EDITORIAL

2019, THE UN-DESIGNATED INTERNATIONAL YEAR OF THE PERIODIC TABLE OF CHEMICAL ELEMENTS: A PERSONAL ASSESSMENT AND EXPLORATION

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One hundred and fifty years ago, 1869, the Russian Scientist Dimitri Mendeleev decided to forgo a planned trip to a cheese factory and, instead, jotted down his blossoming ideas on organizing the known chemical elements by relating atomic weights and chemical properties; ideas that transformed into that icon we know as the Periodic Table, PT.[1] In recognition of this event, the United Nations has designated 2019, the 150th anniversary, as the International Year of the PT.[2]

As in any field of science, Mendeleev had knowledge of prior insights demonstrating periodicity involving groups of elements, and even though his name is synonymous with his creation, many others predating 1869 must be acknowledged and celebrated. It can be said to originate with John Dalton (Fig. 1), who, starting in 1803 introduced the concept of the indivisibility of the atom and who also (with other pioneers such as Avagadro, Berzelius, Dulong and Petit) facilitated the determination of Atomic Weights of the elements.

This latter aspect of the elements was further, and more rigorously, enumerated by Cannizarro (1817), who by adopting hydrogen (H) as

[1]Many excellent books on the PT are available for the general reader: (a) *The Periodic Table: Its Story and its Significance,* Eric Scerri, Oxford University Press, 2006. (b) *The Disappearing Spoon: And Other True Tales of Madness, Love and the History of the World from the Periodic Table of the Elements*, S. Sam Kean, Little Brown and Company, 2010. (c) *The Periodic Table: A Very Short Introduction*, Eric R. Scerri, Oxford University Press, 2011 (d) *The Periodic Table (short story collection)*, Primo Levi, Schocken, 1984.

[2]http://iupac.org/cms/wp-content/uploads/2017/12/Press-Release-International-Year-of-the-Periodic-Table_UN-Proclamation_21-December-2017.pdf

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Figure 1. John Dalton, born Eaglesfield, Cumbria, UK in the cottage on the right where the author resided for a week in 2003. Image: http://what-when-how.com/scientists/dalton-john-1766-1844-english-physicist-chemist-

the standard of mass provided a numerical handle for the elements thereby spawning many periodic relationships from scientists of many interests. A seminal example were the famous Döbereiner's triads ~1817 (Fig. 2). The simple basis of a triad can be exemplified by the alkali metals lithium (Li), sodium (Na) and potassium (K). With its water reactivity intermediate between those of Li and K, Na also has the atomic weight (23) of half that of the combined weights of Li (7) and K (39). The elements chlorine (Cl), bromine (Br), and iodine (I) was another triad he noted. The small arithmetical discrepancy for the halogen triad was overlooked.

It was the combination of both chemical property and numerical analysis that stimulated the world of science. Some investigators got carried away with the numerical side of the insight and concocted relationships such as the triad of carbon (C), nitrogen (N) and oxygen (O), which works for numbers only, 12, 14 and 16, but is not chemically periodic in any real sense. Even more loosely was the proposed triad of titanium (48), tin (119) and tantalum (181), where, indeed, the letter "t" would have been equally as useful!

A significantly more detailed and populated compilation of elements was produced in 1863 by John Newlands in his first

Figure 2. Döbereiner and two of his triads. Image: https://simple.wikipedia.org/wiki/Johann_Wolfgang_D%C3%B6bereiner

classification of the known elements and consisted of 11 groups of triads. These first attempts derived primarily using chemical similarities to create his triads, an early illustration of the need for experimental data as preferential to purely mathematical modeling. However, within a short time he noted the atomic weight regularities where many elements of similar chemical reactivity occurred every eight elements, his so-called Law of Octaves. Had he chosen a title more associated with the classification of the elements, his fame could have been greater; however, his birth place in Lambeth, England, has a plaque signaling him as the discoverer of the Periodic Law (Fig. 3).

Given this extensive earlier work, a more complete classification of all the known elements was a matter of time, focus and commitment. An argument can, and has, been made that French Geologist Alexandre-Émile Béguyer de Chancourtois produced the first true illustration of periodicity and classification of the elements. He remarkably listed the elements in ascending order of atomic weight and wound the strip around a cylinder in a screw-like manner (Fig. 4), noting the elements of similar property aligned vertically. This totally ingenious classification in 1862 predated the more famous, and visually simple Mendeleev product, and is indeed another forerunner of placing the elements into a usable pattern. The fact that a geologist was responsible for the insight may, in part, be responsible for the lack of recognition. Chemists of the day were not familiar with his work, and a detailed illustration of his creation was tardily

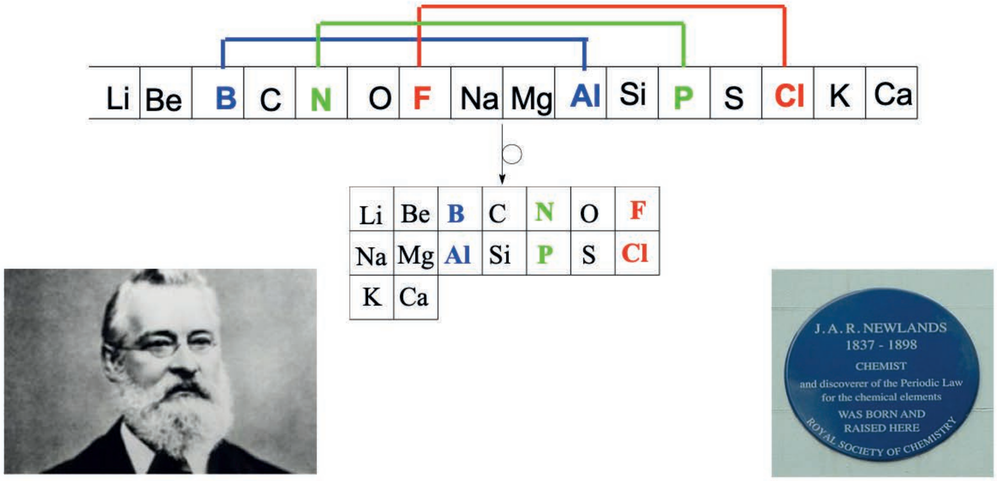

Figure 3. John Alexander Reina Newlands, and his discovery of chemical similarity every eight elements (the noble gases were undiscovered at that time), and birthplace plaque. Images: https://www.elephantandcastle.org.uk/a-brief-history/elements-castle-john-newlands/

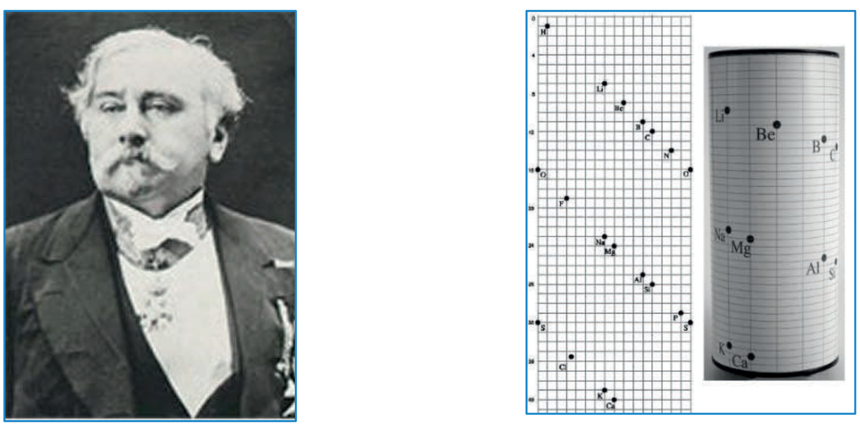

Figure 4. Alexandre-Émile Béguyer de Chancourtois and his Telluric Screw. Images: http://dataphys.org/list/telluric-screw-of-de-chancourtois/

published privately. Since the beauty of the PT is the iconic visual compilation, the lack of a pictorial illustration of the de Chancourtois cylinder, illustrates the maxim “a picture is worth a thousand words” and results in his name being known mainly to the cognescenti. Furthermore, the commonly used English expression for his creation, *The Telluric Screw*, *Vis Tellurique* in French, was seemingly based upon tellurium being centrally located in his completed product together with his geologic understanding that the elements were mainly derived from the earth, Latin *tellus*, *telluris*. Whatever the origin of the title, while evocative, it is not immediately informative as illustrating a periodic relationship of the elements.

So, with this significant background, what was Mendeleev's genius and contribution? Certainly he was in the right place at the right time being privileged to attend the famous Karlsruhe meeting (1860) where Cannizarro formalized the concept of atomic weights of the elements. He was also totally focused and was adamant that any classification of the elements must be based solely on the progressively increasing values of such atomic weights *and* coupled to chemical similarity. For example, there had always been an anomaly in the relative positions of tellurium (Te) and iodine (I) in early tables. Iodine manifestly similar to Br and Cl, and Te clearly not. However, atomic weights indicated I precede Te in his Table, a result that Mendeleev refused to permit, and he even challenged the experimental values of atomic weights. The issue was not resolved until the unraveling of the structure of the atom (a nucleus consisting of protons and neutrons leading to the concept of isotopes), and the final classification of the PT being based upon atomic number, the number of protons.

However, Mendeleev's early Tables had conspicuous gaps that led him to propose unknown, undiscovered, elements, *and*, predict certain properties, physical and chemical. This was the great stroke of insight and confidence in his creation that sealed his fame. For example, the prediction of the missing element, noted as eka-silicon (экасилицій) one place below silicon (Si), was ultimately confirmed by the discovery of germanium (Ge). Others would follow and today the name of Mendeleev is synonymous with the Periodic Table, albeit with high regard, recognition, and gratitude for the preliminary work of those who led him to his discovery/creation.

Our current PT revolves around the truly fundamental atomic number as elucidated by Henry Moseley in 1913. The early scientists were fortunate that the atomic weights are in general twice the atomic number, i.e. the number of protons and neutrons are ~equivalent. As Prout noted in 1815, the atomic weights of the elements are all whole multiples of that of hydrogen (H), thus substitution of atomic weight instead of atomic number had no major negative impact upon the utility of the Mendeleev Periodic Table.

Caveat with respect to chemical reactivity

As noted above, the periodicity and classification, resulting in the Periodic Table as we know it, was derived from a combination of numerics and chemical properties. However, it is important to remember that chemical reactivity is associated with electrons, not protons and neutrons, and these were not part of the historical process described above. It was not until 1897 that J. J. Thompson demonstrated the existence of electrons. At the outset, the reasons for the similarity in chemistry of the various triads, and later the periodic groups, was unclear. We now know this reactivity is due to the electronic configurations of the elements.

Whereas early thinkers had suggested C, N and O as a triad based upon the atomic weight of N being half the sum of the combined weights of C and O, their chemistry is distinctive. These same people could as well have used the triad B, C and N with equal lack of a reactivity basis. We now know these elements have differing valence electronic configurations, $2s^22p^1$ for B; $2s^22p^2$ for C; $2s^22p^3$ for N; thus, their chemistry will be very different and they are not groupable. However, today we also know that the elements are capable of being oxidized and reduced, therefore the hypothetical B^-, C, and N^+ will all be iso-electronic, formalized as $2s^22p^2$, and each is able to form a well-established and stable tetrahydride, $[BH_4]^-$, CH_4 and $[NH_4]^+$ (Fig. 5).

These elemental species do therefore form a clear group, and it can be stated that $B^- = C = N^+$ based upon their electronic configuration, and their bonding properties. However, the products $[BH_4]^-$, CH_4 and $[NH_4]^+$ have decidedly distinct chemistry and $[BH_4]^-$ is a source of

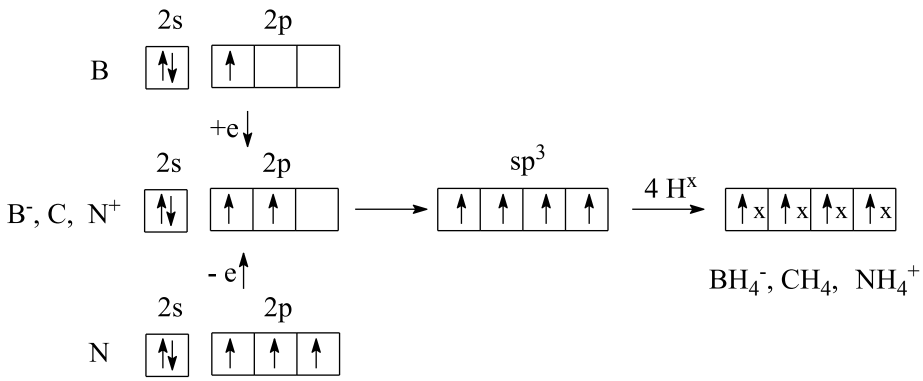

Figure 5. Formation of isoelectronic and isostructural tetrahydrides of B, C and N.

hydride, whereas $[NH_4]^+$ is a source of proton as in equations 1a,b.

$$[BH_4]^- \longrightarrow BH_3 + H^- \qquad (1a)$$

$$[NH_4]^+ \longrightarrow NH_3 + H^+ \qquad (1b)$$

The same concepts can be demonstrated all over the Periodic Table and present much interesting and sometimes challenging chemistry, e.g. I = Xe^+ as in $[IF_3] = [XeF_3]^+$, and $Si^{2-} = P^- = S$, as in $[SiF_6]^{2-} = [PF_6]^- = SF_6$. Such relationships can also be the stimulus for future discoveries.