SCIENCE

VOL. 82 FRIDAY, SEPTEMBER 13, 1935 No. 2124

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. MCKEEN CATTELL and published every Friday by

THE SCIENCE PRESS
New York City: Grand Central Terminal
Lancaster, Pa. Garrison, N. Y.
Annual Subscription, $6.00 Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the Association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

THE STORY OF ISOTOPES[1]

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THIS chapter in the history of science contains much to interest the philosopher and offers many illustrations of that interplay of theory and experiment by which advance takes place. Theory is the scaffolding of science, and just as in ordinary building operations, though some parts of it may only be used for a short time before removal, others may function for so long a period that they may well be mistaken for the permanent structure itself. The postulate of Dalton (1803) that atoms of the same element are equal in weight is a good example of very permanent scaffolding. For over a hundred years it was practically undisputed and on it was founded the major part of atomic chemistry.

About ten years later Prout made the more speculative suggestion that all atoms were made up of primordial particles which he thought might be atoms of hydrogen. On this view the weights of all atoms must be expressed as whole numbers, and if, as Dalton postulated, the atoms of any particular element were all equal in weight, the atomic weights and combining ratios of all elements must be whole numbers also. Chemists soon found that this was certainly not in agreement with experiment; the more results they obtained the more impossible it was to express the atomic weights of *all* the elements as whole numbers, and of the two theories Prout's was the one to be abandoned. In this decision they were perfectly justified for, as it can not be too often emphasized, it is more important for a scientific theory to be simple than for it to be true. Besides it was of little practical importance to chemists if atoms were not equal in weight so long as in all the ordinary operations of chemistry they behaved as though they were.

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[1] Address of the president of the Section of Mathematical and Physical Sciences, British Association for the Advancement of Science, Norwich, September, 1935.

Crookes, however, thought that he had found evidence that they did not so behave, and in his remarkable presidential address to Section B, at Birmingham in 1886, he says: "I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. Later, he developed this idea in connection with his pioneer work on the rare earths. He called the components "meta-elements," but unfortunately for his reputation as a prophet the experimental results on which his idea was founded were later proved to be fallacious, and Dalton's postulate was reinstated as an article of scientific faith more firmly than ever.

Its overthrow, deferred for another twenty years, was one of the many catastrophic results of the tremendous shock due to the discovery of radioactivity. In the rapid development of this, with which the school of Rutherford is so closely associated, the effects of individual atoms, as opposed to those of vast multitudes, were observed for the first time. Chemists could examine elements in the actual process of the making. In 1906 Boltwood observed that his newly discovered element ionium was so similar to thorium that if, by chance, their salts became mixed it was impossible to separate them by any chemical process. Other chemical identities among the products of radioactivity were soon observed and the most painstaking and delicate methods failed to effect or detect the slightest separation.

Discussing these, Soddy, in 1910, boldly stated: "These regularities may prove to be the beginning of some embracing generalization, which will throw light, not only on radioactive processes, but on elements in general and the Periodic Law. . . . 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 generalization underlying his views 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 alpha particle goes back two places in the periodic table; when it loses a beta particle it goes forward one place. It follows that by the loss of one alpha particle followed by two beta 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'[2] 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." It was fortunately possible to put these revolutionary views to an experimental test in the case of one element—lead, the final inactive product of the thorium and uranium transformations. Uranium of atomic weight 238 loses eight alpha particles to become lead of atomic weight 206, while thorium of mass 232 loses six to become 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 complete chemical inseparability of the heavy isotopes formed in radioactive processes passed the most stringent tests and was soon accepted. It was later put to a most ingenious and elegant use by Paneth and Hevesy, who, by adding to an inactive element a small quantity of its radioactive isotope, gave it, so to speak, an indelible label by which its movements and reactions could be followed by the almost infinitely delicate methods of radioactivity. These "radioactive indicators" have been applied to problems of chemistry, otherwise unapproachable, such as the rates of molecular diffusion in the liquid state and the movements of compounds of heavy elements in the sap of living organisms.

The application of the theory of isotopes to elements generally was another matter. 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. This reluctance of orthodox science to accept the theory was, I think, a perfectly natural and healthy reaction. Criticism very seldom destroys enthusiasm and is usually the best stimulant to further research, whereas too immediate a welcome of a new and sensational idea, the outstanding fault of the lay press in dealing with science, may lead to waste of effort. It appears to me a very regrettable thing that, of recent years, it has been repeatedly necessary for experienced research workers to waste their time on the thankless task of disproving the claims of well-

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[2] Of recent years the word ''isotope'' has changed its meaning, and is now used, for lack of another, to designate any atomic species. In the same way the meaning of the word ''mass-spectrograph'' applied by me to one special type of instrument has now been extended to any form capable of analyzing mass-rays. Such changes, though troublesome, are inevitable for the language of science is a living rather than a dead one.—F. W. A.

meaning victims of self-deception, of whom Blondlot, with his N-rays, is the classical example.

The only satisfactory criterion, a method of comparing the masses of individual atoms, was at the time in process of development. This was Sir J. J. Thomson's "parabola" method of positive ray analysis, and here at first all the results seemed to support Dalton's postulate, indeed the appearance on a sensitive screen of a clear-cut parabolic streak, caused by the impact of the atoms of hydrogen, was the first experimental proof that it was in any sense true of any element, previously it had been purely an article of scientific faith. Hydrogen, carbon, nitrogen and oxygen, present either as atoms or molecules, gave parabolas in the positions expected, and it was only when the rare gas neon was examined that an anomaly was observed. Neon, however pure, always gave two parabolas, a strong one at 20 and a weak one at 22. Referring to the latter in January, 1913, Sir J. J. Thomson said: "The origin of this line presents many points of interest; there are no known gaseous compounds of any of the recognized elements which have this molecular weight. Again, if we accept Mendeléef's Periodic Law, there is no room for a new element with this atomic weight. . . . There is, however, the possibility that we may be interpreting Mendeléef's law too rigidly, and that in the neighborhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel and cobalt."

It was my privilege to be associated with him in this work, and as his attenion was fully occupied with the investigation of a parabola of mass 3—now known to be triatomic hydrogen—it fell to my lot to search for a proof that neon was not homogeneous. This I endeavored to do by partial separation of its hypothetical constituents, using as a test its density measured by a quartz micro-balance specially designed for the purpose. The first method, that of fractional distillation from charcoal cooled with liquid air, failed, as we now know was inevitable. The second, diffusion through pipeclay, though extremely tedious, had more success and I was able to announce at the meeting of the association at Birmingham in 1913 that, after thousands of operations, a definite change of density, amounting to about 0.7 per cent., had been achieved. Further data from positive rays were obtained, and, when the war stopped work, there were several lines of reasoning indicating that neon consisted of two bodies of different mass, and that the behavior of these was exactly that predicted by Soddy for isotopes, but none of these was sufficiently strong to carry conviction on so important a conclusion.

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 when work was started again, although I continued for a time to experiment on separation by diffusion by means of an automatic apparatus, I realized that the most satisfactory proof of the existence of isotopes among the elements in general was only to be obtained by much more accurate analysis of positive rays. This was done by means of a sequence of electric and magnetic fields which gave focussed images of fine collimating slits, thus forming a spectrum dependent upon mass alone. This I called a "mass-spectrograph" (see footnote 2). It had a resolving power of about 1 in 130 and an accuracy of mass measurement of 1 in 1,000. This was ample to prove in 1919 that neon consisted, beyond doubt, of isotopes 20 and 22, and that its atomic weight 20.2 was the result of these being present in the ratio of about 9 to 1. Chlorine was found to contain 35 and 37, and bromine, of atomic weight almost exactly 80, and hence expected to be simple, gave two equally intense lines 79 and 81. Other elements were shown to be much more complex. Krypton, the first of these, had six isotopes, 78, 80, 82, 83, 84, 86; xenon and tin even more. 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 the latter being bound together to form the nucleus.

Although the interpretation of mass-spectra was often far from simple owing to the difficulty of distinguishing between lines due to compound molecules and those representing true atomic mass-numbers the analysis of the more suitable elements advanced rapidly. Dempster at Chicago discovered the isotopes of magnesium, calcium and zinc by means of an instrument of his own design with semi-circular magnetic focussing. By 1925, when I replaced my first mass-spectrograph, now in the Science Museum, South Kensington, with one of higher resolving power, information on the isotopic constitution of more than half the elements had already 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 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. Our knowledge of the mechanism of the discharge in both methods is far from complete, so that working with them is still rather an art than a science. The element of luck has played an important part in cases where the properties of the materials are unfamiliar and unfavorable to the conditions of the discharge.

The analysis of the recently discovered element rhenium offers a good example. The only available volatile compound was the heptoxide, a sample of which has been kindly provided by the discoverer Noddack. The vapor of this crystalline solid was first admitted to the discharge bulb, but without success. The solid was then introduced into the bulb itself, and, although its vaporization was so copious that a visible layer was formed on the walls, still no lines were obtained. At this stage the element was abandoned as quite hopeless and preparations were made to go on to another. Purely by chance, this happened to be gold, which it was intended to attack by means of its slightly volatile chloride. This compound gives off chlorine gas when heated, and, as previously it had been noticed that the presence of a halogen gas often stimulated the appearance of lines otherwise faint, it was considered just worth while to make one trial with it *before* the rhenium oxide deposit had been cleaned off the walls. This was successful beyond all hopes. No lines of gold were found, but the rhenium doublet appeared in great strength, giving convincing evidence that it consisted of two isotopes, 185 and 187.

The technique of anode rays is, if anything, even more capricious but, when successful, yields spectra almost free from the lines of compounds and is for this reason particularly suitable for the identification of new isotopes. This method has been recently applied to the large group of the rare earth elements yielding some thirty new isotopes.

From the point of view of the identification of the more abundant isotopes our knowledge is nearly complete. A year ago only four elements, palladium, iridium, platinum and gold, remained without mass-spectrograph data. Dempster has since developed an entirely new method of obtaining suitable rays by using a very intense spark discharge, and I have just heard from him that he has already identified five isotopes of platinum and one of gold. It seems very probable that the last two elements will have yielded before this address is delivered.

In all some 253 stable isotopes are 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 more remarkable is that no odd-numbered element, with the possible extremely rare exception of the isotope of hydrogen of mass 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.

Study of the relative abundance of isotopes in the mixture we still call, for convenience, an element is of interest from two entirely different points of view. In the first place, since it appears to be perfectly invariable in nature, not only in terrestrial but also in meteoric matter, there was a slight hope that a systematic measurement of abundance ratios might disclose some simple relations bearing on the great problem of how the nuclei of atoms were evolved. The relative abundance of isotopes can be estimated by several methods, but that of the most general application is the photometry of mass-spectra. A technique of this was worked out in 1929, and a number of elements examined, but the ratios, obtained in numbers large enough for statistical treatment, showed no groupings other than would have been expected from pure chance. These measurements have a second important practical value. If we know the masses of the isotopes of an element and their relative abundance it is easy to calculate their mean 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.

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 I have stated, my second mass-spectrograph was designed for this and found capable of an accuracy, in favorable cases, of 1 in 10,000. The atom of oxygen 16 was chosen as standard and the percentage divergences expressed in parts per 10,000, called "packing fractions," were determined for a large number of elements. These, when plotted against mass number, were found to lie roughly on a hyperbolic curve. This drops rapidly from hydrogen, passes through a minimum of about -10 in the region of iron and nickel, and then rises gradually, crossing the zero line in the region of mercury. Our knowledge in this field has been notably increased by the brilliant work of Bainbridge, who set up at Swarthmore a powerful mass-spectrograph of an original design which made use of a velocity selector and semicircular focussing. With this instrument he discovered new isotopes of tellurium, rectified results on zinc and germanium, and has made many of the most accurate comparisons of mass so far known.

Fortunately for these comparisons, and particularly so for the extension of an accurate scale of mass to the heavy elements, particles occur in the discharge which carry more than one positive charge. A particle with two charges will give a line corresponding to half its mass, one with three charges will have an apparent mass of one third, and so on. These lines are called lines of the second, third and higher orders. The complex element mercury seems specially provided by nature to help in the work. Not only do its nine isotopes provide a most valuable scale of abundance but it usually occurs in the discharge, to which its presence is advantageous from the point of view of smooth running, and it is unique in its property of forming multiply charged ions. Mercury lines up to the fifth and sixth orders can be detected so that it provides a perfect natural scale, a link between light and heavy atoms absolutely necessary to extend accurate measurements to the latter. The packing fraction of mercury, which is practically zero, was determined by means of its third order line $^{198}Hg^{+++}$.

Of the recent episodes in the story I relate certainly the most sensational is the discovery of deuterium, the heavy isotope of hydrogen. The events leading up to this and following it form a most remarkable sequence. In them the elements of nature seem to have joined in an impish, but fortunately benign, conspiracy to delude the observer and to turn his most sober researches into a sort of blind man's buff.

The first comparison of the masses, now termed "isotopic weights," of the atoms ^{1}H, ^{12}C, ^{14}N and ^{16}O to a high degree of accuracy were made with my second mass-spectrograph and published in 1927. Various methods were used which can not be given in detail here, but since the comparison of H with O could only be done through the intermediate ^{4}He, and even then the ratios measured were very large, little reliance could have been placed on the figure for H unless it could be checked in some quite independent manner. It was possible to do this by means of the close doublet $O—CH_4$, and, when measurements of this appeared to support my values for C and H, I had no reason to doubt their substantial accuracy. In this I have been justified to some extent, for the figures have stood for seven years, and a direct determination of the He,H ratio, made later by Bainbridge, agreed exactly with mine. A further support was afforded by the fact that the figures for the four elements, all then supposed to be simple, agreed within 1 or 2 parts in 10,000 with the accepted chemical atomic weights.

This satisfactory agreement was completely upset in 1929 by the startling discovery of the heavy isotopes of oxygen 17 and 18 which, present in small quantity, had naturally been overlooked on mass-spectra of that element, owing to the technical difficulty of ensuring the absence of the isobaric compound lines OH and OH_2. The discovery was made by Giauque and Johnson by observations on band spectra, which are free from this confusing disability, and the careful quantitative work of Mecke, made later, showed that, owing to the presence of these isotopes, the chemical standard of atomic weight $O=16$ was about 2 parts in 10,000 heavier than the physical one $^{16}O=16$. Examination of compounds of carbon and of nitrogen by the same method showed not only that these elements also contained heavy isotopes ^{13}C and ^{15}N but that their apparent abundance, by a most incredible coincidence, was just about enough to bring their mean weights into line with that of oxygen.

Birge pointed out that to satisfy my low estimate of ^{1}H hydrogen must also contain at least one heavy isotope. 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 ^{2}H was present. Washburn showed that its heavier atoms could be concentrated by the 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 can not 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 reagents in the history of science and certainly one which would have dismayed the founders of the C.G.S. system of units.

Now comes the interesting sequel. Deuterium and its triatomic molecule supply two links, missing before, of the three forming a closed chain of masses by which H can be directly connected with O, given a mass-spectrograph of sufficient resolving power. These links are the doublets D—H_2, at mass 2, C^{++}—D, at mass 6, and O—CH_4 at mass 16. By means of an improved collimator I have recently increased the resolving power of my mass-spectrograph to that necessary to achieve at least a partial separation of the extremely close doublet D—H_2, and to make a much more accurate estimate of the doublet O—CH_4. The latter has disclosed the disturbing fact that this is really wider than I had taken it to be and so no longer confirms the early value of C and H. Provisional work on the wide doublet C^{++}—D_3 makes it reasonably certain that my original value for H is 2 or 3 parts in 10,000 too low, as is also suggested by nuclear transformation experiments. Here we have the pretty paradox of the element discovered providing the means to remove that very discrepancy which seemed to point the way so clearly to its discovery. In view of its valuable results I am not likely to regret my mistake, however serious it turns out to be. The only moral to be drawn from this seems to be that you should make more, more and yet more measurements. Even a bad one *may* be of service, but, fortunately, it will be essential for you to make a considerable number of good ones first, or no notice will be taken of it.

In the field of isotopes, as in so many fields of physical and chemical research to-day, the objective we now aim at is the next decimal place, an elusive object which always appears to be running away from the observer, like a distant spiral nebula. The need for isotopic weights of the highest accuracy is urgent. In artificial radioactivity and transmutation we see the real beginnings of a great new subject, the nuclear chemistry of the future. Its equations can only be founded securely upon direct determinations of masses by the mass-spectrograph, and the nuclear chemist already demands these to an accuracy of 1 in 100,000. I have little doubt we shall be able to provide him with these in the course of a year or two. Armed with reliable equations, and thereby with more and more definite knowledge of nuclear construction, he will transmute and synthesize atoms as his elder brother has done molecules, with results to be wondered at and possibly even misused by his fellow creatures. I foresee a time, not immeasurably far distant, when it will be possible for us to synthesize any element whatever, wherever and whenever we please; alchemy indeed in the service of man.

THE FIFTEENTH INTERNATIONAL CONGRESS OF PHYSIOLOGY

THE CONGRESS AND RUSSIAN PHYSIOLOGY

NEARLY one thousand persons (not all physiologists!) have just returned from a visit to the Soviet Union after attending the fifteenth International Physiological Congress. Every conceivable kindness was shown and honor done to us, and we had the best possible opportunity (in the limited time available) of making ourselves acquainted with Russian physiologists and physiology. We came away filled with affection and regard for our Russian colleagues and deeply touched by their welcome; glad indeed to witness the respect with which they, as scientists, are treated in their country and to appreciate the important position which science, pure as well as applied, and particularly physiology, occupies in the economy of the Soviet Union; moved by the ardor and enthusiasm of the army of young scientific workers; looking forward with hope, not perhaps unmixed with trepidation, to the contributions which these will make to our subject in the next twenty years.

Those twenty years will be critical, and their result will depend very largely upon a factor of which, as yet, the youthful ardor of Russian science takes little obvious account. The devotion of the state to science is proclaimed, and huge resources are lavished upon scientific work. Great new laboratories and scientific establishments are being built and equipped. In a few years there will be literally thousands of enthusiastic workers in physiology and its allied sciences—there were said to be five hundred at the congress. With all this devotion, with all these resources, with all this faith in science—not only for its practical uses, but as an instrument of human culture—is it possible that anything can be missing? One wonders.

In Great Britain and America we are not unacquainted with this problem. The state, as state, may not devote so large a fraction of its resources to the encouragement of scientific work, but our traditions and our particular forms of government—imperfect as in many respects they may be—do in fact allow other and not inconsiderable resources to be so used. The Rockefeller Foundation, the Commonwealth Fund, the buildings and endowments of innumerable universities and institutions of teaching and research throughout America; the ancient and other foundations of the schools and colleges and universities in Great Britain, the endowments of the Royal Society and of various