

Döbereiner revisited

This year is the sesquicentenary of the “birth” of the Periodic Table. A decade ago, at the beginning of 2009, a IUPAC editorial [1] offered “something *old*, something *new*, something *borrowed* and something *blue*” in an issue devoted to IUPAC’s position, *inter alia*, on the periodic table. The periodic table featured in [2] (“Newlands revisited”, henceforward ‘NR’, Fig. 1) was a response to this ongoing debate on the form of the periodic table:

		Groups →													
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Periods ↓	1st	H	He												
	2nd	Li	Be	B	C	N	O								
		F	Ne												
	3rd	Na	Mg	Al	Si	P	S								
		Cl	Ar												
	4th	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni				
Cu		Zn	Ga	Ge	As	Se									
Br		Kr													
5th	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd					
	Ag	Cd	In	Sn	Sb	Te									
	J	Xe													
6th	Cs	Ba	La	Ce	Pr	Nd	Pm	Sa	Eu	Gd	Tb	Dy	Ho	Er	
	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt					
	Au	Hg	Tl	Pb	Bi	Po									
	At	Nt													
	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Ei	Fm	

s
p
d
f
1s ¹
1s ² p ⁶ = Group 0

(Fig. 1)

NR preserves the *old* subgroups (Newlands’ columns) that were a feature of all short forms, although NR would then have been described as a ‘medium form’ (14 groups) in contrast to Mendeleev’s ‘short form’ (8 groups) or Werner’s ‘long form’ (32 groups). NR naturally continues the grouping of the lanthanoids and actinoids whose initial four groups were also included in ‘short form’ tables.

The logic of the arrangement of the s-elements is a *new* feature of NR. It recognizes the chemical subgroups of hydrogen, *viz.* the alkali metals and the halogens, and of helium, *viz.* the alkaline earth metals and the inert gases. It is interesting to note that subgroups differ chemically from each other inversely as the azimuth but decreasingly so, *i.e.* Li:F >> Ca:Zn > La:Lu.

The whole idea of NR is, of course, **borrowed** from Newlands. The group numbers are borrowed from valency but also from electronic structure in that the number of *s*-, *p*-, *d*- or *f*- subgroups (Sommerfeld's 'Nebengruppen') corresponds to the Pauli maximum for each.

Finally, the colour mnemonic reflects that most elementary introduction to chemistry: alkalis turn Litmus **blue**. From this start, the *p*-bloc is red, the transition elements yellow and the "rare earth" elements green, as argued in the NR paper [2].

The numbering of groups I - XIV is unambiguous, it is less than IUPAC's arbitrary 18 groups, it preserves subgroups and satisfactorily accommodates hydrogen and the lanthanoids and actinoids. As required by Leigh [3], this table is clear, simple and brief.

In best Popperian tradition, NR framed a hypothesis predicting a dramatic role for the hitherto obscure [4] thulium as occupying a position between silver and gold in NR's arrangement of the periodic table of chemical elements. A critical test of this hypothesis would be the discovery of monovalent thulium and this has been reported by amateurs Marks and Collins [5] but is yet to be corroborated by professional chemists.

The 'New Gold'

If corroborated, this discovery would demonstrate the logic of, and empirical support for, the hypothesis put forward in [2]. It would mean that thulium could reasonably be considered as bearing the same relationship to silver and gold as cerium does to zirconium and hafnium, neodymium to molybdenum and tungsten, *etc., etc.* Although thulium is unlikely to attain the cachet of silver or gold, it would warrant its exploration for similar purposes, such as jewelry or coinage. It certainly would rescue it from Gray's obscurity [4].

On the wider import of Ir [+9] and Os [-1]

Wang GJ *et al.* [6] report a compound ion of iridium, $(\text{IrO}_4)^+$, demonstrating a valency of +9. This lends further support to the arrangement of NR, with groups reflecting valency. Perhaps Mendeleev, like Sanderson [7], would have expanded his "group VIII" to VIII, IX and X had he known about $(\text{IrO}_4)^+$. A logical expectation may be that some of the heavier lanthanoids or actinoids show a valency such as Cf^{+12} , with positive valencies up to the Pauli maximum for each subshell. The tight binding of *f*-electrons may make this unlikely but no one expected the revision of Abegg's rule that $(\text{IrO}_4)^+$ requires.

After the establishment of Lavoisier's elements, Döbereiner was the first to publish [8] any indication that they may display periodic properties by noting the correlation between chemically similar members of main groups (Mendeleev's *Hauptgruppen*) and the atomic weights of the group members. NR comprises 16 rows and 14 columns but a significant reduction in space can be achieved by adopting Scerri's novel rearrangement [9] of the *s*-bloc (*Fig. 2*), inspired by Döbereiner's triads:

	-1	0	I	II	III	IV	V	VI								
H	He	Li	Be	B	C	N	O									
F	Ne	Na	Mg	Al	Si	P	S	VII VIII IX X								
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					XI	XII	XIII	XIV	
J	Xe	Cs	Ba	La	Ce	Pr	Nd	Pm	Sa	Eu	Gd	Tb	Dy	Ho	Er	
		Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt					
		Au	Hg	Tl	Pb	Bi	Po									
At	Nt	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Il	Cf	Ei	Fm	

(Fig. 3)

which may be described as a Döbereiner-inspired periodic table or “Döbereiner revisited”.

Chemistry revisited

At normal temperatures and pressures (in abnormal ranges it's a different story), few chemists would classify hydrogen with the alkali metals. Probably fewer still would classify helium with the alkaline earth metals. That many physicists do is entirely due to considerations of electronic structure. Yet chemists had applied the Periodic Table to chemistry for half a century before the discovery of electronic structure by Bohr and Sommerfeld.

As far as hydrogen is concerned, it has a Janus-face, both physically and chemically. Its positive ion is in fact an elementary particle, the proton, no more an element than an electron is. This is not to say that protons and electrons play no part in physics or chemistry, rather they are acknowledged as basic constituents of atoms - but hardly, themselves, as atoms.

By contrast, the negative ion of hydrogen constitutes an entity in every respect analogous to the behaviour of ions of any other element. In this sense, the hydride anion is representative of hydrogen *qua* element whereas the hydrogen cation, a free proton, self-evidently and by definition shares the peculiar status of being both a chemical ion and an elementary particle. Since exceptional cases make bad law, we should be wary of ordering chemistry on such an outlier.

For example, Petruševski's argument [10] demonstrates the idiosyncrasy the proton demands and leads to his exiling hydrogen from the periodic table's organization altogether. Protons have a

peculiar chemistry themselves, well illustrated by protonation reactions. Indeed, even electrons appear to demonstrate their own chemistry in the form of electrides, such as the solutions of alkali metals in ammonia. At extraordinary pressures (millions of atmospheres), electrides have even formed “compounds” of helium [11].

Döbereiner first observed periodicity in the form of his triads [8] and hydrogen forms a triad with the halogens not the alkali metals. Its physical existence as a diatomic gas and its chemical behaviour in forming salt-like hydrides with the alkali metals are persuasive empirical evidence for classifying hydrogen with the halogens. As an s^1 element, it is one electron short of a full s -subshell and so, is similar in this respect to d^9 and f^{13} elements and, of course, to the halogens, each of which is one electron short of a full p -subshell. Further, hydrogen’s behaviour with fellow halogens in forming peculiarly active gases reflects the properties of other inter-halogen compounds.

As described in [2], the positions of H and He in the Periodic Table arise from the Sommerfeld ‘*ausspaltung*’ of the first period, with ‘daughter’ subgroups of the halogens and the alkali metals from H and ‘daughter’ subgroups of the inert gases and the alkaline earth metals from He. There is little dispute, **chemically**, that helium belongs in the group of inert gases, Group 0. And, from the **chemical** considerations outlined, hydrogen is more akin to the halogens than the alkali metals despite the indisputable subgroup relationship.

At the level of sp^3 hybridization, the subgroups of the first period are so chemically distinct that they rightly retain the status of ‘main’ groups (Mendeleev’s *Hauptgruppen*). Rather than asking ‘why is Be not an inert gas?’, it is more instructive to ask ‘why is it an alkaline earth metal?’ The explanation given is usually that of sp^3 hybridization, which simply begs the question. To determine which main group should contain H and He, chemical considerations would place the former with the halogens and the latter with the inert gases. Beyond sp^3 , in the d - and f - periods, this division (‘*ausspaltung*’) is explicitly recognized in the allocation of Ca to *Hauptgruppe* II and Zn to *Nebengruppe* II and the more recent allocation [12] of Lu to *Hauptgruppe* III and La to *Nebengruppe* III. Sommerfeld’s *Nebengruppen* are thus the d - elements (the transition series) and the f - elements (the lanthanoids and actinoids), with corresponding main-group valency.

Thus Döbereiner’s first observation of chemical periodicity (expanded and promoted by Gmelin [13]) remains as pertinent today as 190 years ago. Döbereiner’s inspiration is appropriately remembered for this sesquicentenary year.

REFS

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