Looking Backwards and Forwards at the Development of the Periodic Table

by Eric Scerri

Since the periodic table has reached the ripe old age of 150 years it may be an appropriate time to look back at the development of this unique scientific icon. It is also an opportunity to look forwards to any changes that the periodic table may undergo in view of the ever-growing list of new elements that continue to be synthesized. The way that the past and future will be examined in this article will be to follow a main thread that focuses on the number of columns in the periodic table at various stages in its development.

MENDELÉEFF'S TABLE I.—1871.

Series.	Group I. R_2O.	Group II. RO.	Group III. R_2O_3.	Group IV. RH_4. RO_2.	Group V. RH_3. R_2O_5.	Group VI. RH_2. RO_3.	Group VII. RH. R_2O_7.	Group VIII. RO_4.
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Ce=59 Ni=59, Cu=63
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	? Y=88	Zr=90	Nb=94	Mo=96	—=100	Ru=194, Rh=104 Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	? Di=138	? Ce=140	....	....	....	....
9	....	....	....	....	....	....	....	....
10	....	....	? Er=178	? La=180	Ta=182	W=184	....	Os=195, In=197 Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	....	....	
12	....	....	....	Th=231	....	U=240	....	....

Figure 1. Short-form or eight column periodic table as devised by Mendeleev in 1871.

So, let's begin with Mendeleev and the others who discovered chemical periodicity in the 1860s and generally presented their findings in the form of an 8-column table or what has become known as a short-form table (figure 1) [1]. This format has several appealing features which are worth pausing to consider. The first virtue is the simplicity of the short-form. It is based on the notion that chemical and physical properties recur approximately after eight elements and continue to do so. Unfortunately, some of the directness of this presentation is lost on moving to the 18-column format (figure 2) or even wider periodic tables.

A second virtue is that the 8-column table groups together a wide range of elements that share the same highest valency. For examples, beryllium, magnesium, calcium, strontium and cadmium all appear in the second column of the short-form table. Not surprisingly, the 8-column table is still used in certain parts of the world, most importantly in Russia where its most successful version was first discovered by Mendeleev in 1869. The reason why Mendeleev receives the most credit, even though he was the latest among the six independent co-discoverers, has been much debated by historians and philosophers of chemistry.

The usual account is that only Mendeleev made successful predictions of then unknown elements. However, another school of thought disputes the claim that successful predictions are quite so important and proposes that the successful accommodation of already known data is an equally good criterion for the acceptance of scientific theories and concepts [2].

The early periodic tables were required to literally accommodate the 60 or so elements that existed in the 1860s and the relationships between them, which was by no means a trivial task. Today a periodic table must accommodate the presence of about twice that number of elements and their similarity relationships.

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	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Fig 2. 18-column or medium-long form table

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18-column tables

The expansion of the periodic table from an 8-column format to one with 18-columns is not essential but seems to have been generally made some years after the initial discovery of chemical periodicity. There are several reasons why this change was made, some of them scientific and others pragmatic.

First of all, it must be recognized that the periodic table, an object of enormous utility, is man-made. It is not given to us directly by Nature even though chemical periodicity is a scientific fact. The precise form of the periodic table is a form of compromise that aims to serve the majority of scientists and students of science, but it cannot serve all of them at once. For example, chemists who choose to focus primarily on chemical similarities might wish to favor a particular format; chemical educators or experts focusing on atomic structure may favor a different format. The author does not claim that there is one optimal periodic table and yet he believes that it is worth striving to obtain the best possible compromise version that the scientific community can agree upon.

But let me return to the expansion of the table to an 18-column format. One reason for expanding the table in this way is that upon closer inspection chemical periodicity does not invariably operate with a constant repeat distance of eight elements. If one wants to capture chemical similarities among elements more accurately, one must accept that after two period lengths consisting of eight elements each, the repeat length becomes 18 elements. Consider for example the two metals chromium and molybdenum that are very similar chemically but stand 18 rather than 8 elements apart. The 18-column highlights such similarities more effectively than the 8-column version.

Another motivation for the adoption of the 18-column table was that Mendeleev's table displayed certain awkward looking anomalies. The 8-column table can only truly display chemical periodicity if certain short sequences of elements are excluded from the main body of the table. For example, Mendeleev relegated iron, cobalt and nickel to what he labelled as group VIII (figure 1). He did this again for ruthenium, rhodium and palladium as well as osmium, iridium and platinum, all of which elements he termed as transition elements.

In an 18-column table there is no longer any need to exclude these elements. This feature would seem to suggest that an 18-column format shows some advantages in terms of representing all the elements in an evenhanded manner, although as we will see below, the 18-column table introduces another set of 'relegated' elements.

In historical terms the use of an 18-column format has followed a complicated path. Interestingly, even Mendeleev published some medium-long form tables, although his versions contained 17 rather than 18 columns since the noble gases had not yet been discovered [3]. The advent of quantum mechanics and the notion that electrons can be regarded as being situated in distinct shells also seems to have motivated the widespread adoption of a medium-long or 18-column format. Simply put, the 18 groups arise from the fact that, starting with the 3rd main electron shell, electrons occupy s, p and d-orbitals, numbering 9 in all, each of which can be doubly occupied to make a total of 18 electrons and hence the atoms of 18 successive elements, with each one having an additional electron. Since not all electron shells reach their capacity once they contain 8 electrons, it makes perfect sense to expand the periodic table according to the quantum mechanical explanation of chemical periodicity.

32-column tables

However, from the 4th electron shell 14 more electrons can now be accommodated in addition to the previous 18. In the modern terminology we now have f-orbital electrons in addition to the earlier mentioned s, p and d orbital electrons. So why don't we expand the periodic table further to make it into a 32-column format (fig 3)? In fact, an increasing number of textbooks are beginning to show such a long-form periodic table, which again has some advantages and some disadvantages.

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	Cn	Nh	Fl	Mc	Lv	Ts	Og

Fig. 3. 32-column or long form table

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On the plus side, it allows every single element to be incorporated into the main body of the table. The odd-looking footnote to the 18-column table which traditionally houses the f-block elements now disappears. This is an analogous change to the one that occurs on moving from an 8 to an 18-column format that results in the incorporation of certain otherwise excluded elements into the main body of the table. Returning to the 32-column table, this also shows every single element in its correct sequence in terms of increasing atomic numbers as one moves through each period from left to right.

There are some pragmatic downsides, however. Presenting the periodic table in a 32-column format requires that the space for each element must be approximately halved. Worse still, the one or two-letter symbol for each element must now be reduced in size with the risk of rendering them less legible.

What next?

If we continue to follow this line of thinking regarding the progressive expansion of the periodic table we notice that the table may be due for yet a further expansion, at least in principle. Rapid advances have taken place in the synthesis of super-heavy elements in recent years. The f-block of the table has now been completely filled with elements, the most recent additions being nihonium, moscovium, tennessine and oganesson. For the very first time, and also the last time in the foreseeable future, the periodic table has absolutely no missing gaps. At least this state of affairs is true for the current periodic table that houses 118 elements arranged in seven periods.

There is no reason to believe that the periodic table has reached its end point and there are several current initiatives that are aimed at producing elements 119, 120 and beyond. The discovery of elements 119 and 120 will be easily accommodated by tagging two new spaces directly below francium and radium in either the 18 or 32-column formats. However, as soon as element 121 is synthesized, it will become necessary to introduce a new kind of footnote to the table to house what will be formally known as the g-block elements.

On the other hand, if we insist that all elements be placed together in the main body of the table and that all elements are numbered sequentially we will have no choice but to introduce a 50-column wide table! But this will only be the formal beginning of the g-block since theoretical calculations predict that the first element with a true g-orbital electron will be approximately element number 125 [4].

Interesting issues connected with the onset of new blocks of the table

Each time that a new kind of orbital occurs in the Aufbau and the sequence of increasing atomic numbers, a new kind of problem also seems to arise.

The first time that a d-orbital electron appears is in the atom of scandium, or element 21. In this case the claim that the atom contains a d-electron is not merely formal but is supported by much spectroscopic evidence. The problematical aspect concerns the fact that 3d orbital electrons only begin to appear after the 4s orbital has been occupied in the case of the atoms of potassium and calcium.

The vast majority of textbooks state that in the case of scandium the final electron to enter the atom, in terms of the fictitious but useful Aufbau scheme, is a 3d electron. This view immediately creates a problem when it comes to explaining the ionization behavior of the scandium atom. Experimental evidence clearly shows that the 4s electrons are preferentially ionized in scandium. If the 3d orbital had really been the final one to enter the atom it ought to be the first to be ionized, which runs contrary to the experimental facts. Almost every textbook proceeds to simply fudge the issue, in order to maintain that 4s electrons enter the atom first but are also the first to depart during the ionization process, something that clearly makes no sense in energetic terms [5].

The problem was clarified relatively recently by the theoretical chemist Eugen Schwarz who pointed out that in fact the 3d orbital electrons are preferentially occupied in scandium, followed by the 4s electrons and thus explaining perfectly why it is that 4s electrons are the first to be ionized [6]. However, it appears that Schwarz wants to throw out the "Aufbau baby with the bathwater." Schwarz correctly points out that the Madelung rule fails for all except the s-block elements. This is the rule that purports to show the relative energies of all the orbitals, and is part of the staple diet of high school and first-year undergraduate chemistry courses. However, any dismissal of this well-known mnemonic would be rather unfortunate since it still succeeds in listing the differentiating electron in all but about 20 atoms in the entire periodic table.

My reason for saying this is that as we move through the periodic table there is no denying that the differentiating electrons in potassium and calcium are 4s electrons while for scandium and most of the following transition metal atoms the differentiating electron is of the 3d variety. The Madelung rule therefore still rules when it comes to discussing the periodic table as a

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H 1																															He 2
Li 3	Be 4																									B 5	C 8	N 7	O 8	F 9	Ne 10
Na 11	Mg 12																									Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20															Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38															Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71	*La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103	*Ac* 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

H 1																																He 2
Li 3	Be 4																										B 5	C 8	N 7	O 8	F 9	Ne 10
Na 11	Mg 12																										Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20																Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38																Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	*Lu* 71		Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	*Lr* 103		Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

H 1																															He 2
Li 3	Be 4																									B 5	C 8	N 7	O 8	F 9	Ne 10
Na 11	Mg 12																									Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20															Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38															Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	*Lu* 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	*Lr* 103	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

Figures 4–6 (top to bottom): Three different long-form periodic tables with differences highlighted. Figure 4 (top): Version with group 3 consisting of Sc, Y, La, Ac. The sequence of increasing atomic number is anomalous with this assignment of elements to group 3, e.g., Lu (71), La (57), Hf (72). ***Figure 5 (middle):*** Second option for incorporating the f-block elements into a long-form table. This version adheres to increasing order of atomic number from left to right in all periods, but with lanthanum located at the start of a 15-element block. ***Figure 6 (bottom):*** Third option for incorporating the f-block elements into a long-form table. This version adheres to increasing order of atomic number from left to right in all periods, and groups Sc, Y, Lu and Lr together as group 3.

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whole, as opposed to the occupation and ionization behavior of a single element such as scandium as discussed above [7].

First appearance of an f-electron

In principle, or using the Madelung rule, we find that f-orbital electrons begin to appear in the atom of lanthanum or element 57. However, according to experimental evidence this event occurs at the next element cerium (Z = 58). Notice how this delayed onset is analogous to the delayed onset of g-electrons that was described above.

If one consults current versions of the periodic table one finds that there are at least three versions that are on offer. In the majority of textbooks and wall-chart periodic tables we find lanthanum located in the d-block directly below the atom of yttrium (figure 4). In a smaller number of currently available periodic tables one finds lanthanum located at the start of a 15-element wide f-block (figure 5); and yet a third version places lanthanum at the start of a 14-element wide f-block (figure 6).

As a result of these alternative tables there are three different ways of regarding group 3 of the periodic table. According to the first option group 3 consists of scandium, yttrium, lanthanum and actinium (figure 4). In the second option, which features a 15-element wide f-block, group 3 contains a mere 2 elements, namely scandium and yttrium (figure 5). Finally, the third form of the periodic table implies that group 3 should be regarded as containing scandium, yttrium, lutetium and lawrencium (figure 6). What is a student of chemistry, or even a professional chemist to make of all of this?

A further complication is that neither chemical and physical evidence on the elements concerned, nor microscopic evidence in the form of electronic configurations, provide an unambiguous resolution of the question. One possible way to try to resolve the issue is to consider a 32-column table representation, and return to the main theme of this article. It turns out that in a 32-column table that also maintains all the elements in their correct sequence of increasing atomic number, the 3rd option would seem to be the most reasonable choice [8].

Needless to say, it is important for IUPAC to be in a position of recommending a compromise periodic table that most effectively conveys the largest amount of information to the largest group of users. Since the periodic table is a human construct there is no absolutely correct version of the periodic table. My own personal recommendation is that group 3 should be considered as consisting of scandium, yttrium, lutetium and lawrencium and that the f-block should formally begin at lanthanum even though the atom of lanthanum does not actually contain an f-electron. It remains to be seen what the recommendations of the working group will be [9].

What does not seem to be well known, even though Jeffery Leigh has written an article on the subject in this very magazine, is that there is currently no officially recommended IUPAC periodic table even though it regularly publishes one [10]. Now that the periodic table has reached 150 years it may be time for IUPAC to take the plunge and go ahead and recommend one official table.

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