losing the ability of explicitly indicating secondary and tertiary relationships by means of broken and dotted tie-lines.

The second of these tables, known as the "medium block" table, is shown in figure 10. It has become increasingly popular since about 1945 and is currently the table of choice in most textbooks and reference books, although it is distinctly inferior to both the full step-pyramid table and the double-appendix table when it comes to illustrating subtler levels of chemical similarity. It is created from the full step-pyramid table by pulling down the F-block as an appendix, closing up the resulting gap in the D-block, and splitting apart the P-block to eliminate the diagonal offsets.

Placement Problems

All three of the modern periodic tables shown in figures 8-10 have been modified to incorporate the tentative resolution of three long-standing placement problems. The first of these involves the placement of hydrogen and, to a lesser extent, the placement of helium. Most current tables either place H in the Li group of the main block, along with the alkali metals (Li-Fr), or in the F group of the main block, along with the halogens (F-At). Yet others attempt to compromise by simultaneously placing hydrogen in both positions or by floating it in space above the rest of the table. The problem with helium is less apparent. There is no doubt that chemically it resembles the noble gases in the Ne group (Ne-Rn) of the main block. However, when it comes to valence electron counts, it should be classified with the alkaline-earth metals (Be-Ra) in the Be group of the main block.

The resolution of these ambiguities lies in the recognition that H and He form a separate electronic block. They are in fact simultaneously related to all of the above groups, but by means of secondary and tertiary, rather than primary relationships. Thus H and He exhibit secondary isodonor relationships with the alkali metals and alkaline earth metals by virtue of their

Figure 9. The Sanderson "double-appendix" version of the periodic table.

valence-electron counts, and tertiary isoacceptor relationships with the halogens and noble gases by virtue of their valence-vacancy counts.

The second placement problem involves the question of where the transition or D-block ends. An increasing number of textbooks now display periodic tables in which the elements of the Zn group (Zn, Cd, and Hg) are listed as transition metals or D-block elements. In actual fact, the evidence overwhelmingly indicates that these elements never make use of either d-electrons or d-type valence vacancies in their chemistry. They are in fact main-block or P-block elements whose valence manifolds contain only s- and p-levels. Thus the D-block or transition block begins with the Sc group and ends with the Cu group, as is most clearly shown in Sanderson's double-appendix table.

The third and final problem involves the placement of La and Ac. Should they be counted as the first members of the D-block in periods 6 and 7, with the F-block

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European AB American ABA ACS 1-18		IA VIII B IA VIII A 1 18		1 H He												
IA IIA IA IIA 1 2											IIIB IVB VB YIB YIIB YIIIB IIIA IVA YA YIA YIIA YIIIA 13 14 15 16 17 18					
2 Li Be	IIIA	IVA	VA	VIA	VIIA	VIIIA	IB	IIB	B	C	N	O	F	Ne		
3 Na Mg	IIIB	IVB	VB	VIB	VII B	VIII B	IB	IIB	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 Cs Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7 Fr Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	110	111	112	113	114	115	116	117	118
No Labels Provided in Any of the Systems																
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 10. The popular “medium-block” version of the periodic table.

beginning at Ce and Th, or should they be considered as the first members of the F-block, with the D-block beginning at Lu and Lr? The problem arises because there are no f-electrons in the ground-state configurations of La and Ac. As in the case of hydrogen, most textbooks attempt to resolve this issue by simultaneously placing La and Ac in both positions. However, an analysis of the chemical and physical evidence seems to support the second of these choices and the interpretation of La and Ac as F-block elements having irregular electronic configurations. Thus the F-block in periods 6 and 7 begins at La and Ac and ends with Yb and No. It is true that La and Ac are also related to Sc and Y in the first group of the D-block, but this is a secondary relationship based on identical valence-electron counts, rather than a primary relationship based on identical valence manifolds.

Mendeleev’s short-form table of 1871 contained a total of 12 periods or series, which he numbered using Arabic numerals. However, from period 4 onwards, these periods were not equivalent, since the even-numbered periods each ended with a collection of elements in Group VIII, whereas the odd-numbered peri-

ods did not. Early 20th-century versions of the short-form table occasionally reduced the number of periods from twelve to seven by pairing these higher odd and even periods in order to form the A and B branches of a smaller set of super-periods. Thus periods 4 and 5 of Mendeleev’s table became the A and B branches of period 4 in the newer short-form tables, periods 6 and 7 became branches A and B of period 5, etc.

Arabic numerals are still used to denote periods in the modern table. However, the period numbers have now been given an underlying physical interpretation by making them correspond to the quantum number of the outermost valence shell for the atoms in the period in question. This numbering scheme is used in all three of the modern periodic tables given in figures 8-10.

Group Labels

In his table of 1871 Mendeleev used Roman numerals to denote his valence groups. With the advent of the A and B subperiods, it became customary to also talk about the A and B branches of each valence group. Thus Be and

Mg were described as simply being in Group II but, beginning with period 4, it was necessary to further distinguish between those elements in Group IIA (Ca-Ra), which fell on the A branches of the corresponding periods, and those in Group IIB (Zn-Hg), which fell on the B branches. This method of modifying the group numbers is now known as the European AB method, and is illustrated in the first line along the top of the medium-block table in figure 10. It should be noted that most American textbooks fail to recognize that these modifiers only apply to the elements in periods 4 and higher.

A second method of modifying Mendeleev's Roman numeral system, known as the American ABA system, is shown in the second line along the top of the table in figure 10. The precise origins of this method are not known, though it appears to have first been used by the American chemist, Horace Deming, in his popular general chemistry textbook of 1923. This method essentially associates the A modifier with main-block elements and the B modifier with transition-block elements. Because of its loose correlation with electronic blocks, this method was widely adopted by American chemists after World War II. However, the method fails to provide similar modifiers for both the H-He block and the inner-transition or F-block. In addition, it incorrectly implies that the members of the Zn group are transition or D-block elements.

A third method, adopted by the American Chemical Society (ACS) and the International Union of Pure and Applied Chemistry (IUPAC) in 1990, is shown in the third line along the top of the table in figure 10. This method eliminates both the AB modifiers and the Roman numeral valence labels. Instead the groups are simply counted and numbered accordingly as 1-18. Group labels now function as enumerators rather than as descriptors, since they no longer provide information about valence-electron counts. Unfortunately this method is largely tied to the peculiarities of the medium-block form of the periodic table. It totally ignores the 14 groups in the F-block and forces one to incorrectly classify both H and He as main-block elements.

A fourth method, based on the S, P, D, F block labels listed in Table 1, is shown at the top of the double-appendix table given in figure 9. Each group label consists of an Arabic numeral corresponding to the total valence-electron count for the members of the group in question and is prefixed by a modifier indicating the electronic block to which the group belongs. Since these block modifiers directly correlate with the size of the overall valence manifold, the number of valence-shell vacancies for each group is easily calculated by means of equation 3.

In addition to these various numerical methods, most of the groups in the main-block also have traditional descriptive names, many of which predate the discovery of the periodic law. These are summarized in Table 2. It is also possible to systematically identify each group by using the name of the first element in the group. This practice is becoming increasingly common in the textbook literature and was used earlier when reference was made to the Li group, the Zn group, etc.

Electronic	Descriptive	Traditional
P1	Li group	alkali metals
P2	Be group	alkaline-earth metals
P3	B group	none
P4	C group	adamantogens
P5	N group	pnictogens
P6	O group	chalcogens
P7	F group	halogens
P8	Ne group	noble gases

Table 2. Electronic, descriptive, and traditional names for the groups of the main-block elements in the periodic table.

Select Annotated Bibliography

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