CLASSIC PAPER PRESENTATION

ISOTOPES AND ATOMIC WEIGHTS

Dr F. W. Aston
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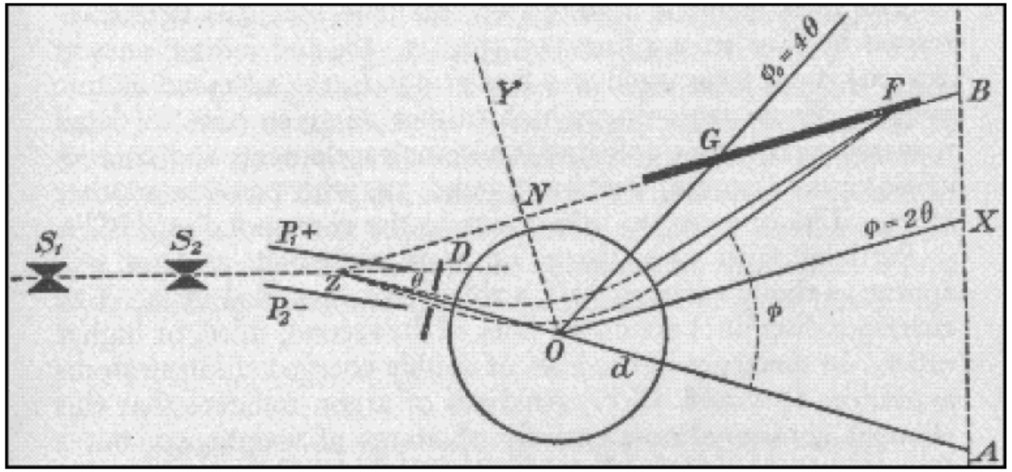
In the atomic theory put forward by John Dalton in 1801 the second postulate was: "Atoms of the same element are similar to one another and equal in weight." For more than a century this was regarded by chemists and physicists alike as an article of scientific faith. The only item among the immense quantities of knowledge acquired during that productive period which offered the faintest suggestion against its validity was the inexplicable mixture of order and disorder among the elementary atomic weights. The general state of opinion at the end of last century may be gathered from the two following quotations from Sir William Ramsay's address to the British Association at Toronto in 1897:

This idea was placed on an altogether different footing some ten years later by the work of Sir Ernest Rutherford and his colleagues on radio-active transformations. The results of these led inevitably to the conclusion that there must exist elements which have chemical properties identical for all practical purposes, but the atoms of which have different weights. This conclusion has been recently confirmed in a most convincing manner by the production in quantity of specimens of lead from radio-active and other sources, which, though perfectly pure and chemically indistinguishable, give atomic weights differing by amounts quite outside the possible experimental error. Elements differing in mass but chemically identical and therefore occupying the same position in the periodic table have been called "isotopes" by Prof. Soddy.

At about the same period as the theory of isotopes was being developed by the radio-chemists at the heavy end of the periodic table an extremely interesting discovery was made by Sir J.J. Thomson, which carried the attack into the region of the lighter and non-radio-active elements. This was that, when positive rays from gases containing the element neon were analyzed by electric and magnetic fields, results were obtained which indicated atomic weights roughly 20 and 22 respectively, the accepted atomic weight being 20.2. This naturally led to the expectation that neon might be a mixture of isotopes, but the weight 22 might possibly be due to other causes, and the method of analysis did not give sufficient accuracy to distinguish between 20 and 20.2 with certainty. Attempts were made to effect partial separation first by fractionation over charcoal cooled in liquid air, the results of which were absolutely negative, and then by diffusion, which in 1913 gave positive results, an apparent change in density of 0.7 percent between the lightest and heaviest fractions being attained after many thousands of operations. When the war interrupted the research, it might be said that several independent lines of reasoning pointed to the idea that neon was a mixture of isotopes, but that none of them could be said to carry the conviction necessary in such an important development.

By the time work was started again the isotope theory had been generally accepted so far as the radio-active elements were concerned, and a good deal of theoretical speculation had made as to its applicability to the elements generally. As separation by diffusion is at the best extremely slow and laborious, attention was again turned to positive rays in hope of in creasing the accuracy of measurements to the require degree. This was done by means of the arrangement illustrated in Fig. 1. Positive rays are sorted into an extremely thin ribbon by means

of parallel slits S_1S_2, and are then spread into an electric spectrum by means of the charged plates P_1P_2. A portion of this spectrum deflected through an angle [theta] is selected by the diaphragm D and passed between the circular poles of a powerful electromagnet O the field of which is such as to bend the rays back again through an angle [phi] more than twice as great as [theta]. The result of this is that rays having a constant mass (or more correctly constant m / e) will converge to a focus F, and that if a



photographic plate is placed at GF as indicated, a spectrum dependent on mass alone will be obtained. On account of its analogy to optical apparatus, the instrument has been called a positive-ray spectrograph and the spectrum produced a mass-spectrum.

Plate IV [N.B. not included in the document available to me - John Park] shows a number of typical mass-spectra obtained by this means. The number above the lines indicates the masses they correspond to on the scale O = 16. It will be noticed that the displacement to the right with increasing mass is roughly linear. The measurements of mass made are not absolute, but relative to lines the mass of which is known. Such lines, due to hydrogen, carbon, oxygen, and their compounds, are generally present as impurities or purposely added, for pure gases are not suitable for the smooth working of the discharge tube. The two principal groups of these reference lines are the C_1 group due to C (12), CH (13), CH_2 (14), CH_3 (15), CH_4 or O (16), and the C_2 group 24 - 30 containing the very strong line 28, C_2H_2 or CO. In spectrum i. the presence of neon is indicated by the lines 20 and 22 situated between these groups. Comparative measurements show that these lines are 20.00, 22.00 with an accuracy of one-tenth per cent., which removes the last doubt as to the isotopic nature of neon.

The next element investigated was chlorine; this is characterized by four strong lines 35, 36, 37, 38, and fainter ones at 39, 40; there is no trace of a line at 35.46, the accepted atomic weight. From reasoning which cannot be given here in detail it seems certain that chlorine is a complex element, and consists of isotopes of atomic weights 35 and 37, with possibly another at 39. The lines at 36, 38 are due to the corresponding HCl's.

Particles with two, three, or more electronic charges will appear as though having half, a third, etc., their real mass. The corresponding lines are called lines of the second, third, or higher order. In spectrum ii. the lines of doubly charged chlorine atoms appear at 17.5 and 18.5. Analyzes of argon indicate that this element consists almost entirely of atoms of weight 40, but a faint component 36 is also visible. Spectra v, vi. are taken with this gas present; the former show the interesting third order line at 13 1/2. Krypton and xenon give surprisingly complex results; the former is found to consist of no fewer than six isotopes, the latter of five (spectra viii. and ix.). Mercury is certainly a complex element probably composed of five or six isotopes, two of which have atomic weights 202 and 204; its multiply charged atoms give the imperfectly resolved groups, which are indicated in several of the spectra reproduced in Fig. 2.

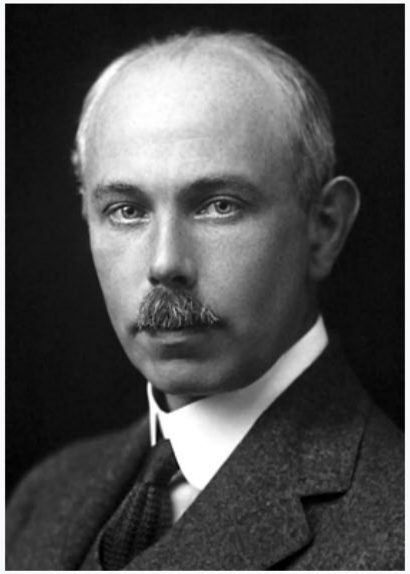
By far the most important result obtained from this work is the generalization that, with the exception of hydrogen, all the atomic weights of all elements so far measured are exactly whole numbers on the scale O = 16 to the accuracy of experiment (1 in 1000). By means of a special method (see *Phil. Mag.* May, 1920, p. 621), some results of which are given in spectrum vii., hydrogen is found to be 1.008, which agrees with the value accepted by chemist. This exception from the whole number rule is not unexpected, as on the Rutherford "nucleus" theory the hydrogen atom is the only one not containing any negative electricity in its nucleus.

The results which have so far been obtained with eighteen elements make it highly probable that the higher the atomic weight of an element, the more complex it is likely to be, and that there are more complex elements than simple. It must be noticed that, though the whole number rule asserts that a pure element must have a whole number atomic weight, there is no reason to suppose that all elements having atomic weights closely approximating to integers are therefore pure.

The very large number of different molecules possible when mixed elements combine to form compounds would appear to make their theoretical chemistry almost hopelessly complicated, but if, as seems likely, the separation of isotopes on any reasonable scale is to all intents impossible, their practical chemistry will not be affected, while the whole number rule introduces a very desirable simplification into the theoretical aspects of mass.

BACKGROUND

Francis William Aston
FRS



Aston in 1922

Born	1 September 1877 Harborne, Birmingham, England
Died	20 November 1945 (aged 68) Cambridge, England
Nationality	English
Citizenship	British
Alma mater	Mason College (as issued by University of London) Trinity College, Cambridge
Known for	Mass spectrograph Whole Number Rule Aston Dark Space[1]

Awards	Mackenzie Davidson Medal (1920) Nobel Prize for Chemistry (1922) Hughes Medal (1922) John Scott Medal (1923) Paterno Medal (1923) Royal Medal (1938) Duddell Medal and Prize (1944)
	Scientific career
Fields	Chemistry, physics
Institutions	Trinity College, Cambridge
Doctoral advisor	Percy F. Frankland[*citation needed*]
Other academic advisors	J. J. Thomson John Henry Poynting[1] William A. Tilden[1]