Atomic weights: From a constant of nature to natural variations

N E Holden

High Flux Beam Reactor, Brookhaven National Laboratory, Upton NY USA 11973

Abstract

The concept of Atomic Weight of an element as a constant of nature has played a key role in science for almost two hundred years. Two centuries ago, it helped provide credence to the atomic theory of matter. One hundred fifty years ago, the periodicity in the properties of various elements as a function of their atomic weight helped lead to the discovery of the Periodic Table and the classification of the chemical elements. Early in this present century this constant of nature concept was shaken when elements were found, which had different atomic weight values as well as different radioactive properties but they had the same chemical properties and therefore were located in the same position in the Periodic Table. To solve this problem, the concept of isotopes was born. Finally fifty years ago, the variation in nature of the composition of the stable isotopes in carbon and oxygen was found, which led to a variation in their respective atomic weights. Now mass dependent chemical reactions, nuclear reactions both natural or man-made and radioactive decay processes force us to accept the idea that atomic weights are more likely to vary in nature than they are to be constants of nature. What should we expect from atomic weights in the future?

Introduction

The world is made up of an apparently endless variety of substances; if each one is an entity in itself, the nature of matter must be forever incomprehensible. The Greeks first introduced the idea of atoms as elementary constituents of matter, but their atom was a vague general idea unattached to any specific facts or processes. John Dalton introduced his atomic theory and his table of atomic weights at the start of the 19th century. The Periodic Table was constructed using the periodicity of the chemical properties of elements in the ascending order of the atomic weights of these elements. As a result, the world was now made up of a moderate number of different real substances related in a single system and the nature of matter became comprehensible, but why did it take almost seventy years from the inception of the atomic weight concept to the publication of the Periodic Table?

In the first decade of the twentieth century, new substances were being discovered, almost daily, which had similar chemical properties to existing elements but with different atomic weight values. Bewildered scientists could not decide where to place these new discoveries in the Periodic Table. Did this invalidate the concept of atomic weights as a useful, chemical tool?

Treating the variation in the lead atomic weight as a special case, atomic weights were still considered to be constants of nature into the latter half of this century. Has this view changed? Is the atomic weight concept still useful today? We will investigate these questions in detail below.

Prehistory

The ancient Greeks first developed the idea 2500 years ago that matter was composed of atoms (Greek: indivisible). They taught that all matter was composed of four elements; fire, water, air and earth (Holden 1984). The 16th century alchemist Paracelsus added to those elements sulphur, salt and mercury.

In the seventeenth century, the Irishman Robert Boyle denied both the Greek notion that the basic elements were fire, water, air and earth and Paracelsus' salt, sulphur and mercury. He developed chemical analysis - the technique for breaking down substances into their most elemental parts. He defined an element as a material that could be identified by scientific experiment and could not be broken down into still simpler substances. This is the definition that is still in use today.

The French scientist Antoine Lavoisier revolutionized chemistry by introducing accurate weighing. He determined that a given amount of matter has a total mass as measured by a weight, which remains the same when it changes in chemical combination, whether in the solid, liquid or gaseous state. The French chemist Joseph Proust's analyses showed that a particular chemical compound always contained the same elements united in the same definite proportion by weight.

Dalton's atomic theory

The English school-teacher John Dalton tested Proust's law and noted that the same elements combined in different proportions to produce different substances. In his atomic theory, all matter was made up of particles called atoms, which were alike in everything except their weight. In chemical reactions, atoms preserved their identity and are not destroyed. When Dalton published his atomic theory, he included tables of atomic weight values (Dalton 1805).

Dalton assigned weights to atoms and expressed the relations between atoms of elements in precise numerical terms. It is possible to assign relative weights by determining the ratio in which elements reacted with each other. Having assigned hydrogen as his reference atom with atomic weight one, he calculated atomic weights by comparing weights of other atoms with that of hydrogen. When two elements combine in a compound, it is insufficient to merely determine the percentage of each element in the compound. One must also determine the valence of each element in the compound. Valence is a measure of how many atoms of one element combine with an atom of the other element, *e.g.* is water HO, or H_2O, or perhaps H_2O_2? Dalton assumed that if only one compound of two elements is known, it contains one atom of each element. This led to many difficulties in the application of his atomic theory. Equivalent weights (atomic weight/valence) were quoted rather than atomic weights.

Although his calculations were wrong, the principle was correct. However, the listing of atomic weights for some elements and fractions of atomic weights for other elements was very confusing and persisted for half a century.

The English physician, William Prout (Prout 1815) noted that Dalton's atomic weight values of elementary gases were nearly exact multiples of that of hydrogen and suggested that hydrogen was the primordial matter from which all elements are formed. For a while, it appeared that a number of atomic weight values agreed with this "Law". Testing the "Law" led to a major measurement effort of atomic weight values over the remainder of the century.

The Italian physicist Amedeo Avogadro suggested (Avogadro 1811) that all gases under the same conditions of temperature and pressure contain the same number of molecules and a molecule (Greek: a small mass) may contain more than one atom. He made a distinction between the chemical atom (smallest part of matter that can enter into combination) and physical molecule (smallest particle that can exist in a free state). This could have helped to solve the equivalent weight problem but unfortunately he used the term molecule throughout his discussion with a series of qualifying adjectives; integral, constituent and elementary. In those days, the terms atom and molecule were often used interchangeably. Some scientists understood Avogadro to imply that there could be half-atoms. This confusion caused Avogadro to be ignored for half a century.

The French physicist, Joseph Gay-Lussac determined (Gay-Lussac 1809) that gases form compounds with each other in simple (numerical) volume ratios proving that Dalton's idea of combining gases by weight alone was insufficient.

Atomic weights and the periodic table

At the Karlsruhe Congress in September 3-5, 1860, about 140 of the leading European chemists met to formulate an area of agreement among chemists regarding the nature of atoms and molecules and to reach a consensus with respect to a mutually satisfactory atomic weight scale. The Italian chemist, Stanislao Cannizzaro

presented his "Sketch of a Course in Theoretical Chemistry" (Cannizzaro 1858), where he called attention to the value of Avogadro's distinction between atoms and molecules as an organizing device for the interpretation of chemical phenomena. Lother Meyer and Dimitri Mendeleev both attended this congress and subsequently developed periodic tables of the chemical elements based on revised atomic weight values. Mendeleev left open spaces, when no known element filled that space (Mendeleev 1869). He also predicted the properties of these unknown elements. When scandium, gallium and germanium were discovered over the next sixteen years and agreed with Mendeleev's predicted chemical properties and atomic weight, the periodic table was established and the usefulness of atomic weights was further enhanced.

As mentioned above, Prout's law spurred chemists to prodigious effort to measure atomic weights during the nineteenth century. Compare the Table from 100 years ago (Clarke 1896) with that of the International Commission for 1959 (the last one prepared on the oxygen = 16 scale). The elements not included in the 1895 Table were the noble gases and some rare earths, which had yet to be separated. Two thirds of the 1895 values listed agree to better than 1% and almost 40% agree to better than 0.1% with the 1959 values.

Radioactivity and atomic weights

At the end of the 1800s, many scientists felt that future progress was to be looked for in the measurement of variations in the sixth decimal place of fundamental constants such as the atomic weights. Roentgen's discovery (Roentgen 1895) of X-rays followed by Becquerel's radioactivity discovery (Becquerel 1896) quickly changed that viewpoint.

As radioactive materials were studied, many substances were being found with various atomic weight values. The English chemist, Frederick Soddy, showed (Soddy 1911) the chemical identity of mesothorium (^{228}Ra) and radium. In 1913, he concluded that there were chemical elements with different radioactive properties and different atomic weights but with the same chemical properties and therefore occupying the same position in the Periodic Table. He coined the word "isotope" (Greek: in the same place) to account for these radioactive species.

The study of the natural radioactive decay chains for thorium and uranium led to speculation that these parent isotopes, ^{232}Th and ^{238}U would decay into different daughter isotopes of lead, ^{208}Pb and ^{206}Pb, respectively. The lead from radioactive minerals should differ in atomic weight according to the proportion of uranium and thorium in the mineral. The atomic weight value for "common" lead (from a non-radioactive source material) was measured to be 207.2 (Baxter & Wilson 1908). Soddy & Hyman (1914) measured lead in a thorium silicate mineral to have an atomic weight value of 208.4. Richards & Lembert (1914) measured the atomic weight of lead in uranium minerals as low as 206.4.

Could stable lead be made up of a mixture of isotopes, each of a different whole number atomic weight? Was the overall atomic weight a fraction only because it was

an average? Radioactivity contributed to this problem in the case of lead, but what about the case of non-radioactive elements?

J J Thomson discovered the electron, which was found to be over a thousand times less massive than even the lightest atom. He then studied the rare gas neon in 1912 by sending a stream of cathode ray electrons through the neon gas. These cathode ray electrons knocked some electrons off of neon atoms, which left these neon atoms with a positive electric charge, so-called neon ions. In the combined presence of a magnet and an electric field, the neon ions move in a curved path. If all neon ions had the same mass, all would follow the same curve. If some were more massive than others, the more massive ones would curve less. Thomson detected the neon ions at the end of their path on a photographic plate. He measured the darkening of the plate and found two locations which from the amount of curvature had to be ^{20}Ne and ^{22}Ne. The intensity of darkening indicated amounts of 90% and 10%, respectively. The overall atomic weight of neon, 20.2, was the average atomic weight of these two isotopes. Thomson's instrument, the fore-runner of the "mass spectrometer", was the first one capable of separating isotopes.

The Englishman, Francis W Aston used a mass spectrograph (Aston 1929) to analyze a sample of lead showing lines on the photographic plate at masses 206, 207 and 208 with intensities of 100, 10.4 and 4.5, respectively. Aston concluded that mass 207 must be the end product of the actinium radioactive decay series and was probably derived from an isotope of uranium and it would have a mass of 235. ^{235}U was found six years later.

Lead has four isotopes, of which only ^{204}Pb is not produced from radioactive decay. The American physicist, Alfred Nier used this peak as a reference in a mass spectrometer. He showed (Nier 1938) that the relative abundances of the lead isotopes varied widely even in common lead, which had a nearly constant atomic weight value. Nier's work on lead's isotopic composition was also useful for dating purposes and the measurement of geological time (Nier 1939).

There is no longer a case of an element like lead having varying isotopic compositions but a constant atomic weight because atomic weights are now determined by isotope mass spectrometry almost exclusively (De Bièvre 1973).

The atomic weight scale

The atomic weight scale H = 1 was originally conceived used by Dalton and was used for 100 years. The Commission on Atomic Weights changed to the O = 16 scale with it's 1906 report (Holden 1984). Both hydrogen and oxygen were thought to not have isotopes. The discovery of oxygen isotopes in infrared spectra (Giauque & Johnson 1929a,b) led to a situation where the chemists scale of O = 16 differed from the physicists scale of ^{16}O = 16. When a variation was found in oxygen's atomic weight in water versus air (Dole 1935), this implied a variation in the isotopic composition of oxygen and the two scales took on a small but variable difference. In

April 1957 at a hotel bar in Amsterdam, Nier suggested (Holden 1984) that the ^{12}C = 12 scale be adopted because of carbon's use as a secondary standard in mass spectrometry. Physicists' approval was obtained, and in 1961 the atomic weights were officially given on the ^{12}C = 12 scale for the first time (Cameron & Wichers 1962).

Variations

Although the atomic weight scale difficulty had been solved, another problem began to plague the Atomic Weights Commission. Nier & Gulbransen (1939) had made measurements on carbon which showed 5% variation in the isotopic composition. The atomic weight would vary depending on the source of the material studied. Although the lead atomic weight variation could be ignored, the variation in carbon and in oxygen, mentioned earlier, made it apparent that atomic weights were not constants of nature. Variations in many light elements have since been found as well as variations due to radioactive decay in a parent affecting the isotopic composition and atomic weight of the daughter. For 30 years, restrictions on quoted atomic weight values have acknowledged these variations.

Speculations and conclusions

After the problem with lead, Richards had speculated on whether the supposed constant atomic weight magnitudes in chemistry were really variable? If so, how much effort should be expended in determining atomic weight values? One must determine the detailed variation to understand causes of the variation. Evaluations of isotopic compositions have been added to the responsibility of the Atomic Weights Commission. Examples will illustrate some of the interesting problems that are now addressed.

Reference has already been made to the use of the isotopic variations in uranium dating of geological times. There are a host of other dating methods which involve selecting a decay system with the same magnitude of half-life as the age of the material to be studied.

Boron is an element with a large probability for reacting with neutrons, so boron was used as a standard for measuring other elements. However, these measurements at different laboratories gave dissimilar results, which was traced to the use of boron samples with different atomic weights and isotopic composition at these labs. This variation now restricts the accuracy with which the atomic weight of boron can be quoted.

In 1972, uranium ore from the Oklo mine in Gabon, West Africa was shown to contain too low an amount of ^{235}U compared to normal uranium. Additional analyses indicated that the ^{235}U had been burned up in a natural fission chain reaction under the ground about 2 billion years ago. The isotopic composition of various chemical elements was not consistent with normal samples of these elements but was consistent with the yield of the various isotopes as produced in the fission process (Ruffenach et al. 1980). These variations are now made note of when reporting the standard atomic weight values.

Table I.

Comparison of 1895 & 1959 atomic weight values based on oxygen = 16.000 scale

Element	1895	1959	Element	1895	1959	Element	1895	1959
Actinium	Unknown	(227)	Glucinum	9.08	(Beryllium)	Praseodymium	143.5	140.92
Aluminum	27.11	26.98	Gold	197.24	197.0	Promethium	Artificial	(145)
Americium	Artificial	(243)	Hafnium	Unknown	178.50	Protactinium	Unknown	(231)
Antimony	120.43	121.76	Helium	Uncertain	4.003	Radium	Unknown	(226)
Argon	Uncertain	39.944	Holmium	Unlisted	164.94	Radon	Unknown	(222)
Arsenic	75.09	74.92	Hydrogen	1.008	1.0080	Rhenium	Unknown	186.22
Astatine	Unknown	(210)	Indium	113.7	114.82	Rhodium	103.01	102.91
Barium	137.43	137.36	Iodine	126.85	126.91	Rubidium	85.43	85.48
Berkelium	Artificial	(249)	Iridium	193.12	192.2	Ruthenium	101.68	101.1
Beryllium	(Glucinium)	9.013	Iron	56.02	55.85	Samarium	150.0	150.35
Bismuth	208.11	208.99	Krypton	Unknown	83.80	Scandium	44.0	44.96
Boron	10.95	10.82	Lanthanum	138.6	138.92	Selenium	79.0	78.96
Bromine	79.95	79.916	Lead	206.92	207.21	Silicon	28.40	28.09
Cadmium	111.93	112.41	Lithium	7.03	6.940	Silver	107.92	107.873
Calcium	40.08	40.08	Lutetium	Unknown	174.99	Sodium	23.05	22.991
Californium	Artificial	(251)	Magnesium	24.29	24.32	Strontium	87.61	87.63
Carbon	12.01	12.011	Manganese	54.99	54.94	Sulfur	32.07	32.066
Cerium	140.2	140.13	Mendelevium	Artificial	(256)	Tantalum	182.6	180.95
Cesium	132.89	132.91	Mercury	200.0	200.61	Technetium	Artificial	(99)
Chlorine	35.45	35.457	Molybdenum	95.98	95.95	Tellurium	127.07	127.61
Chromium	52.14	52.01	Neodymium	140.5	144.27	Terbium	160.0	158.93
Cobalt	58.93	58.94	Neon	Unknown	20.183	Thallium	204.15	204.39
Columbium	94.0	(Niobium)	Neptunium	Artificial	(237)	Thorium	232.63	(232)
Copper	63.60	63.54	Nickel	58.69	58.71	Thulium	170.7	168.94
Curium	Artificial	(247)	Niobium	(Columbium)	92.91	Tin	119.05	118.70
Dysprosium	Unlisted	162.51	Nitrogen	14.04	14.008	Titanium	48.15	47.90
Einsteinium	Artificial	(254)	Nobelium	Artificial	(254)	Tungsten	184.84	183.86
Erbium	166.3	167.27	Osmium	190.99	190.2	Uranium	239.59	238.07
Europium	Unknown	152.0	Oxygen	16.000	16.000	Vanadium	51.38	50.95
Fermium	Artificial	(253)	Palladium	106.36	106.4	Xenon	Unknown	131.30
Fluorine	19.03	19.00	Phosphorus	31.02	30.975	Ytterbium	173.0	173.04
Francium	Unknown	(223)	Platinum	194.89	195.09	Yttrium	88.95	88.91
Gadolinium	156.1	157.26	Plutonium	Artificial	(242)	Zinc	65.41	65.38
Gallium	69.0	69.72	Polonium	Unknown	(210)	Zirconium	90.6	91.22
Germanium	72.3	72.60	Potassium	39.11	39.100			

Many elements are produced which are enriched in less abundant isotopes and are used as tracers in medical diagnoses of processes in humans when use of radioactive tracers is not appropriate, *e.g.* in children and pregnant women. Note should be made that standard atomic weight values may not apply to these "doctored" elements.

Carbon has two stable isotopes, ^{12}C and ^{13}C. The study of diet uses the ^{13}C abundance variation in the two major photosynthetic pathways; C_3 plants - wheat, rice, beans and nuts, are depleted in ^{13}C relative to atmospheric CO_2 and as compared to C_4 plants, such as corn and sugar cane, which come from warm environments. Similarly, nitrogen has two stable isotopes, ^{14}N and ^{15}N. The abundance of ^{15}N is enhanced in marine plants relative to land plants. This can be used to study changes in diet, when our ancestors moved from a hunting society to one dependent on marine life and on to the cultivation of plants.

Earth and planetary science studies the isotopic anomalies (Shima 1989; Shima & Ebihara 1989) in meteorites and moon rocks to understand differences in processes of origin of the solar system $1-1.5 \cdot 10^{10}$ years ago compared to the earth some 4 or $5 \cdot 10^9$ years ago.

We have seen how the concept of atomic weights has evolved over the past two centuries. There was much interest when atomic weights were considered constants of nature and even more interest now that they are known to be variable. The demonstrated uses (de Laeter 1988, 1990; de Laeter *et al.* 1992) of the underlying fundamental isotopic compositions exceed the few examples cited and I anticipate even more extensive uses of isotopes will be found in the future.

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