

# The straight dope on isotopes

A century ago this month, Frederick Soddy described and named isotopes in the pages of *Nature*.

**Brett F. Thornton** and **Shawn C. Burdette** discuss how chemists have viewed and used isotopes since then — either as chemically identical or chemically distinct species as the need required and technology allowed.

Ernest Rutherford visited Stockholm in December 1908 to receive the Nobel Prize in Chemistry for his “investigations into the disintegration of the elements, and the chemistry of radioactive substances”<sup>1</sup>. Rutherford, a famously reluctant chemist, had hoped to be recognized for physics, but the discovery of radioactivity had deeply intertwined physics and chemistry more than at any time before or after. Investigations into radioactivity were accompanied by a multitude of reports describing new substances, tentatively called radio-elements, but in 1908 almost no one knew how to classify them. Mendeleev’s periodic table lacked enough gaps to accommodate all the new substances being found in samples of uranium and thorium, and some chemists even suggested that the periodic table was no longer a valid way to organize elements.

After the Nobel ceremony, Rutherford met with two chemists from Uppsala University, Daniel Strömholm and a young Theodor Svedberg. Strömholm and Svedberg were attempting to crystallize radio-elements for chemical characterization. Using these methods, they hypothesized that the radio-elements radium, thorium X and actinium X were actually the same chemical element<sup>2</sup> and, therefore, should be grouped together on the periodic table. Today these species are recognized as <sup>226</sup>Ra, <sup>224</sup>Ra and <sup>223</sup>Ra. Rutherford was highly sceptical of the Swedes’ suggestion, and although discouraged, Strömholm and Svedberg cautiously published their results<sup>2,3</sup>, which were largely ignored. Had they been bolder in making their claims, the pair might have been credited with discovering isotopes, as Svedberg would speculate much later.

The evidence of chemically inseparable elements became more undeniable in May 1913 when J. J. Thomson reported that neon seemed to be made of two gases with masses 20 and 22 (ref. 4). *Nature* then published Frederick Soddy’s proposal on 4 December 1913, which hypothesized that isotopes were “chemically identical elements of the same nuclear charge”<sup>5</sup>. The name isotope, from Greek words meaning ‘same place’, had been suggested to Soddy at a dinner party<sup>6</sup>. Soddy’s Nobel Prize speech nine years



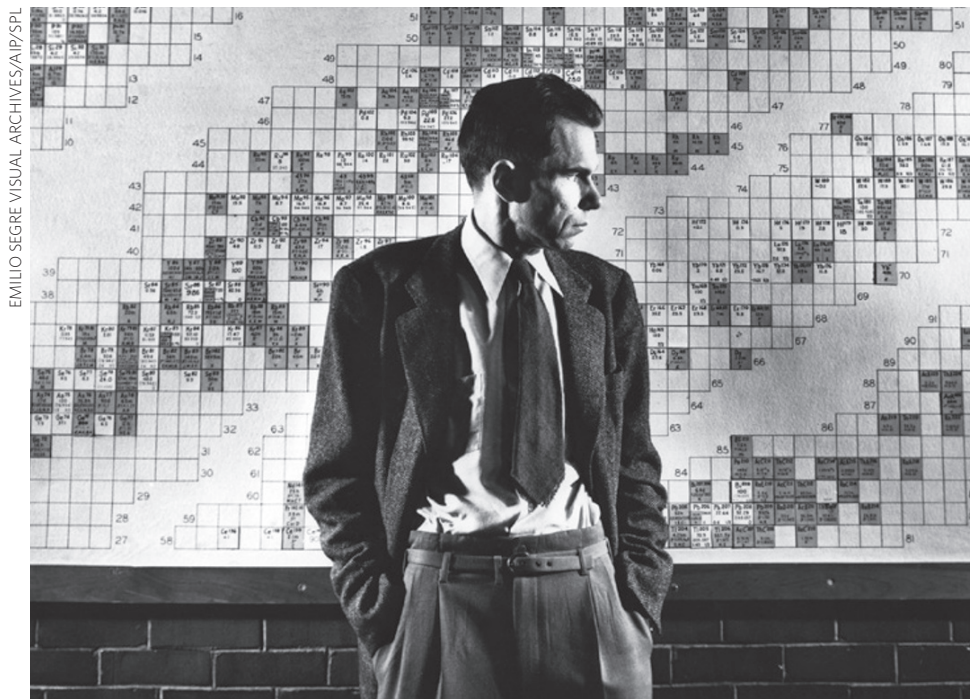
The origin of ‘isotopes’.

later summarized the events surrounding the realization of isotopy, and included an apologetic acknowledgement of Strömholm’s and Svedberg’s research. Much of the early work leading to the rationalization of isotopes was based on classical chemistry techniques rather than physics-based methods, and isotopes were put on a solid footing just before Moseley’s X-ray studies firmly established that each element has a unique atomic number<sup>7</sup>.

Soddy described isotopes as having “identical outsides but different insides”<sup>8</sup>. We now know that the ‘outsides’ — the electrons — cause all of an element’s isotopes to exhibit the same chemistry. The protons and neutrons — the ‘insides’ — are spectators to the interactions of valence electrons. This was the original, but philosophically troubling, understanding<sup>9</sup>. Some chemists believed that isotopes must be chemically distinct. How could isotopes of a single element, made up of atoms that were different, have identical chemical properties? Earlier work had demonstrated that thorium and ionium, now known as two isotopes of thorium, seemed to have the same atomic emission

spectrum<sup>10</sup>. Though there was much debate, Georg Hevesy and Friedrich Paneth’s critical experiments demonstrated that, to their limits of accuracy, isotopes of lead behaved identically in an electrochemistry experiment<sup>11</sup>. They concluded that an element’s chemistry does not depend on which isotope it is. Although the early experimenters were limited to studying only the relatively few isotopes that occur naturally on Earth, that limit soon lapsed.

Today there are about 3,000 known isotopes, and there could be 3,000–4,000 more<sup>12</sup>. Most isotopes are short-lived radioactive species. Elevating only stable isotopes to element-like status would be unwieldy and, for most chemistry, unnecessary; however, subtle problems with treating isotopes as chemically equivalent entities soon emerged. When Harold Urey discovered <sup>2</sup>H in 1931, deuterium was quickly shown to have different chemical properties from <sup>1</sup>H. Although the hypothesis that isotopes were chemically identical was refuted long ago, we still teach students that an element’s isotopes exhibit the same chemistry. How far do the real differences extend? The



Soddy's work opened a fertile area of chemistry research. Pictured here, Glenn Seaborg, discoverer of many isotopes, stands in front of an isotope chart.

doubled mass of deuterium with respect to protium represents the most extreme case: the differences are so pronounced that hydrogen isotopes have special names.

In 1946, Urey reviewed instances where isotopes of elements besides hydrogen behaved differently<sup>13</sup>. This marked the beginning of stable isotope studies, and a shift to viewing isotopes as being chemically distinct instead of identical. Although this had been realized much earlier for deuterium, the phenomenon was now recognized as being a possibility for the entire periodic table. Urey introduced the idea of using oxygen isotopes to deduce seawater paleotemperatures in 1948 (ref. 14). In natural and artificial systems, a tiny preference for one isotope over another in a frequently repeated reaction, such as carbon fixation by plants, will lead to a differential isotope fractionation in the reactants and products.

What is the nature of isotopes for chemists today? Aside from the pioneers endeavouring to create new isotopes (or elements), isotopes are tools for chemists. Those isotopic tools fall into two broad categories: (1) tools that assume isotopes of an element are chemically identical; and (2) tools that assume they are chemically distinct. Tools that assume isotopes are chemically identical exploit isotopes as tracers. For example, elucidating a biological process by observing the flow of a spike of radioactive <sup>14</sup>C through the system. Such tracer uses were exploited very early, even before the word 'isotope' was coined<sup>15</sup>.

Alternatively, the kinetic isotope effect (KIE) is based on mass-induced variations in chemistry. Chemical bonding interactions with a heavy isotope will usually occur more slowly than with a lighter one. Molecules with the lighter isotopes in reactive positions become depleted relative to the analogous molecules with heavier isotopes at the same location. The larger the mass difference, the larger the KIE. Reactions involving C–H bonds are about 6–10 times faster than C–D bond reactions, whereas substituting <sup>13</sup>C for <sup>12</sup>C only slows reactions by about 1.04 times.

When carbonic anhydrase captures CO<sub>2</sub>, <sup>12</sup>C is preferentially incorporated into the plant's tissues. The measurement of isotope fractionation, the 'delta' notation<sup>16</sup> ( $\delta^{13}\text{C}$ ), is shown in equation (1). The  $\delta$  represents the deviation of an isotope ratio in a sample from the isotope ratio in a standard material. The zero value for  $\delta$  is defined a standard material. For carbon, the standard is Vienna Pee-Dee Belemnite, a synthetic standard based on fossilized cephalopods, but other element isotope standards are based on less obscure materials such as seawater.

$$\delta^{13}\text{C} = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{standard}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{standard}}} \times 1,000 \quad (1)$$

Typical  $\delta$  values for reactions are a few to tens of parts per thousand, or per mille (‰),

although there is great variability.

Atmospheric CO<sub>2</sub> has a  $\delta^{13}\text{C}$  of about  $-8\text{‰}$ ; in plants,  $\delta^{13}\text{C}$  is about  $-28\text{‰}$ . A positive  $\delta^{13}\text{C}$  means that the sample is <sup>13</sup>C-enriched relative to the standard; a negative value means that the sample is depleted in <sup>13</sup>C. Variations in these values can be used in elucidating food webs and which plants animals preferentially eat.

Kinetic isotope effects have an impact, though often imperceptibly, on most chemical reactions. The average mixture of an element's isotopes varies slightly as matter moves through various systems on Earth. Most (74) of the first 92 elements have more than one isotope used in calculating their atomic weights, therefore these atomic masses are subject to variability. As far back as 1951, the IUPAC atomic weight revisions included a disclaimer about the atomic weight of sulfur because of variations found in natural materials. Advances in analytical and separation technologies have slowly led to the requirement for more footnotes in each succeeding revision. Six decades later, 12 elements have atomic weights that are given as ranges, not single values<sup>17,18</sup>.

As elements become heavier, the KIE and relative differences in isotope masses become smaller. In bromine, <sup>79</sup>Br and <sup>81</sup>Br differ in mass by less than 3%. Advances in experimental techniques have recently allowed bromine isotope fractionation to be measured in atmospheric methyl bromide, a naturally occurring and anthropogenically produced ozone-depleting gas. Knowing the relative amounts of <sup>79</sup>Br and <sup>81</sup>Br in CH<sub>3</sub>Br may help explain the uncertainties in its sources and sinks in the environment. Measuring  $\delta^{81}\text{Br}$  of CH<sub>3</sub>Br means trapping and separating an 8 parts-per-trillion component of the atmosphere, and noting variations in isotopic composition at a parts-per-thousand level. So far,  $\delta^{81}\text{Br}$  of CH<sub>3</sub>Br has been observed in the 0 to 1.75‰ range where 0‰ is the bromine composition of seawater<sup>19</sup>, providing a new tool for distinguishing amongst the many natural sources and sinks of CH<sub>3</sub>Br.

The KIE doesn't explain all isotope effects however. Some reactions were observed to behave in exactly the opposite fashion of what the KIE would predict, with heavier isotopes found to be more reactive. In the 1970s, the magnetic isotope effect was elucidated. This effect arises because of chemical reactions preferring to conserve electron and nuclear spin<sup>20</sup>. For instance, Mg has three stable isotopes: <sup>24</sup>Mg and <sup>26</sup>Mg are spinless and non-magnetic, whereas <sup>25</sup>Mg has a nuclear spin and is magnetic, and can participate in electron–nuclear hyperfine coupling during reactions, potentially

introducing alternative reaction pathways. In contrast, bromine's two stable isotopes have the same nuclear spin, so Br cannot exhibit magnetic isotope effects.

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The ability to measure isotope effects has slowly spread to higher atomic numbers. With more of the periodic table now available, the applications of isotope fractionation measurements<sup>21</sup> will continue to grow. Measuring more than one isotope system in a molecule, or multidimensional isotope analysis, can enable very detailed sourcing of samples. Isotopes are the workhorses of geochemistry, tracers built into the fabric of Earth and the universe. Isotopes have proved invaluable at elucidating many aspects of the Earth's history<sup>22</sup>. Farther afield, isotopes are useful for understanding not only the atmosphere of Mars, but the history of the atmosphere of Mars<sup>23</sup>.

For nearly a century, isotopes have been invisible to most chemists, but that is changing in small steps. Shifting isotope compositions mean that the atomic weights are no longer universal constants<sup>24</sup>. Students of chemistry often learn about the simpler uses of isotopes based on chemical identicalness, though this is now changing<sup>25,26</sup>. The unique chemical nature of an element's individual isotopes becomes more apparent when analysed at finer scales, reflecting a century of improvements in analytical chemistry.

So what are isotopes to a modern chemist? What will they be in another hundred years? Chemical curiosities, an area of active research, or a vital tool? The answer, ultimately, may depend on what type of chemist you are. □

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