Isotopes

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THE subject of isotopes is particularly suitable for inclusion in this special issue of NATURE, for it is just twenty-five years since Soddy published the first valid proof of their existence. The earlier speculations of Crookes and others had been found to rest on unsound observations. Discussing apparent chemical identities among the products of radioactivity, Soddy said : "Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several of different atomic weights, or that any atomic weight is not merely a mean number". The basis of his evidence was the law connecting radioactivity and chemical change, in the discovery and enunciation of which he played so prominent a part. This law asserts that a radioactive element when it loses an α-particle goes back two places in the periodic table ; when it loses a β-particle it goes forward one place. It follows that by the loss of one α-particle followed by two β-particles, the atom, though weighing four units less, will have regained its nuclear charge and returned to its original place.

Such changes result in bodies to which Soddy applied the following words : "The same algebraic sum of the positive and negative charges in the nucleus when the arithmetical sum is different gives what I call 'isotopes' or 'isotopic elements' because they occupy the same place in the periodic table. They are chemically identical, and save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical also". Since the radioactive disintegration of uranium should result in lead of atomic weight 206, and that of thorium in lead of atomic weight 208, Soddy maintained that the lead found in uranium minerals should be lighter and that in thorium minerals heavier than ordinary lead, of atomic weight 207·2.

The idea that ordinary elements could consist of atoms of different mass received great opposition, for it appeared quite incompatible with such facts as the constancy of chemical atomic weight, the apparently perfect homogeneity of elementary gases, and the almost incredible invariability of such accurately measurable constants as the electrical conductivity of mercury independent of its source. Nor was it at first supported by the only available method of comparing the weights of individual atoms, Sir J. J. Thomson's parabola analysis of positive rays, which was then being perfected, for such elements as hydrogen, carbon, nitrogen and oxygen gave only single parabolas. Neon, on the other hand, gave two parabolas, the one expected at 20 and a second fainter one at 22. Experimental evidence indicating partial separation of the hypothetical constituents of this element by diffusion was obtained in 1913, and when the War stopped work, there were several lines of reasoning suggesting that it consisted of isotopes, but none of these was sufficiently strong to carry conviction.

During the War, Soddy's prediction concerning the atomic weights of leads from uranium and thorium minerals had been triumphantly vindicated by some of his most severe critics, the experts in chemical atomic weights, and it was realised that the most satisfactory proof of the isotopic nature of neon could be obtained by much more accurate analysis of its positive rays. An instrument using a focusing device capable of a resolution of 1 in 130 and an accuracy of 1 in 1,000 was set up in 1919 by the writer and called a 'mass-spectrograph', a term which has now been extended to all devices capable of analysing mass-rays. This instrument not only proved that neon was a mixture of atoms having weights, or mass numbers, 20 and 22, but also that chlorine consisted similarly of isotopes 35 and 37, and indeed that the majority of all elements were complex. Thus krypton, the first element shown to be multiple, had six isotopes, 78, 80, 82, 83, 84, 86. Of the greatest theoretical importance was the fact that the weights of the atoms of all the elements measured, with the exception of hydrogen, were whole numbers to the accuracy of measurement. This 'whole number rule' enabled the simple view to be taken that atoms were built of two units, protons and electrons, all the former and about half of the latter being bound together to form the nucleus.

The analysis of the elements advanced rapidly, Dempster in America discovering the isotopes of magnesium, calcium and zinc by means of an instrument of his own design having magnetic focusing. By 1925, when the first mass-spectrograph was dismantled to be replaced by a more powerful one, information on the isotopic constitution of more than half the elements had been obtained. The new instrument was designed primarily for measuring the minute variations of the masses of atoms from the whole number rule, and had a resolving power ample for the heaviest elements. By its means the search for isotopes has been carried on until a few months ago.

The difficulty of obtaining the necessary rays for analysis varies enormously from element to element. Two main devices are employed: the ordinary gas discharge which requires the element to be volatile or form suitable stable volatile compounds; and the anode ray discharge, in which the halide or other compound of the element is treated as the anode in a discharge at low pressure The inert gases are particularly suitable to the first method, the alkali metals to the second, other groups of elements being intermediate. The largest group recently investigated was that of the rare earths. These yielded to anode ray methods, and during the work some thirty new isotopes were discovered.

From the point of view of the identification of the more abundant isotopes, our knowledge is nearly complete. Of the more common elements all but four—palladium, iridium, platinum and gold—have yielded definite information on their isotopic constitution. The resistance of these four is due to their chemical properties, which make the production of their rays peculiarly difficult. In all, some 247 stable isotopes are now known, of which seven were discovered by observations on optical spectra, and have since been confirmed by the mass-spectrograph. This large assembly shows many empirical laws, of which perhaps the most remarkable is that no odd numbered element, with the possible extremely rare exception H^3, has more than two isotopes. Even elements are not so limited. The most complex element so far observed is tin, with eleven isotopes ranging in mass number from 112 to 124. One of the most astonishing results is that, for practically every natural number up to 210, a stable elementary atom is known, many are filled twice over and a few three times with 'isobares', that is, atoms of the same weight but different chemical properties. Schemes of tabulation of all the known species have led to the prediction of isotopes and to theories of nuclear structure to account for their occurrence.

Instead of the original view that the nuclei of atoms consisted of protons and electrons, it is now considered more likely that they are built of protons and neutrons. In either case the binding forces holding the particles together must represent loss of energy, that is, loss of mass. Hence it is that the atom of hydrogen has abnormally high mass, and that the accurate determinations of divergences from the whole number rule are of such profound theoretical importance. As has been stated, my second mass-spectrograph was designed for this and found capable of an accuracy in favourable cases of 1 in 10,000. The atom of oxygen, 16, was chosen as standard and the percentage divergencies called 'packing fractions', were determined for a large number of elements. These when plotted against mass number were found to fall roughly on a hyperbolic curve. Our knowledge in this field has been notably increased by the brilliant work of Bainbridge, who, by means of a powerful mass-spectrograph of original design set up at Swarthmore, discovered new isotopes of tellurium, rectified results on zinc and germanium and made many of the most accurate comparisons of mass so far known.

The relative abundance of the isotopes of an element can be measured in several ways, the most general being by photometry of mass spectra. From this and the masses of the isotopes it is easy to calculate the mean atomic weight. This with proper corrections can be used to check the chemical atomic weight. During the past six years, nearly every atomic weight has been determined by this purely physical method, which has the great advantage of being, in general, independent of purity and requiring an almost infinitesimal quantity of material.

The masses of the atoms H^1, C^{12}, N^{14} and O^{16} as determined by the second mass-spectrograph and published in 1927 agreed to 1 part in 10,000 with the accepted chemical atomic weights of these elements, but shortly after, observations on band spectra made by Giauque and Johnson showed the presence of heavier isotopes 17 and 18 in oxygen. Their abundance determined by Mecke was such that the chemical unit of atomic weight O was about 2×10^{-4} greater than the physical one, O^{16}. Carbon and nitrogen were found later to possess heavier isotopes, and Birge pointed out that to satisfy the values hydrogen must have them also. Urey took up the problem and, happily unaware of the real uncertainty in the figures concerned, with the collaboration of Brickwedde and Murphy fractionated liquid hydrogen and proved by examination of the Balmer lines that H^2 was present. Washburn showed that its heavier atoms could be concentrated by electrolysis of water. This method was developed so rapidly and brilliantly by Lewis that, soon after its discovery, pure 'heavy water' had been obtained in appreciable quantity.

The isotope of hydrogen of mass 2 cannot be treated as a normal isotope. Its exceptional difference in mass enables it to be separated with comparative ease in a pure state. It has been given the name deuterium, symbol D, and heavy water (D_2O) is now obtainable in quantity at reasonable prices, one of the most surprising and interesting reagents in the whole history of science.