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Four-Figure 2016 Atomic Weights: Time to Review our table

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Many readers might wonder what can be new about atomic weights and why such a subject deserves even a short paper in *Chemistry Views* magazine. Despite common belief, atomic weights are not constants of nature. Scientists' ability to measure these values is regularly improving, so one would expect that the accuracy of these values should be improving with time. However, as will be explained below, variations have been measured in the atomic-weight value of many chemical elements found in different natural sources that greatly exceed the accuracy in the measurement of any one sample of the element. Unless you know the origin of the source of your sample, this natural variation limits the accuracy that can be assigned to the atomic weight of the element in your sample. It is therefore the task of the IUPAC (International Union of Pure

and Applied Chemistry) Commission on Isotopic Abundances and Atomic Weights (CIAAW) to regularly review atomic-weight determinations and release updated values. This short paper points out that according to the recent (2013) review to be published in *Pure and Applied Chemistry* [ref. 1] even the most simplified table abridged to four significant digits (and therefore periodic tables, which present these values) needs a few tweaks and couple of updates. Moreover, according to the most recent 2015 release [ref. 2], one more update is also now needed for the element ytterbium.

What is an Atomic Weight?

An atomic weight of an element E, symbol $A_r(E)$, is the sum of the products of the relative atomic mass and the fraction of the amount of each stable and long-lived radioactive isotope of that element in a given sample. Because relative atomic masses are known with high accuracy, the atomic weights of elements having only one stable or long-lived radioactive isotope are also known with high accuracy. For example, gold-197 (^{197}Au) is the only stable isotope of gold and its relative atomic mass (atomic weight) $= A_r(^{197}\text{Au}) = 196.96657$, expressed to 8 digits. Thus, gold's atomic weight, $A_r(\text{Au})$, can be expressed relatively accurately as 196.96657, which would be rounded to 197.0 in a four-digit table. For elements with more than one stable or long-lived radioactive isotope, the accuracy of an atomic weight is substantially lower because the accuracy with which the fractional amounts of each isotope in a given specimen can be determined is lower. For example, lithium has two stable isotopes, ^6Li and ^7Li , having relative atomic masses, respectively, of 6.0151229 and 7.0160034, expressed to 8 digits. But the best measurement of the fractions of ^6Li and ^7Li in a specimen give 0.07589 ± 0.00024 and 0.92411 ± 0.00024 , respectively, which yields an atomic weight, $A_r(\text{Li})$, of $6.0151229 \times 0.07589 \pm 0.00024 + 7.0160034 \times 0.92411 \pm 0.00024 = 6.9400 \pm 0.0002$. Analytical uncertainty in the measurement of the amounts of the two lithium isotopes in a sample limits the atomic weight of lithium to an accuracy of only five digits. The natural variation of the fraction of the amount of ^7Li in a sample further limits the atomic weight, as shown in Figure 1 for selected lithium-bearing materials. The fraction of the amount of a specified isotope in a sample is also called the mole fraction, the amount fraction, the atom fraction, or the isotopic abundance. Note that atomic weights are

dimensionless quantities. Because relative atomic masses are scaled (expressed relative) to one-twelfth the mass of a carbon-12 atom, atomic weights are dimensionless.

Figure 1. Variation in atomic weight with mole fraction of ^7Li of some lithium-bearing materials (modified from [ref. 3]). Alternative names for the mole fraction of ^7Li are isotopic abundance of ^7Li , the ^7Li fraction, and the ^7Li amount fraction.

Many Standard Atomic Weights Are Not Constants of Nature

Although many of us were taught that atomic-weight values found on the Periodic Table in our chemistry classrooms are constants of nature, it has been known for more than half a century that atomic weights of many elements are not constants of nature. However, only in the past few years was the IUPAC Table of **Standard Atomic Weights** updated to clarify this fact by replacing single-value atomic-weight values by **Atomic-weight Intervals** [refs 3 and 4]. For example, starting in the 2009 Table, the atomic weight of lithium was changed from 6.941 ± 0.002 to $[6.938, 6.997]$ to indicate that the atomic weight of naturally occurring lithium samples, which includes normal chemical reagents, can range between 6.938 and 6.997, depending upon the source of the material (Figure 1). Obviously, if one knows the source of lithium in a sample, one may have a more accurate value for the atomic weight. However, if the source is unknown, the value of the atomic weight could be at one or the other extreme shown in figure 1. These extremes are the end-points of the atomic-weight interval quoted in Table 1. In the past, the atomic weight was quoted as a mid-point and the range as an uncertainty. However, many users were aware of published atomic-weight values for samples, which were more precise and chose those literature values over the IUPAC recommendations thinking that they had the best value for their sample. The interval notation was introduced to inform users about the basic problem of natural variations of amounts of isotopes of elements and why the choice of a more precise literature value is incorrect unless that value corresponded to the same source as their own sample of the element.

Today, the standard atomic-weight values of 12 elements are best reported as intervals; these are hydrogen, lithium, boron, carbon, nitrogen, oxygen, magnesium, silicon, sulfur, chlorine, bromine, and thallium. For these 12 elements, the standard atomic weight is given as an atomic-weight interval with the symbol $[a, b]$ to denote the set of atomic-weight values in **normal materials**; thus, $a \leq \text{atomic-weight value} \leq b$. Symbols a and b denote the lower and upper bounds of the interval $[a, b]$, respectively. A normal material was defined by the CIAAW ([ref. 3] and references therein). The CIAAW recognized that some users of atomic-weight data only need representative values for the 12 elements having interval atomic-weight values, such as for

trade and commerce. For these purposes, the CIAAW provides conventional atomic-weight values (Table 2).

Influence of Variations of Mole Fractions (Isotopic Abundances)

Variations in mole fractions of **stable** (non-radioactive) and long-lived **radioactive isotopes** give rise to the variabilities observed in atomic weights of many elements. While the atomic weight of an element can be determined in any material, the standard atomic weight represents the atomic weight of an element in all normal terrestrial materials. All stable (non-radioactive) **isotopes** and thirty-six radioactive isotopes, which have very long half-lives, contribute to the determination of the standard atomic weights, giving rise to expanded uncertainties in many elements having two or more stable or long-lived radioactive isotopes.

Despite regular improvements in analytical instrumentation, the ranges in isotopic abundances of normal materials prevent more precise values of atomic weight from being determined for many elements, for example, argon, nickel, copper, zinc, selenium, strontium, and lead [ref. 1].

Uncertainties of atomic weights are also examined and reported regularly by the CIAAW.

Readers interested in more details should refer to the full text of Commission reports and the careful annotations conveyed in the footnotes, see [refs. 1 and 3].

Rounded Values to Four Significant Figures

Forty years ago, the first Table of Atomic Weights to Four Significant Figures, based on the 1975 values, was developed under guidance of the CIAAW and published by the IUPAC Committee on Teaching of Chemistry [ref. 5]. In more recent years, similar tabulations were also published in the IUPAC scientific journal, *Pure and Applied Chemistry*, along with detailed Commission biennial reviews. The Commission recognized that the details and number of significant digits reported in the full Table of Standard Atomic Weights (e.g., up to 9 digits for aluminium (aluminum) or fluorine, or even 10 digits for caesium (cesium)) exceeds the need and interests of many users. The abridged table was also published with the expectation that subsequent changes would be minimal.

As a retrospective review of such changes, we present in Table 1 the four-digit atomic-weight values (either published or deduced) over time for elements from hydrogen through uranium since the seminal 1961 report by A. E. Cameron and E. Wichers [ref. 6]. This report was the first element-by-element review of all of the atomic-weight values by the Commission, and it corresponded with changing the atomic-mass standard from oxygen-16 to carbon-12. From examination of Table 1, one can see that the expectation of minimal changes in atomic-weight values was a valid prediction. Except for five elements (lithium, boron, sulfur, titanium, and germanium), the four-digit standard atomic-weight values have not changed over five decades by more than 1 digit in the last place. For three of these elements (lithium, boron, and sulfur), the differences are due to recognition of **natural isotopic fractionation in normal materials**. The improvements in the two others, titanium and germanium, are due to the use of isotope-ratio mass spectrometry to determine more accurate isotopic abundances and thus more accurate values of atomic weight [ref. 7].

Reviewing the values reported in the 2013 table [ref.1] does trigger the update of two four-digit standard atomic-weight values, and these concerned the elements selenium and molybdenum. The recent 2015 release [ref.2] triggers an additional update for the element ytterbium. In these cases, the revisions are due to improved measurements using high-accuracy mass spectrometry.

In its most recent report, the Commission did not publish a Table of the Standard Atomic Weights abridged to 4 significant digits. Still, if you already routinely consult a table abridged to 4 significant digits, ensure you update your table with these latest values. As we keep telling our students to do well in chemistry; let us be sure not to give them any out-of-date tables ...

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Table 1. Four-place table of atomic-weight values of hydrogen through uranium compared through the years

[*, value may differ from the atomic weights of the relevant elements in some normal materials because of a variation in the isotopic abundances of the element's stable isotopes; uncertainty in standard atomic weight larger than ± 1 appears in parentheses, following the last significant digit to which it is attributed.]

At No	Symbol	Value 1961	Value 1975	Value 1983	Value 2007	Value 2009	Value 2011	Value 2013	Value 2015	<i>Current value</i>
1	H	1.008				[1.007, 1.009]				[1.007, 1.009]
2	He	4.003								4.003
3	Li	6.939	6.941*	6.941(2)		[6.938, 6.997]				[6.938, 6.997]
4	Be	9.012								9.012
5	B	10.81	10.81*	10.81	10.81*	[10.80, 10.83]				[10.80, 10.83]
6	C	12.01				[12.00, 12.02]				[12.00, 12.02]
7	N	14.01				[14.00, 14.01]				[14.00, 14.01]
8	O	16.00				[15.99, 16.00]				[15.99, 16.00]
9	F	19.00								19.00
10	Ne	20.18								20.18
11	Na	22.99								22.99
12	Mg	24.31	24.31*	24.31			[24.30, 24.31]			[24.30, 24.31]
13	Al	26.98								26.98
14	Si	28.09				[28.08, 28.09]				[28.08, 28.09]
15	P	30.97								30.97
16	S	32.06	32.06*	32.07	32.07*	[32.05, 32.08]				[32.05, 32.08]
17	Cl	35.45				[35.44, 35.46]				[35.44, 35.46]
18	Ar	39.95	39.95*	39.95						39.95
19	K	39.10								39.10
20	Ca	40.08	40.08*	40.08	40.08*					40.08*
21	Sc	44.96								44.96
22	Ti	47.90		47.88(3)	47.87					47.87
23	V	50.94								50.94
24	Cr	52.00								52.00
25	Mn	54.94								54.94
26	Fe	55.85								55.85
27	Co	58.93								58.93
28	Ni	58.71	58.70	58.69						58.69
29	Cu	63.54	63.55							63.55

30	Zn	65.37	65.38	65.39(2)	65.38(2)		65.38(2)
31	Ga	69.72					69.72
32	Ge	72.59		72.59(3)	72.64	72.63	72.63
33	As	74.92					74.92
34	Se	78.96		78.96(3)		78.97	78.97
35	Br	79.91	79.90			[79.90, 79.91]	[79.90, 79.91]
36	Kr	83.80			83.80*		83.80*
37	Rb	85.47			85.47*		85.47*
38	Sr	87.62	87.62*	87.62	87.61*	87.62*	87.62*
39	Y	88.91					88.91
40	Zr	91.22			91.22*		91.22*
41	Nb	92.91					92.91
42	Mo	95.94			95.96(2)*	95.95*	95.95*
43	Tc	-----	(97)	98.91	-----		
44	Ru	101.1			101.1*		101.1*
45	Rh	102.9					102.9
46	Pd	106.4			106.4*		106.4*
47	Ag	107.9			107.9*		107.9*
48	Cd	112.4			112.4*		112.4*
49	In	114.8					114.8
50	Sn	118.7			118.7*		118.7*
51	Sb	121.8			121.8*		121.8*
52	Te	127.6			127.6*		127.6*
53	I	126.9					126.9
54	Xe	131.3			131.3*		131.3*
55	Cs	132.9					132.9
56	Ba	137.3					137.3
57	La	138.9					138.9
58	Ce	140.1			140.1*		140.1*
59	Pr	140.9					140.9
60	Nd	144.2			144.2*		144.2*
61	Pm	-----	(145)	144.9	-----		
62	Sm	150.4			150.4*		150.4*
63	Eu	152.0			152.0*		152.0*
64	Gd	157.3			157.3*		157.3*
65	Tb	158.9					158.9
66	Dy	162.5			162.5*		162.5*
67	Ho	164.9					164.9

68	Er	167.3	167.3*			167.3*
69	Tm	168.9				168.9
70	Yb	173.0	173.1*		173.0*	173.0*
71	Lu	175.0				175.0
72	Hf	178.5				178.5
73	Ta	180.9				180.9
74	W	183.9		183.8		183.8
75	Re	186.2				186.2
76	Os	190.2	190.2*			190.2*
77	Ir	192.2				192.2
78	Pt	195.1				195.1
79	Au	197.0				197.0
80	Hg	200.6				200.6
81	Tl	204.4		[204.3, 204.4]		[204.3, 204.4]
82	Pb	207.2	207.2*	207.2	207.2*	207.2
83	Bi	209.0			209.0*	209.0
84	Po	-----	(209)	210.0	-----	
85	At	-----	(210)	210.0	-----	
86	Rn	-----	(222)	222.0	-----	
87	Fr	-----	(223)	223.0	-----	
88	Ra	-----	(226)	226.0	-----	
89	Ac	-----	(227)	227.0	-----	
90	Th	232.0			232.0*	232.0*
91	Pa	-----	(231)	231.0		231.0
92	U	238.0	238.0*	238.0	238.0*	238.0*

Notes:

Value 1961, four-digit values based on those published in the *Comptes Rendus* of the 21st Conference of IUPAC, Montreal, 2-5 August 1961 and reproduced in *JACS* 84 4175 (1962) as "The Report of the International Commission on Atomic Weights" (1961). This report constituted the most significant atomic weights table of the middle twentieth century and was authored by A. E. Cameron and E. Wichers [ref. 6]. This report corresponded with the change in the atomic mass standard from oxygen-16 to carbon-12 and provided the first of a number of element-by-element reviews of all of the atomic-weight values by the Commission.

Value 1975, the first Table of Atomic Weights to Four Significant Figures was published in *Int. News Chem. Educ.* 2 (June 1975) and developed under guidance of the Commission on Atomic Weights by the IUPAC Committee on Teaching of Chemistry, and it was

based on the 1975 values published by the Commission in *PAC* 47(1) 75–95 (1976).

<http://pac.iupac.org/publications/pac/pdf/1976/pdf/4701x0075.pdf>

Value 1983, four-digit values based on the 1983 values published by the Commission in *PAC* 56(6) 653-674 (1984).

<http://pac.iupac.org/publications/pac/pdf/1984/pdf/5606x0653.pdf>

Value 2007, four-digit values as published in *PAC* 81(11) 2131-2156 (2009), *Atomic Weights of the Elements 2007*

<http://pac.iupac.org/publications/pac/pdf/2009/pdf/8111x2131.pdf>. In this report, the Commission actually evaluated and published standard atomic weight tables abridged to four and five significant figures, a practice that was repeated in the subsequent two reports.

Value 2009, four-digit values as published in *PAC* 83(2) 359–396 (2011), *Atomic Weights of the Elements 2009*

<http://pac.iupac.org/publications/pac/pdf/2011/pdf/8302x0359.pdf>. In addition, to include abridged values, this report coincides with the first publication of atomic-weight values expressed as intervals for selected elements. Specifically, the standard atomic weights of 10 elements having two or more stable isotopes were changed to reflect the variability of atomic-weight values in natural terrestrial materials.

Value 2011, four-digit values as published in *PAC* 85(5) 1047–1078 (2013), *Atomic Weights of the Elements 2011*.

In this report, two more elements reported in terms of intervals to reflect the common occurrence of variations in the atomic weights of those elements in normal terrestrial materials.

Value 2013, four-digit values based on the latest values published by the Commission in *PAC* 2016, in press, doi: 10.1515/pac-2015-0305. In this report, the Commission discontinued the publication of standard atomic weight tables abridged to four significant figures; instead, it released an unabridged table and a table abridged to five significant figures.

Value 2015, four-digit values based on the CIAAW release of 24 Aug 2015 (ref.2)

Current value, Cumulative values as deduced from all previous reports.

The full text of the *PAC* references cited above (except 2016) is directly accessible from

<http://www.iupac.org/publications/pac/series/atomicweights/>

Table 2. Conventional atomic weights abridged to four digits

[For users needing an atomic-weight value for an unspecified sample, such as for trade and commerce, the following values are provided, which are abridged from conventional atomic weight values (ref 1).]

Element name	Symbol	Atomic number	Reference atomic weight
hydrogen	H	1	1.008
lithium	Li	3	6.94
boron	B	5	10.81
carbon	C	6	12.01
nitrogen	N	7	14.01
oxygen	O	8	16.00
magnesium	Mg	12	24.31
silicon	Si	14	28.09
sulfur	S	16	32.06
chlorine	Cl	17	35.45
bromine	Br	35	79.90
thallium	Tl	81	204.4

Glossary of Terms:

amount fraction (mole fraction or isotopic abundance) – the amount of a given isotope in a sample divided by the total amount of all stable and long-lived radioactive isotopes of the chemical element in the sample.

atomic weight (relative mean atomic mass) – the sum of the products of the relative atomic mass and the **mole fraction** of each stable and long-lived radioactive isotope of that element in the sample. The symbol of the atomic weight of element E is $A_r(E)$, and the symbol of the atomic weight of an atom (isotope) element E having mass number A is $A_r(^A E)$. Because relative atomic masses are scaled (expressed relative) to one-twelfth the mass of a carbon-12 atom, atomic weights are dimensionless.

atomic-weight interval – the upper and lower bounds determined for the **Standard Atomic Weight** of an element when its isotopic and atomic weight variations in **normal material** exceed the measurement uncertainty of its standard atomic weight. It is determined by an IUPAC project by evaluation of peer-reviewed scientific publications, and currently only 12 elements have been evaluated and assigned atomic-weight intervals.

half-life (radioactive) – the time interval that it takes for the total number of atoms of any radioactive isotope to decay and leave only one-half of the original number of atoms.

isotope – one of two or more species of atoms of a given element (having the same number of protons in the nucleus) with different atomic masses (different number of neutrons in the nucleus). The atom can either be a **stable isotope** or a **radioactive isotope**.

natural isotopic fractionation – variation in the mole fractions (isotopic abundances) of an element in various substances. These variations arise because stable isotopes of an element have slightly different physical and chemical properties, giving rise to partitioning of these isotopes in substances. These fractionations of isotopes commonly are proportional to differences in their relevant isotope masses.

normal material – a reasonably possible source for an element or its compounds in commerce, for industry or science; the material is not itself studied for some extraordinary anomaly and its mole fractions (isotopic abundances) have not been modified significantly in a geologically brief period.

radioactive decay – the process by which unstable (or radioactive) isotopes lose energy by emitting alpha particles (helium nuclei), beta particles (positive or negative electrons), gamma radiation, neutrons or protons to reach a final stable energy state.

radioactive isotope – an atom for which **radioactive decay** has been experimentally measured (also see half-life).

stable isotope – an atom for which no radioactive decay has ever been experimentally measured.

Standard Atomic Weight – an evaluated quantity assigned by the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW) to encompass the range of possible atomic weights of a chemical element that might be encountered in all samples of normal terrestrial materials. It is comprised of either an interval (currently for 12 elements) or a value and an uncertainty (a Standard Atomic Weight Uncertainty), and currently there are 72. A Standard Atomic Weight is determined from an evaluation of peer-reviewed scientific publications.

Standard Atomic-weight Uncertainty – the uncertainty part of the **Standard Atomic Weight** of an element not having an **Atomic-weight Interval**. It is based on both the measurement uncertainty of the atomic weight in a representative sample and the interval over which known variations in atomic weights among normal terrestrial materials have been reported.