The Impact of Depleted $^6\text{Li}$ on the Standard Atomic Weight of Lithium

by Norman E. Holden

Lithium is one of a handful of elements whose stable isotopic ratio varies in natural terrestrial samples to the extent that the resulting atomic weight variation exceeds the measurement uncertainty on the value. As a result, the standard atomic weight of lithium is more accurately characterized as a range of atomic weight values from 6.9387 to 6.9959. Lithium has become the least accurately known atomic weight because of the existence and the distribution in the distant past of some chemical reagents, which were depleted in the $^6\text{Li}$ isotope of natural lithium. This background story brings to light an interesting page of history.

Lithium is an element with only two stable isotopes, $^6\text{Li}$ and $^7\text{Li}$, and so there is only one stable isotope ratio involved (see Figure 1). The standard isotopic reference material for lithium, $\text{IRMM-016}$, has a measured stable isotope ratio that leads to a mole fraction for $^6\text{Li}$ of 0.0759 (which corresponds to an isotopic abundance of 7.59%) and a mole fraction for $^7\text{Li}$ of 0.9241 (which corresponds to the isotopic abundance of 92.41%). The product of each isotope’s atomic mass and its isotopic abundance, summed over both isotopes leads to a calculated value of 6.94 for the atomic weight of lithium. For the isotopically fractionated lithium samples with depleted $^6\text{Li}$ in our story, the mole fractions in the extreme case would be $^6\text{Li}$ is 0.02007 (or isotopic abundance of 2.007%) and $^7\text{Li}$ is 0.97993 (or isotopic abundance of 97.993%).

These mole fractions lead to a value of about 7.00 for the atomic weight of the lithium sample that is depleted in $^6\text{Li}$.

At this point, let it be noted that the isotopic abundance values are also weighting factors that relate the thermal neutron absorption cross section (or probability that a neutron reaction will occur) of each stable isotope to the thermal neutron absorption cross section of the natural chemical element. In the case of lithium, the thermal neutron cross section reaction for one of its isotopes, $^6\text{Li}$, had an interesting impact on the atomic weight of lithium in reagents found on the shelves of chemists.

The majority of the thermal neutron absorption in the various target chemical elements usually involves the neutron capture reaction. In this reaction, the neutron projectile is absorbed by the target nucleus and any excess energy created in this process is released by the emission of a gamma-ray photon. This energy release allows the product nucleus to decay from the excited state to the normal ground state. However, in the case of a $^6\text{Li}$ target nucleus, a much larger contribution to the absorption cross section results from the neutron reaction: $^6\text{Li} (n, \alpha) ^3\text{He}$. The neutron cross section for this reaction has a very large value. The value is approximately 940 barns† (or $940 \times 10^{-28}$ m$^2$), compared to values of a milli-barn (or 1 x $10^{-31}$ m$^2$) for typical neutron capture cross sections in light elements.

From the late 1940s to the early 1950s, a number of nations, which had previously developed and tested nuclear fission weapons, were attempting to construct thermonuclear weapons of mass destruction (or in the vernacular, hydrogen bombs). The approach involved the use of the $^2\text{H}^3\text{He}$ reaction (or DT reaction), which released a large amount of energy. The successful method that was suggested for producing this reaction was to irradiate lithium deuteride with neutrons. To improve the efficiency for generation of the tritium component, the lithium sample was enriched‡ in $^6\text{Li}$.

† The International System of Units (SI) has a unit of area of meters$^2$ (m$^2$). The barn can be expressed as $10^{-28}$ m$^2$. (The history of the origin of the name of the unit “barn” would also make an interesting story). The large value of 940 barns for the neutron isotopic cross section of $^6\text{Li}$ would correspond to a natural element cross section of about 71 barns (which is also a relatively large value) for “normal” lithium. This large value led to the use of natural lithium as a neutron cross section standard. For isotopically fractionated lithium depleted in $^6\text{Li}$, the natural elemental cross section would be about 19 barns. Neutron cross-section measurements that were made relative to the lithium standard that was depleted in $^6\text{Li}$ would be too low by almost a factor of 4.

‡ It is interesting to note that the $^7\text{Li}$ component of the lithium deuteride also provided a source of additional tritium. It was not initially realized that the cross section at high neutron energies for the reaction $^7\text{Li} (n, 2n)$ was so significant. Since there was not a very large source of $^6\text{Li}$ available at the start, the initial lithium was not very highly enriched and this lithium had a significant amount of $^7\text{Li}$ in it. The total yield (energy release) from the explosion of the first dry lithium deuteride weapon’s test was two and one half times greater than originally anticipated and this had unexpected consequences.
Rather than waste all of the leftover by-product of these isotopically fractionated lithium samples, this by-product, which would be enriched in $^7\text{Li}$, was commercially distributed in laboratory reagents. Because of the fact that the enrichment of $^6\text{Li}$ was part of a classified military weapons program, the general scientific community and the public were never provided information that the lithium being distributed in the chemical reagents was depleted in $^6\text{Li}$. This distribution resulted in labels on containers of reagents, which had incorrect atomic weight values listed on them.

The isotopic fractionation of lithium was first noted when measurements of the neutron cross section of various materials, that were normalized to the natural lithium standard cross-section value, provided results that were much lower than those same cross sections when measured against all other neutron cross-section standards. The large discrepancy in the isotopic abundance of $^6\text{Li}$ in reagents was later measured via neutron activation analysis and by mass spectrometric measurements. The detection of this problem was published in the open scientific literature at various times in 1958, 1964, 1966, 1968, 1973, and 1997, with ever increasing depletion of $^6\text{Li}$ in the commercial samples noted. Figure 2 shows the variation in isotopic composition and atomic weight of selected lithium-bearing materials. Note that lithium enriched in $^7\text{Li}$ has made its way into ground waters (see Figure 2), and the lithium isotopic composition has been used as an environmental tracer to identify lithium compounds in waste waters down gradient of a mental institution using pharmaceuticals containing lithium (T. Bullen, U.S. Geological Survey, written communication).

Although many of lithium’s elemental properties would not affected by the use of depleted lithium, the incorrect atomic weight would lead to errors in the concentration of the lithium being used. It has a major effect when isotopically fractionated lithium is used as a reference in mass spectrometric measurements. In the neutron cross-section field, natural lithium was eliminated as a measurement standard more than half a century ago because of the problem of depleted $^6\text{Li}$.

The atomic weight of terrestrial and commercial lithium sources varies between 6.9387 and 6.9959. If the standard isotopic reference material’s atomic weight is recommended, the value would be 6.94 ($\pm$0.002), where the number in parentheses indicates the uncertainty needed to cover the isotopically fractionated lithium sources, which is an uncertainty of about 0.9% (see Figure 2). If a value were recommended that is accurate to one in the last quoted digit, the atomic weight becomes 6.9 ($\pm$1), and an uncertainty of about 14%. In either case, lithium is the element with the least accurate atomic weight, and all because of the unacknowledged distribution of depleted $^6\text{Li}$ in chemical reagents in the distant past.

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Figure 2. Variation in atomic weight with isotopic composition of selected lithium-bearing materials (modified from reference 2). Isotopic reference materials are designated by solid black circles. The previous (2007) standard atomic weight of lithium was $6.941 \pm 0.002$.
may be using. If the published value of the standard atomic weight in the Commission’s report is not of adequate accuracy for a particular application when the uncertainty budget is determined, one needs to measure the atomic weight value for the specific sample.

References


Norman Holden <holden@bnl.gov> works at the National Nuclear Data Center of the Brookhaven National Laboratory, in Upton, New York. He is a member of the IUPAC Inorganic Chemistry Division and is actively involved in multiple projects. He is chair of the project to develop an isotopic periodic table for the educational community, and of another on the assessment of fundamental understanding of isotopic abundances and atomic weights of the chemical elements.

Stamps International

R is for Rutherford

He may well be the best-known scientist born and raised in New Zealand and the most famous physicist to receive the Nobel Prize in Chemistry (1908). Ernest Rutherford was born in 1871 in a rural community near Nelson, on the South Island of New Zealand. He received his early education at local schools and then attended Canterbury College (1890–1895), where he obtained B.A., M.A., and M.Sc. degrees in math and physics and did research on the magnetic properties or iron exposed to high-frequency oscillations. After a three-year stint at Trinity College in Cambridge, England, he accepted a position as a professor of physics at McGill University in Montreal, where he conducted most of the work that led to the Nobel Prize “for his investigations into the disintegration of the elements and the chemistry of radioactive substances.” He subsequently investigated the nature of alpha rays and established the nuclear structure of the atom while at the University of Manchester (1907–1919). From there, he succeeded J.J. Thomson as head of the famous Cavendish Laboratory at Cambridge, where he remained until his death in 1937. A talented experimentalist and gifted mentor, he is regarded as one of the most important scientists of the 20th century. Element 104 (rutherfordium, Rf) is named after him.

The stamp illustrated herein is part of an eclectic set of 26 stamps (A through Z . . . ) issued by New Zealand Post on 6 August 2008 to celebrate the achievements and cultural heritage of New Zealanders. Thus, G is for Goodnight Kiwi, a beloved cartoon character that used to signal the end of nightly broadcasts on New Zealand television, and K is for Kia Ora, a traditional Maori greeting that literally means “be well” but is indistinctly used to say hello or goodbye. Rutherford, coincidentally bestowed with the honor of representing the letter R stamp on the centennial of his Nobel Prize, is the only scientist portrayed on the set. He may have spent most of his professional career in Canada and the UK, but there’s little doubt that most people in New Zealand consider him a source of national pride, a cultural icon, and a symbol of kiwi ingenuity.

Written by Daniel Rabinovich <drabinov@uncc.edu>.