Just 20 years ago, while completing his chairmanship of the IUPAC Commission on Atomic Weights, Norman Holden prepared and published in Chemistry International *(1984, issue No.1) an early historical review of the International Commission on Atomic Weights. Since then, his interest of the topic has not faded, and au contraire, he has now reviewed, extended, and updated the historical review to a length far beyond the space available here. The excerpts below are extracted from the historical review, which is available online at <www.iupac.org/publications/ci/2004/2601/1_holden.html>. The full text is equivalent to about 20 pages and includes more than 100 references.*

Atomic Weights and the International Committee: A Brief Historical Review

Norman E. Holden, when chairman of the commission from 1979-1983.

by Norman E. Holden

The International Committee on Atomic Weights (ICAW) has a long and colorful history dating back for over a century. Initially, the task was to provide the chemical community and trade and commerce with the most accurate atomic weight values for the chemical elements. For over the past half century, the isotopic composition of the stable (or very long-lived) isotopes of those elements has taken on a larger role, until today the atomic weight values are determined by mass weighting the isotopic abundance values. There was much interest in the atomic weight values when they were considered constants of nature and the building blocks of the periodic table and even more now that they are known to be variable.

Background

Just two hundred years ago, the English schoolteacher, John Dalton, presented the first table of atomic weight values in a paper entitled *On the Absorption of Gases by Water and Other Liquids*. (The table was first read on 21 October 1803 to the Manchester Literacy and Philosophical Society, and than published in 1805.) Since hydrogen had the smallest atomic weight value, Dalton chose that element as his reference scale unit, hydrogen = 1, and he calculated atomic weights by comparing weights of other atoms with that of hydrogen. Values given in the table indicate that Dalton grasped the ideas of constant composition in compounds and of multiple proportions. However, he did not account for the valence of each element in the compound. Dalton's later tables, published in 1808 and 1810, show a marked improvement in accuracy but the values are still difficult to recognize because of these errors in valence (i.e., some equivalent weights [atomic weight/valence] are quoted rather than atomic weights).

By the end of the nineteenth century, atomic weight had taken on the concept of a constant of nature like the speed of light, but the lack of agreement on accepted values created difficulties in trade. All parties were not translating quantities measured by chemical analysis into weights in the same way. With so many different values being reported, the American Chemical Society (ACS), in 1892, appointed a permanent committee to report on a standard table of atomic weights for acceptance by the Society. Frank W. Clarke, who had been appointed a committee of one, presented his first report at the 1893 annual meeting.

In 1897, the Deutsche Chemische Gesellschaft appointed a working committee to report on atomic weights. The committee, chaired by Hans Landolt (Berlin), published its first report in 1898. In contrast to Clarke, who presented a review of every atomic weight value published during the year along with his recommended values, the German committee merely gave the table with its estimated best value for each element. The committee argued for the adoption of the O = 16 scale and invited other chemistry organizations to appoint delegates to an international body. The resulting International Committee on Atomic Weights (ICAW) began with 57 chemists. The committee's first report, published in 1901, was a table on the O = 16 scale, which appeared as a flyleaf in issue 1 of the *Chemische Berichte* in 1902.

The ICAW soon decided to elect a smaller committee of three members to avoid the difficulties and delays of corresponding among a large group. The top three vote getters, Clarke, Karl Seuber, and Thomas Edward Thorpe, were elected. This committee reported annually (except for 1918) until 1921. In 1913, the committee became formally affiliated with the International Association of Chemical Societies (IACS), which had been formed two years earlier. The ICAW was charged with publishing an updated Table of Atomic Weights every year. Although the IACS was formally dissolved in 1919, the ICAW continued to publish its annual tables until 1922.

In 1918, a conference of scientists from allied (countries at war with the Central Powers) scientific academies withdrew from the IACS and formed the International Research Council (IRC). A year later, at the Inter-allied Chemical Conference in London, the allied chemical societies of Belgium, England, France, Italy, and the United States formed the International Union of Pure and Applied Chemistry (IUPAC), which would function—with autonomous powers—as the chemical section of the IRC.

At the first IUPAC conference, held in 1920 in Rome, the IUPAC Council met and established a series of committees: one on atomic weights, one on tables of constants, and one on patents, as well as an Institute of Chemical Standards. The council requested that the old ICAW be asked to continue its work. In 1921, the committee on atomic weights was reorganized, enlarged, and renamed the Committee on Chemical Elements. This committee, in addition to providing atomic weight values, was also asked to cover the discovery of isotopes in radioactive and non-radioactive elements. Tables of radioactive elements and their principal constants, a table of isotopes, and a table of atomic weights were to be prepared.

At a meeting in Paris in 1922, the Committee on Chemical Elements voted to publish the table of isotopes and of radioactive elements the following year and to continue the old committee's table of 1921–1922 if a new general table of atomic weights could not be completed in time. The committee published a completely revised atomic weight table in 1925, but did not revise the table again until after 1930. In 1928, after being criticized for failing to publish an annual table of atomic weights for many years, the committee was reorganized into three separate committees: one dealing with atomic weights, one with atoms, and one with radioactive constants.

Frank W. Clarke

The Atomic Weights Scale

The atomic weights scale of H = 1 was originally used by Dalton and (except for Berzelius' time) had been used for approximately 100 years when the ACS and the German committees began reporting their tables. Lothar Meyer (one of the first developers of the periodic table) and Seubert had published on the hydrogen scale, but Wilhelm Ostwald (a member of the German committee who later won the Nobel Prize for chemistry for catalysis) and Bohuslav Brauner (member of the Committee on Chemical Elements) strongly urged the adoption of the O = 16 scale. Clarke reported his table on both scales, while the German committee used the O = 16 scale exclusively and argued for its adoption. As a result of a vote within the German Committee in 1899, the first international table was published on the O = 16 scale. However, after vigorous protests from certain parties, doubt was expressed as to whether a majority opinion could ever be accepted as final in such theoretical matters. As a result, the smaller ICAW continued publishing the annual tables on both scales until a consensus could be reached.

Beginning with the 1906 report, however, the ICAW used the O = 16 scale following a new survey of the larger committee. Thus, the scale was settled for some 30 years, except for a brief discussion in 1920 on going back to the hydrogen scale. Beginning in the 1930s, when the neutron was discovered and the structure of nuclei was accepted to be a combination of protons and neutrons, H = 1 became a near impossible choice as a reference for atomic weights. The atomic number of heavy elements would not represent the number of nuclides in the nucleus in an H = 1 scale.

In 1929, the discovery of the two oxygen isotopes, ^{17}O and ^{18}O by Giauque and Johnston led to a situation in which the chemist's scale of O = 16 differed from the physicist's scale of ^{16}O = 16. When Dole reported the variation in oxygen's atomic weight value in water versus air, this implied a variation in the isotopic composition of oxygen and the two scales took on a small but a variable difference. The ICAW briefly discussed the atomic weight standard in their 1932 report, where they considered ^{1}H = 1, ^{4}He = 4, ^{16}O = 16 and O = 16 before choosing to follow Aston, who argued that the two scales satisfied everyone's requirement.

The variable scale difference was of great concern to Edward Wichers (president of ICAW beginning in 1949) and for a number of years he attempted to have the ICAW fix the difference between the two scales by definition. This would effectively define the isotopic composition of oxygen to be a particular value in nature. Failing with this solution, he solicited proposals for an alternate scale that would be acceptable to both the physics community as well as to the chemists worldwide.

Edward Wichers

Alfred Nier

Josef Mattauch

In April 1957, Alfred Nier suggested to Josef Mattauch (both were members of ICAW) that the ^{12}C = 12 mass scale be adopted because of carbon's use as a secondary standard in mass spectrometry. Also, ^{12}C = 12 implied acceptable relative changes in the atomic weight scale, (i.e., 42 parts-per-million [ppm] compared to 275 ppm for the ^{16}O = 16 scale [which would not be acceptable to chemists]). Enthusiastically, Mattauch made a worldwide effort in the late 1950s to publicize the ^{12}C = 12 scale and obtain the physicist's approval, while Wichers obtained the chemist's approval.

Following the approval of the International Union of Pure and Applied Physics General Assembly in Ottawa, Canada, in 1960 and the IUPAC General Assembly at Montreal, Canada, in 1961, the atomic weights were officially given on the ^{12}C = 12 scale for the first time in the 1961 report. Mattauch and his colleagues combined data on direct nuclidic mass measurements with data on measured binding energies and beta decay energies derived from the masses to produce a consistent least squares fit of all nuclidic masses. This mass data was combined with the isotopic compositions to provide atomic weight values used in that 1961 Atomic Weights report.

Expanded Topics for the Commission

In the years between when the mass scale change occurred and 1969, there were relatively few changes in the atomic weights table. In the 1969 report, a table of radioactive isotopes with half-life values and a table of atomic masses of selected isotopes were included, and definitions of terms of atomic weight, isotope, nuclide, and normal material were introduced. These definitions led to an interdivisional fight within IUPAC with various terminology committees about these terms, not the least of which was "atomic weights" itself. The various discussions that followed would continue over a decade until the IUPAC General Assembly at Davos, Switzerland, in 1979.

The fallout from the terminology wars was discussed in the commission's meetings at both the 1971 IUPAC Washington, D.C., General Assembly and the 1973 IUPAC Munich, FRG, General Assembly. In the 1971 report, there was a discussion as well as a graph of the relative precision of the atomic weight values of all elements across the periodic table. The two tables of half-life values and atomic masses from the 1969 report were combined into a single table in the 1971 report.

With the increased importance of the isotopic abundance measurements in the determination of the atomic weights, the commission's name was changed at the 1979 IUPAC General Assembly in Davos, Switzerland, to Commission on Atomic Weights and Isotopic Abundances. A new definition of atomic weight was presented, which indicated that atomic weights could be defined for a sample. Tables of standard atomic weights published by the commission referred to best knowledge of the elements in natural terrestrial sources (this is still the case today). Atomic weight (mean relative atomic mass) of an element from a specified source was defined as "the ratio of the average mass per atom of the element to $^{1}/_{12}$ of the mass of an atom of ^{12}C." From this point on, the commission presented the most accurate available values for those who needed to use them, but the concept of accuracy implies the existence of a true value and the definition doesn't recognize the existence of one true value for every element.

The Growing Importance of Isotopic Compositions

For the 1981 IUPAC General Assembly in Leuven, Belgium, the Commission decided to publish its report in *Pure and Applied Chemistry* in two separate parts for the first time (i.e., the *Atomic Weights of the*

Elements, 1981 and the *Isotopic Compositions of the Elements*, 1981).

At the 1983 IUPAC General Assembly in Lyngby, Denmark, the Commission changed its method for expressing uncertainties in atomic weight values. Previously these uncertainties were restricted to one of two values, (i.e., either ± 1 or ± 3). Beginning with the 1983 report, these uncertainties could now take on any digit from ± 1 up to ± 9. Another change with the 1983 report dealt with the treatment of elements with no stable isotopes. For radioactive elements with no unique naturally occurring isotopic composition from which an atomic weight could be calculated with five or more figure accuracy without prior knowledge of the sample, the concept of a standard atomic weight has little meaning. So scientists dealing with non-terrestrial samples were warned to exercise caution when the isotopic composition or atomic weight of a non-terrestrial sample was required.

At the 1999 IUPAC General Assembly in Berlin, Germany, the Working Party on Non-terrestrial Data reported on the processes explaining isotopic variations and provided a table of anomalous isotopic compositions in extra-terrestrial materials due to decay of radioisotopes.

More recently, at the 2001 IUPAC General Assembly in Brisbane, Australia, the commission emphasized the great importance of the isotopic abundance values as the sole source (along with the atomic mass values of the stable isotopes) for determining atomic weight values for the elements. The commission once more changed its name to the Commission on Isotopic Abundances and Atomic Weights (CIAAW). At the conclusion of the Brisbane General Assembly, changes to the IUPAC bylaws and statutes resulted in the termination of all commissions, but after discussions, the IUPAC Council approved the reestablishment of the CIAAW.

Normally in the period between IUPAC General Assemblies, the members of the commission and the various subcommittees perform the literature search for data from the journal and document sources and an initial assessment of the results and impact on the database. In the period after the Brisbane General Assembly, it was determined that although IUPAC approved continuation of the commission, it was to be without commission funding. It had been concluded that without adequate funding, there would be no commission meeting in 2003. This thinking continued for more than one and one half years, until the president of the IUPAC Inorganic Chemistry Division, Gerd Rosenblatt, made funds available to bring together all members of the commission and subcommittees in Ottawa to discuss the future course of the commission.

As a result of the above confusion, no preparatory work for the scientific agenda had been done to analyze the data and recommend updated values for the Table of the Standard Atomic Weights. At the 2003 IUPAC General Assembly in Ottawa, Canada, the commission chose not to publish a report on Atomic Weights for 2003 (for the first time in almost 40 years). The commission and the subcommittees discussed the future work of these bodies and a mechanism for the funding for continued operation either within IUPAC or outside of the IUPAC framework. Tiping Ding (Chinese Academy of Geological Sciences, Beijing, China) was elected chairman to replace Philip Taylor and Michael Wieser (University of Calgary, Alberta, Canada) was elected secretary to replace Robert Loss at the conclusion of the meeting.

One atomic weights publication that did appear in a pre-print form at the time of the Ottawa General Assembly was another element-by-element review called *EXER-2000*. This 115-page document had been the result of the six-year effort by the members of the 1997 working party and it was written in a similar manner to the earlier Subcommittee on the Assessment of Isotopic Composition review.

Norman Holden <holden@bnl.gov> has been involved with IUPAC for over 30 years and is today a titular member on the Inorganic Chemistry Division. Since 1974, he has been at the National Nuclear Data Center of the Brookhaven National Laboratory, in Upton, New York, USA.

The full version of this historical review, which includes sections on Uncertainties and Annotations and The Naming of Natural and Synthetic Elements, is available at

www.iupac.org/publications/ci/2004/2601/1_holden.html

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