The Role of Triads in the Evolution of the Periodic Table: Past and Present

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It has been suggested by various authors that an improved form of the periodic table might be the left-step form, as first proposed by Charles Janet, in which helium is placed among the alkaline earths *(1)*. The present author's previous support for this form of representation was not motivated by any chemical intuition concerning the element helium, but rather by a desire for greater regularity in the form of the periodic table. In common with other authors, the present author has also suggested that the left-step table reflects the manner in which electrons occupy atomic orbitals more directly than the conventionally used medium-long form table *(2)*.

The left-step table (Figure 1) allows one to display the $n + \ell$ rule very prominently contrary to the medium-long form. Successive periods are identified with increasing values of $n + \ell$, the sum of the first two quantum numbers denoting the atomic orbital in which the differentiating electron is located. Meanwhile, the medium-long form is based on numbering successive periods with increasing values of just the first quantum number, *n*. Consequently, when using the medium-long form, one encounters complications starting with the fourth period, which involves the filling of the 4s orbital followed by the 3d and 4p orbitals successively.

Dual Sense of the Concept of "Element"

In our previous work the justification for ignoring the apparent clash with chemical intuition regarding helium, was essentially philosophical and formed the main motivation for that proposal. Although it is not well known, Mendeleev repeatedly argued that the periodic system is not primarily a classification of the elements regarded as simple substances (Lavoisier's elements) but, more correctly, a classification of elements regarded as basic substances. The terminology being used here is not Mendeleev's but rather due to Paneth who, sometime later, wrote,

> I suggested that we should use the term "basic substance" whenever we want to designate that which is indestructible in compounds...and that we should speak of a "simple substance" when referring to the form in which such a basic substance, not combined with any other, is presented to our senses *(3)*.

Mendeleev himself makes the distinction between the two senses of the term element in a number of passages, including the following,

> It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous substance, and as a *material* but invisible *part* of a compound. Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, that, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is contained in mercury oxide; it only contains the substance of the elements, just as steam only contains the substance of ice, but not ice itself, or as corn contains the substance of the seed but not the seed itself *(4)*.

To state the distinction otherwise, simple substances are the manifestation of the elements considered as basic substances, the latter being the more fundamental of the two senses of the term "element". Admittedly the terminology is a little unfortunate since the labels "basic" and "simple" appear to place the two senses of the term element on the same epistemological level. The intention however is that basic substances are to be regarded as more fundamental. Be that as it may, we will retain Paneth's terminology in view of the importance of the writings of this author in which the distinction is perhaps more clearly established than elsewhere in the literature *(5)*.

We have previously suggested that concentrating on elements as basic substances means that one could ignore the apparent absurdity of placing helium among the alkali earths since elements as basic substances do not possess properties in the macroscopic sense. Strictly speaking an element as a basic substance possesses no properties but as Mendeleev suggested it should be attributed just one characteristic—atomic weight, or in present day terms—atomic number.

However, one aspect, having to do with triads of elements, is troubling in this otherwise elegant left-step periodic system. The use of the left-step table results in the loss of a triad involving helium, neon, and argon.

Triads

Although triads were highly instrumental in the discovery of the periodic system, the concept of atomic weight triads be-

																														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	Co	Ni	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	Db	Sg	Bh	Hs	Mt	Ds	Rg									

Figure1. Left-step periodic table.

came somewhat neglected following the accurate determination of atomic weights.

But as argued in a recent book, once one accepts that the more correct ordering principle for the elements is atomic number the concept of triads makes a significant return, at least in about half of all conceivable triads in the modern table *(6)*. Using the atomic numbers of chlorine, bromine, and iodine for example the middle element is not just the approximate mean of the atomic numbers of the flanking elements but the exact mean.

If one looks for an atomic number triads among the elements helium, beryllium, and magnesium within the left-step table one encounters a serious discrepancy. Moreover, the conventional placing of helium among the noble gases gives a perfect atomic number triad. So why would one want to lose an atomic number triad by adopting the left-step table? This we suggest now is a serious objection against the repositioning of helium in the way that is carried out in the left-step table. As will be argued, the existence of atomic number triads represents a fundamental aspect of periodic classification because it depends just on atomic number which, as mentioned above, is the one essential criterion for the characterization of elements as basic substances.

A Brief History of Triads

Perhaps the earliest hints of any numerical regularity among the atomic weights of the elements was discovered as early as 1817 by Döbereiner. He was the first to notice the existence of various groups of three elements, subsequently called triads, that showed chemical similarities. In addition, such elements displayed an important numerical relationship, namely that the equivalent weight, or atomic weight, of the middle element is the approximate mean of the values of the two flanking elements in the triad.

In 1817 Döbereiner found that if certain elements were combined with oxygen in binary compounds, a numerical relationship could be discerned among the equivalent weights of these compounds. Thus when oxides of calcium, strontium, and barium were considered, the equivalent weight of strontium oxide was approximately the mean of those of calcium oxide and barium oxide. The three elements in question, strontium, calcium, and barium were said to form a triad.

$$\mathrm{SrO} = \frac{\mathrm{CaO} + \mathrm{BaO}}{2} = \frac{59 + 155}{2} = 107$$

Though Döbereiner was working with weights that had been deduced with the relatively crude experimental methods of the time, his values compare rather well with current values for the triad:

$$104.71 = \frac{56.08 + 153.33}{2}$$

Döbereiner's observation had little impact on the chemical world at first but later became very influential. He is now regarded as one of the earliest pioneers of the development of the periodic system. Very little happened regarding triads until twelve years later, in 1829, when Döbereiner added three new triads. The first involved the element bromine, which had been isolated in the previous year. He compared bromine to chlorine and iodine, using the atomic weights obtained earlier by Berzelius:

$$\mathrm{Br} = \frac{\mathrm{Cl} + \mathrm{I}}{2} = \frac{35.470 + 126.470}{2} = 80.970$$

The mean value for this triad is reasonably close to Berzelius' value for bromine of 78.383. Döbereiner also obtained a triad involving some alkali metals, sodium, lithium, and potassium, which were known to share many chemical properties:

$$\mathrm{Na} = \frac{\mathrm{Li} + \mathrm{K}}{2} = \frac{15.25 + 78.39}{2} = 46.82$$

In addition he produced a fourth triad:

$$\mathrm{Se} = \frac{\mathrm{S} + \mathrm{Te}}{2} = \frac{39.239 + 129.243}{2} = 80.741$$ [1]

Once again, the mean of the flanking elements, sulfur (S) and tellurium (Te), compares well with Berzelius' value of 79.5 for selenium (Se).

Döbereiner also required that, in order to be meaningful, his triads should reveal chemical relationships among the elements as well as numerical relationships. On the other hand he refused to group fluorine, a halogen, together with chlorine, bromine, and iodine, as he might have done on chemical grounds, because he failed to find a triadic relationship between the atomic weights of fluorine and those of these other halogens. He was also reluctant to take the occurrence of triads among dissimilar elements, such as nitrogen, carbon, and oxygen, as being in any sense significant even though they did display a triadic numerical relationship.

Suffice it to say that Döbereiner's research established the notion of triads as a powerful concept, which several other chemists were soon to take up with much effect. Indeed, Döbereiner's triads, which would appear on the periodic table grouped in vertical columns, represented the first step in fitting the elements into a system that would account for their chemical properties and would reveal their physical relationships.

Later Work on Triads

It is probably fair to say that much time was wasted by other researchers in trying to uncover triads where they simply did not exist. Some pioneers, including Mendeleev, made it a point to turn their backs on numerical approaches such as Prout's hypothesis and the search for triads. This attitude certainly seems to have paid dividends for Mendeleev in that he made progress where others had failed to do so.

The problem with triads, as well as the other important numerical hypothesis due to Prout, is easy to discern in retrospect. It is simply that atomic weight, which both concepts draw upon, is not the most fundamental quantity that can be used to systematize the elements. The atomic weight of any element depends on the particular geological origin of the sample examined. In addition, the atomic weight of any particular element is an average of several isotopes of the particular element.

Mendeleev's Path to Mature Periodic System

Many historians have examined in detail the path that Mendeleev took in arriving at his early periodic tables. It seems to be agreed that the first key document, which still exists, consists of a letter sent to Mendeleev. On the back of the letter Mendeleev

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	Co	Ni	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	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Figure 2. Long-form periodic table.

sketched some rudimentary ideas on how best to arrange the elements into a coherent system.

This letter, which is held in the Mendeleev archives, is dated February 17, 1869, which is also the date of the famous first table that Mendeleev produced. The letter is from one Alexei Ivanovich Khodnev, secretary of the Free Economic Society in St. Petersburg, inviting Mendeleev to the visit to a cheese factory where he was due to conduct an inspection. On the back of the letter Mendeleev has made a comparison of the following atomic weights:

23	39	85	133
7 or 14	24	65	112
16 or 9	15	20	21

Historians differ regarding the precise assignment of elements to these values. In particular they disagree with respect to the identity of the element depicted as 7 or 14. According to some it is twice the atomic weight of lithium, while others maintain that it is beryllium using an older value for its atomic weight.

Na	K	Rb	Cs
2 Li?	Mg	Zn	Cd

Kedrov, and after him Dimitriev, conclude that the first entry in the second row should be twice the weight of lithium *(7)*. In any case it is clear that Mendeleev is groping his way towards a horizontal relationship by examining differences in atomic weights and is starting to see hints of almost constant differences in some cases such as Rb/Zn and Cs/Cd. We suggest that his endeavor was in the same spirit as the search for triads. The only difference being that in the case of a triad one seeks two differences between the weights of three elements rather than just two as Mendeleev was doing in these early attempts.

A similar activity is found in Mendeleev's first attempt at a periodic system as presented in a hand-written table. If one examines the calculations that he is carrying out one finds again an attempt to compute differences between the atomic weights of elements in the columns of his table. For example Mendeleev writes the number 27 in smaller writing below the symbols for potassium (Zn – K = 65 – 39 = 27) and again below rubidium (Cd – Rb = 112 – 85 = 27).

It appears that, in the space of a single day, February 17th 1869, Mendeleev not only began to make horizontal comparisons but also produced the first version of a full periodic table that included most of the known elements. Moreover, Mendeleev's overall approach consists of looking at atomic weight differences in conformity with the general principle of triads even though he was not specifically identifying triads in the manner of Döbereiner.

Mendeleev's Use of Triad-Like Concepts To Make Predictions

Mendeleev went to some length to distance himself from the use of numerical relationships such as Prout's relationship and the notion of triads. However, it is quite clear that many of his predictions of the properties of new elements involve the notion of triads. The triads he considered were sometimes vertical, or horizontal, or at times the combination of both vertical and horizontal triads.

In the various editions of his textbook, and in the publications dealing specifically with his predictions, Mendeleev repeatedly illustrates his method using the known element selenium as an example. The atomic weight of selenium was known at the time and so could be used to test the reliability of his method. Given the position of selenium and the atomic weights of its four flanking elements,

	S (32)	
As (75)	Se ?	Br (80)
	Te (127.5)	

the flanking atomic weights can be averaged to yield approximately the correct value for the atomic weight of selenium:

$$\frac{32 + 75 + 80 + 127.5}{4} = 79$$

Atomic Number Triads

The atomic weight of any particular elements is not a fundamental property in that it depends upon terrestrial contingencies concerning isotopic abundances. Atomic number, on the other hand, is fundamental and more correctly characterizes the distinction between one element and the next. The adoption of atomic number has an intriguing consequence on triads that has seldom been discussed. This is the fact that approximately 50% of all vertical triads based on atomic number, rather than atomic weight, is mathematically exact. This remarkable result is easy to appreciate by referring to the long-form of the modern periodic table (Figure 2).

By considering elements from rows 1, 2, and 3, such as helium, neon, and argon one obtains a perfect atomic number triad,

He	2
Ne	10 = (2 + 18) / 2
Ar	18

or from rows 3, 4, and 5, for example,

																												H	He	Li	Be	1,2
																								B	C	N	O	F	Ne	Na	Mg	3
																								Al	Si	P	S	Cl	Ar	K	Ca	4
														Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	5
														Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	6
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	7
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg										8

Figure 3. New proposed periodic table. Numbers at the right of table denote values of $n + \ell$ for each period and not principal quantum numbers.

P 15
As 33 = (15 + 51) /2
Sb 51

or from rows 5, 6, and 7,

Y 39
Lu 71 = (39 + 103) / 2
Lr 103

Alternatively any triads taken from combinations of elements in rows 2, 3, 4 or 4, 5, 6 and so on, do not give perfect triads. The reason why this works so perfectly, albeit in only about 50% of possible triads, is because the length of each period repeats just once in the long-form periodic table, with the exception of the very first short period. The full sequence is 2, 8, 8, 18, 18, 32, presumably 32, and so forth.

So if one selects any element at random there is a 50% chance that the element above and below the selected element, in the same column of the periodic table, will have atomic numbers at an equal interval away from the original element. If this is the case, then it follows trivially that the second element in the sequence will lie exactly mid-way between the first and third elements. In numerical terms, its atomic number will be the exact mean of the first and third elements, or in other words the atomic number triad will hold perfectly. All one needs to do is to pick a middle element from the first of a repeating pair of periods. Thus about half of all the elements are good candidates for beginning a triad. This phenomenon is therefore a mathematical consequence of the fact that all periods repeat (except for the first one) and that the elements are characterized by whole number integers.

It would appear that the original discoverers had accidentally stumbled upon the fact that the length of most periods of elements repeat. What held them back was that these repeat distances vary in length and, of course, the fact that they were operating with the vagaries of atomic weight data. It is somewhat amusing to think that the ancient notion triads of elements, which was initially so productive but later and later came under criticism, should now emerge as being essentially correct, and that the reason for its correctness is now fully understood. It might also be mentioned that a recent article in this *Journal* has proposed using atomic weight triads to predict the atomic weights of the trans-lawrencium elements *(8)*.

The aim of the present article is to elevate the role of triads to an even greater extent. Since triads are now expressed in terms of atomic numbers they coincidentally characterize the elements as basic substances. In other words they characterize the true basis for periodic classification compared with the elements as simple substances, as argued by Mendeleev and more recently by Paneth and other authors.

The New Proposal

Finally let us turn to the new periodic table, which it is claimed restores a fundamental role to triads. Rather than relocating helium to the alkaline earths and thereby losing a perfect triad (He, Ne, Ar), we propose to relocate hydrogen into the halogen group, thereby gaining one completely new perfect triad (H, F, Cl) as shown in Figure 3.

In chemical terms this proposal is certainly more conservative and more generally plausible to chemists, than the relocation of helium, although this is not the reason for suggesting it here. In addition, the relocation of hydrogen is supported in some respects on chemical grounds as has been argued previously by many authors *(9)*.

Conclusion

We are not under any illusion that chemical educators or governing bodies of chemistry will readily accept this new proposal. It is being suggested to promote further discussion on the presentation of the periodic system and because it appears to rest on the fundamental criterion of elements as basic substances. Of course even the medium-long form table (not shown) utilizes atomic number for the purposes of ordering the elements in what might be termed primary classification. What is being proposed here is that triadic relationships between atomic numbers can also serve for the purpose of secondary classification, namely the placement of elements in groups or columns.

As suggested in the title of the present article, we believe that the periodic table, which initially arose from the discovery of atomic weight triads, can now be further enhanced by recognizing the fundamental importance of atomic number triads. In addition one should recognize the more fundamental nature of the elements as basic substances rather than as simple substances, and that the periodic system is primarily a classification of the former. Whereas we previously suggested that these aims were best served by the left-step table we now favor the revised left-step table shown in Figure 3.

The proposed new table retains most of the feature of the Janet left-step table but does not commit one to placing helium in the alkaline earths. The regular form of the table represents an advantage over the medium-long form and the closer connection with electron-shell filling that the left-step table offers is maintained with the small disadvantage that two values of $n + \ell$, namely 1 and 2, appear in the same first row.

The new proposed version does not alleviate the concern that some authors voice in wanting to maintain the metals on the left and non-metals on the right of the table. We suggest that such a desideratum does not necessarily reflect the most fundamental aspects of the elements as basic substances whereas the left-step and its new variant do. The latter two forms aim to represent elements as basic substances as well as establishing a closer connection with fundamental aspects of electron-shell filling, and consequently with quantum mechanics, than the medium-long form table does. Finally, we have recently published another new table that differs only in shape from the one proposed here *(10)*.

Note

1. This seems to be a printer's error since the mean should be 84.241.

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