IUPAC and the Periodic Table

by G.J. Leigh

The Periodic Table is now regarded as such a fundamental part of current chemical research and teaching that it is salutary to learn that this prominence is a relatively recent development. IUPAC was established in its present form in 1919, but the roots of the Table go back much further. The general realization of the value of the Periodic Table to rationalize and teach chemistry has only come about since the new flowering of inorganic chemistry, which can be dated to the 1960s. Today the most popular form of the Table and its updating and dissemination owe much to IUPAC, though this was not always the case.

5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.95 [39.792, 39.963]

Figure 1 *Typical element entries taken from a long form of the Periodic Table, https://iupac.org/what-we-do/periodic-table-of-elements/. See back cover of this issue.*

Figure 1 is taken from a Periodic Table of the Elements published by IUPAC on 1 December 2018. It represents the second and third periods, with the lighter elements of Groups 13-18. Each element square contains an atomic number, an atomic name, an atomic symbol and as many as three atomic weights. IUPAC is deeply concerned both with the general form of the Periodic Table and with the contents of each elemental entry. Note that IUPAC always uses a long form to display the Table, but this has not discouraged chemists from devising other arrangements, such as circular, spiral and even three-dimensional.

Attempts to systematize the chemistry of the elements in a logical fashion are more than 200 years old. The general acceptance of atomic theory, often ascribed to the influence of Dalton who published his ideas in 1805, was the beginning of the modern scientific systemization of the inorganic chemistry. It encouraged a more quantitative approach to inorganic chemical studies and the appearance of lists of so-called atomic weights. These were then relative combining weights, and are essentially those still used today. They are not related to the real weights of atoms. Döbereiner was an early systematiser who recognised the existence of triads, such as lithium + sodium + potassium, chlorine + bromine + iodine, and calcium + barium + strontium as early as 1817 [1]. In such triads the atomic weight of the middle element is roughly the mean of the atomic weights of the other two members. The recognition of weight relationships was extended further by Newlands [2] who enunciated his Law of Octaves. He noted that

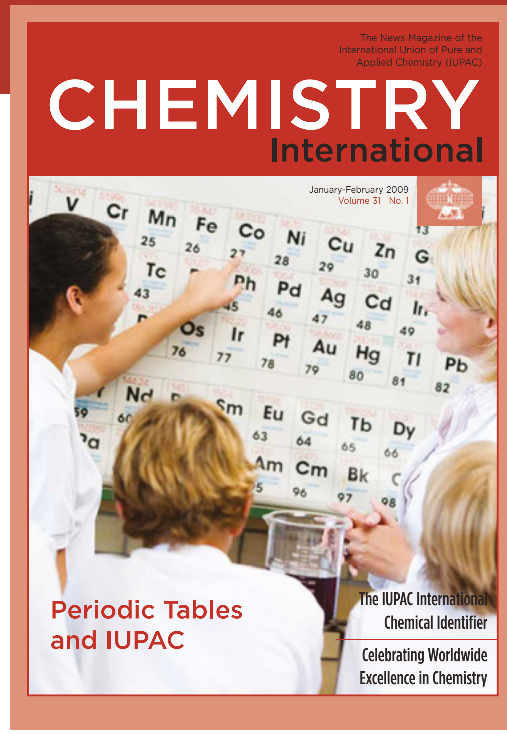
292

ONE OF MENDELEJEFF'S TABLES, MODIFIED

Li 7	....	....	....	....	....	....	....	....	....	....	Gl 9	B 11	C 12	N 14	O 16	F 19
Na 23	....	....	....	....	....	....	....	....	....	....	Mg 24.3	Al 27	Si 28.3	P 31	S 32	Cl 35.5
K 39	Ca 40	[Sc] 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7	Cu 63.6	Zn 65.4	[Ga] 70	[Ge] 72.5	As 75	Se 79.2	Br 80
Rb 85.5	Sr 87.6	Y 89	Zr 90.6	Cb 93.5	Mo 96	....	Ru 101.7	Rh 103	Pd 106.7	Ag 108	Cd 112.4	In 115	Sn 119	Sb 120	Te 127.5	I 126.9
Cs 133	Ba 137.4	La 139	Ce 140	Nd 144.3	....	....	....	....	....	....	....	....	....	....	....	....
....	....	Yb 173.5	....	Ta 181.5	W 184	....	Os 191	Ir 193	Pt 195	Au 197	Hg 200.6	Tl 204	Pb 207	Bi 208	....	....
....	Ra 226	....	Th 232.4	....	U 238.2	....	....	....	....	....	....	....	....	....	....	....

TEXT BOOK OF CHEMISTRY

Figure 2. An early text-book example of a periodic table, taken from Alexander Smith, Intermediate Text Book of Chemistry, Century Co., New York, 1919.



See reference 7 in Chem Int January 2009

groups of related elements are separated in weight order by seven other elements, and he even drafted a form of periodic table, though essentially with periods and groups at right angles to the modern usage. These advances would have been impossible without the wider determination of many atomic weights relative to hydrogen which was assigned the atomic weight of 1 and the recognition that some elements can exhibit more than one combining weight, an expression of what we would now understand is due to variable valency [3]. The first proponent of a modern form Periodic Table was Mendeleev who proposed what we would now regard as a short form [4]. Atomic weights were regarded as a basis for systematization until after 1913, when the significance of atomic number and hence basic elemental electronic structure was described by Moseley [5]. This eventually gave rise to the long form of the Table, and also to the many variants which are in circulation today. A very early and detailed adoption of Moseley's proposals for the employment of atomic numbers is to be found in the text of A Smith (1919), Intermediate Text Book of Chemistry, Century Co., New York. Figure 2, reproduced from page 292 of this book, shows a modified Mendeleev Periodic Table, which still retains atomic weights rather than atomic numbers, but leaves appropriate gaps for missing elements, except for hydrogen which is ignored and but it does include glucinium, which is now known as beryllium. There are no group or period numberings.

All this happened before IUPAC was formally constituted in 1919, and IUPAC still does not have an official format for the Table, though its discussions and recommendations generally use a clear and easily readable long form. However, it does promulgate official formalisms and rules governing the Table content.

The short form of the Table, essentially an extension of Mendeleev's format, was the first to be widely adopted. However, it was developed in contradictory forms on different sides of the Atlantic. For example, in the USA and Chemical Abstracts, the group of elements indicated by the symbols IVA was indicated by the symbols IVB on the European side of the Atlantic. There could have caused considerable confusion in the mind of a reader unaware of the place of origin of a particular paper and of the difference usages. The resolution of this contradiction involved the wider adoption of the long form of the Table and has been clearly and objectively described [6].

It was recognised by Ölander in 1956 [7] that this problem could be avoided by using a long-form numbering scheme for the various Groups. He suggested numbering them 1-17, though this was not generally adopted. Although the 1970 IUPAC Red Book [8] made no mention of a Periodic Table, it did list groups of elements designated by numbers and the letters A and B. Thus Group 3A was listed as Sc, Y, La (including the lanthanoids) and Ac (including the actinides), whereas Group 3B included Ga, In, and Tl. The AB confusion still reigned until 1970 when the ACS proposed the current 1-18 Group numbering, which is best appreciated in a long form Periodic Table. There was considerable discussion between the ACS and IUPAC concerning the introduction of the 1-18 numbering and its value. Many older chemists did not see the need to agree to such formalisms, but the IUPAC Commission on the Nomenclature of Inorganic Chemistry eventually accepted and recommended it after some discussion. The next version of the Red Book (1990) [9] contains a long form of the Periodic Table with this numbering, though apparently copyrighted by IUPAC and Kurt Samuelsson! Such a long form is as official as IUPAC recommends, but IUPAC now makes formal recommendations as to how all the contents of the Table in each element square such as those exemplified above should be modified as chemistry develops. Currently IUPAC is sponsoring a detailed discussion upon the preferable formulation for the elements in Group 3 of the Table. This has been a subject of discussion for some years. IUPAC now adjudicates for the international chemistry community on all changes and formalisms likely to affect the detailed presentation of Periodic Tables. That includes names, symbols, and atomic weights.

Atomic number rather than atomic weight now defines the place of a given element in the element series. This will not change. There are now no "missing elements" such as those which puzzled Mendeleev and his contemporaries, and which led him to suggest where unknown elements might occur in the Table. Before the Inorganic Chemistry Division of IUPAC undertook to consider claims for new elements, there was no obvious public method for the chemical community to assess the reliability of the individual claims or to approve the suggested names and symbols, though the Atomic Weights Commission attempted to do so. For example, element 86, now called radon, Rn, was discovered in 1899. It had originally been identified as "radium emanation", and was designated in early literature as Em and even Ra Em, though no general decision to adopt such symbols was ever made.

Since World War II, new synthetic heavy elements have been synthesized in several different countries, starting with element of atomic number 93, neptunium, Np. When these "new" elements began to appear, they originated in the United States. During the Cold War, the Soviet Union was eager to show the world that it could also synthesize new elements, and meetings of the IUPAC Commission on the Nomenclature of Inorganic Chemistry sometimes provided a battle ground where representatives from each of these two countries made efforts to undermine claims to new elements made by the other. This was an uncomfortable experience for those members of the Commission who were not of Soviet or US nationality [10]. There was also an accepted rule within the Commission that the name of a living scientist should not be used in the name for a new element. This rule has now been superseded, though not without some initial spirited discussion [10]. It became evident that an internationally acceptable procedure was needed for assessing and naming a claim to have prepared a new element. Since these new elements are as much a product of high-energy physics as of chemistry, the procedure now used is one in which IUPAC collaborates with IUPAP in assessing claims.

The current limit of recognised elements concludes with element 118, oganesson, Og. When new elements are claimed, IUPAC and IUPAP jointly consider whether the claim is scientifically satisfactory. If the science is accepted, then the discoverers are asked to suggest a name and symbol, and IUPAC then assesses whether the name would prove acceptable to the international community. This exercise was last undertaken and published in 2016 when the discoveries of the elements with Z = 113, 115, 117, and 118 were confirmed [11] and then the names and symbols for these elements nihonium, moscovium, tennessine, and oganesson were officially recognised and recommended for inclusion in the Periodic Table. For an account of these discoveries see [12]. Criteria for acceptable sources used when proposing new names have also recently been published [13].

In the past, there was considerable literature concerning unprepared elements, and it became necessary to devise a system of provisional element names and symbols to assist such discussions. To this end, Joseph Chatt, then Director of the Unit of Nitrogen Fixation at the University of Sussex, proposed the system of provisional names and symbols based upon atomic number, which IUPAC adopted. In this system, a set of syllables derived from classical sources, but recognizably representing each number from 0 to 9, is sufficient to identify any element of a given atomic number even if the element has not been prepared and has no recognised name and symbol [14]. For example, element 118, designated by IUPAC by the provisional symbol Uuo and the provisional name ununoctium; it is now officially named oganesson. The validity of claims to its initial preparation were the matter of some dispute, but it seems to have been prepared on more than one occasion in different laboratories between the years of 2002 and 2006. The synthesis was officially accepted after assessment in 2015. Oganesson concludes both a Group and a Period in the Periodic Table. If element 119, ununnovium, symbol Uun, ever appears, its position in the Table will have to be decided by the community and IUPAC. It is tempting to suggest it would be a new alkali metal in Group 1, below francium. A discussion of these matters can be found in [15].

Atomic weights have been a concern of IUPAC since the 1920s. The history of the Atomic Weights Commission (now known as the Commission on Isotopic Abundances and Atomic Weights, CIAAW) has been described in detail by Holden, and shows that the need to determine internationally agreed-upon atomic weights was understood long before IUPAC was formally established in 1919 [16]. The formation of the Commission itself was a consequence of the realization that the determined values of atomic weights depended upon the isotopic composition of the samples employed, and these varied with place of origin. In addition, the determination of atomic weights is now based upon physical methods of great accuracy and no longer relies, as it did originally, on simple test-tube chemical analysis. The Commission was first established in 1899 and now operates under the auspices of the Inorganic Chemistry Division of IUPAC. In its early days it was responsible for naming elements, and it was involved in discussions such as whether element 74 should be named tungsten or wolfram. Its recommendations were not always accepted by all countries, and some national variants in spelling, such as aluminum and aluminium, still persist. Today name recommendations are made only for use in English since it may not be possible to devise names which satisfy all international requirements. For example, recommended names such as tennessine for element 117 may cause discomfort to users of Spanish, which does not normally use combinations of letters such as “ss” and “nn”.

CIAAW attempts to keep the chemistry community aware of the latest and best estimates of the atomic weights and isotopic compositions of the elements. It generally reports every second year on the atomic weights of the elements and on their isotopic compositions. Each value is usually cited to five significant figures. For some elements it cites maximum and minimum values which arise from the differing isotopic compositions of the samples studied, which come from sources of different origins. For a recent summary of data see www.sbcs.qmul.ac.uk/iupac/AtWt/. This range is indicated in the IUPAC 2016 Table for most of the lighter elements, where variations may have greater practical significance, such as the study of biological systems. In such cases the Table also gives a satisfactory mean value. Heavier elements are generally given a best mean value, with the exceptions of thallium and bromine, for which ranges are also provided. The 2017 report of the CIAAW also adds a weight range for argon [17].

In conclusion, IUPAC was not involved in the development of the Periodic Table, but once the Union became established in 1919 it has kept notice of the various changes made, and since its widespread adoption for teaching and rationalizing chemistry it has been the prime international authority for developing and adopting changes in its content, including new elements, and their atomic numbers, names, symbols, and atomic weights.

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