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Theodore William Richards and the Periodic Table

James B. Conant

In the fall of 1913, a young German chemist arrived in Cambridge, Massachusetts, and was soon at work in the Wolcott Gibbs Memorial Laboratory of Harvard University. Among the Harvard graduate students in chemistry, of whom I was one, it was rumored that the newcomer, Max E. Lembert, had been sent by Kasimir Fajans of Karlsruhe, to carry out experiments under the direction of our Professor Theodore William Richards. He had brought with him, so it was said, samples of lead which Fajans believed would prove to have a different atomic weight from ordinary lead—a most extraordinary prediction.

There was no secret about the undertaking. That the enterprise was a consequence of the recently promulgated theories of Fajans and Soddy was soon made evident from what Lembert said. Indeed, before many weeks had passed, he himself expounded Fajans' views to an audience of Harvard chemists. He made clear why he was in Cambridge and what he was doing. He expected that the lead he had brought with him would prove to be identical chemically and spectroscopically with ordinary lead, but would have a significantly different atomic weight.

In 1913 I was just starting on a doctoral thesis in organic chemistry. My work bench was in Boylston Hall, across the Harvard Yard from the Wolcott Gibbs Laboratory, where Richards had provided facilities for Lembert. I do not recall ever having had the privilege of even shaking the hand of the foreign visitor. I remember Lembert's lecture, however, for a highly personal reason. One of my sisters met the young German scientist at some social occasion in Boston. In the course of the conversation Lembert mentioned that he had recently given a lecture at Harvard about his work. My sister volunteered the information that her brother was a graduate student in Cambridge, starting research in organic chemistry under the direction of E. P. Kohler. She added that of course her brother must have heard the lecture in question, and must have enjoyed it. To which Lembert replied (according to my sister's report) that, if her brother was a good organic chemist, he must have thought the lecture complete nonsense.

I recall being a bit surprised at hearing how Lembert thought his exposition of Fajans' theory would probably be received. That the hypothesis was bold and—if confirmed—revolutionary, all of us young chemists around Cambridge would have readily agreed. But we were not as skeptical as Lembert's remark to my sister seemed to imply. I think he must have reflected the attitude of some of Fajans' older colleagues in Karlsruhe, who may well have challenged the new ideas. After all, Kasimir Fajans was only 26 years old, and only a *privat dozent.*

Fajans' Hypothesis

What Lembert had to tell us was based on what Fajans had published early in the year, in *Physikalische Zeitschrift* (*1*) and in *Berichte* of the German Chemical Society (*2*). He had put forward a comprehensive scheme for placing the members of three different radioactive disintegration series in the periodic table. The relation of one member to the preceding one, according to the radioactive displacement law, depended on whether the transformation connecting them was accompanied by the emission of an alpha particle or a beta ray. The end product of each series was assumed to be identical with lead chemically, but to have an atomic weight different from that of ordinary lead. Fajans, in a footnote to the paper published in the *Physikalische Zeitschrift*, had stated that the assumption was to be tested by determination of the atomic weight of "lead and bismuth samples which will be obtained from uranium minerals free of thorium and thorium minerals free of uranium." If he was correct, the atomic weight of lead from radioactive minerals would be significantly different from that of ordinary lead.

Soddy's Monograph

Early in 1914 a small monograph by Frederik Soddy of Glasgow appeared on the library shelves—*Chemistry of the Radio-elements*: Part II, *The Radio-elements and the Periodic Law* (*3*). I remember the volume well. In it was set forth with great clarity the relation of one radioacitve element to another in a series of spontaneous transformations starting with uranium; in a second series, starting with thorium; and in a third, starting with actinium.

A new word was introduced into the vocabulary of the chemist. "It will be of great convenience," wrote Soddy in his monograph, "if some new word is employed to express this newly revealed complexity of matter. The words 'iso-

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The author is president emeritus of Harvard University. This article is adapted from an address delivered 29 December 1969 at the Boston meeting of the AAAS.

tope' and 'isotopic' suggest themselves. Henceforward a group of two or more elements occupying the same place in the Periodic Table and being in consequence chemically non-separable and identical, will be referred to as a group of isotopes and within the group, the separate members will be referred to as isotopic."

Soddy went on to explain that "it may not even be the general rule that only one isotope is stable." (Fajans had expressed the same idea in his paper.) The possibility that any one of the elements might be a mixture of isotopes was envisioned. Soddy raised the question whether or not common lead was a mixture of the final nonradioactive products of three disintegration series.

The question in Soddy's monograph, which we read in the first months of 1914, was being answered, we knew, by Lembert. His work was common knowledge in the Harvard laboratories in the winter of 1913–1914. And I think we younger men fully expected that his determination would show that lead from radioactive minerals had an atomic weight not far from 206.07, as Fajans' hypothesis predicted. (The atomic weight of common lead is 207.19.)

Some of our professors were more cautious in their reaction to the new ideas. Indeed, the reluctance of the older chemists to embrace without reserve the "new chemistry" may have been the very reason why we who were young were so certain that Fajans and Soddy were right. I remember well that, when we gossiped among ourselves about the senior members of the staff of the chemistry department, we were likely to characterize our elders as hopelessly conservative.

A Revolutionary Discovery

I have no recollection of how the news spread among Lembert's acquaintances that he had, indeed, made the predicted, but nonetheless revolutionary, discovery. I think it must have been that we were all so convinced that Fajans and Soddy were right that there was no surprise when we heard of Lembert's findings, which were to be the basis for the paper by Richards and Lembert in the *Journal of the American Chemical Society* (*4*) (received by the editors on 16 May 1914) and a brief note in *Science* of 5 June 1914 (*5*). Five samples of lead from radioactive minerals were found to have atomic weights considerably below the accepted value for common lead (207.19). Fajans reported Lembert's results to a meeting of the Bunsen Society in Leipzig on 21 May 1914. After Lembert's presentation, Otto Hönigschmid of Prague spoke of his own atomic weight determinations with different samples of lead. The conclusion was the same. It is interesting to note that Hönigschmid had been at Harvard a few years before to learn Richards' methods. Therefore, a biographer of Richards' could claim that it was by the application of his procedures, by either Lembert or Hönigschmid, that chemical evidence of the existence of isotopes was first obtained. As Sir Harold Hartley pointed out in his Theodore William Richards Memorial Lecture (*6*), the difference between the atomic weight of ordinary lead and of lead from radioactive minerals was the only conclusive evidence in support of the theory of isotopes prior to Aston's work in 1919.

Cautious Interpretation

As joint authors, Richards and Lembert reported as would the most conservative investigator. They considered all the possibilities they could think of which would explain what were labeled "amazing" results. These possibilities included the following: there might be an unknown substance mixed with ordinary lead which produces the lower atomic weight yet has the same spectrum as lead itself; or else this unknown substance gives no lines whatever in the ultraviolet range; or else the presence of a large bulk of lead hides or obscures the spectrum of the foreign admixture; or else ordinary lead is a similar mixture in somewhat different proportion. Now comes the reserved judgment of a cautious investigator. "It is perhaps premature," write the authors, "to decide between the alternatives but all are of interest, the first and last, of course, being the most revolutionary."

Richards' attitude remained cautious. In his Phi Beta Kappa address at Harvard on 19 June 1916, in reporting on his atomic weight investigations (which had covered many years), he stressed the amazing constancy of the atomic weight of the elements irrespective of their source. And the sentence introducing the results obtained by himself and Lembert hardly does justice to the revolutionary nature of the findings. The report, probably the first to a general audience, of the determination of the atomic weight of lead from radioactive ores was as follows.

> Although thus we know only one kind of copper and iron and silver, evidence has recently been discovered which points toward the existence of at least two kinds of metallic lead. Every sample of ordinary lead always has exactly the same atomic weight as every other sample; but lead from radioactive minerals—lead which seems to have come from the decomposition of radium—has neither the same atomic weight nor the same density as ordinary lead, although in many properties, including their spectra, they seem to be identical. This recent conclusion, reached only two years ago at Harvard, has been confirmed in other laboratories, and it now seems to be beyond question. Whatever may be the ultimate interpretation of the anomaly, the solution of this cosmic conundrum must surely give us a new idea of the essential nature of matter.

This use of the word *anomaly* seems a bit odd, yet Richards, in his presidential address before the Christmas meeting of the American Association for the Advancement of Science, as late as 1918 was still speaking of the "interesting speculations by Drs. Russell, Fleck, Soddy and Fajans and others." These speculations are characterized as having "interpreted in extremely ingenious and plausible fashion the several steps of the changes [in the disintegration series] and [provided] the reasons why the end products of the decomposition both of uranium and thorium should be very similar to lead if not identical to it."

An explanation of Richards' cautious interpretation of Lembert's results is to be found, I think, in his persistent doubts about the reality of the alleged *spontaneous* disintegration of an element. I recall Richards telling me in either 1921 or 1922 that he was far from convinced that any element ever spontaneously distintegrated. What was observed might be due to the action of some sort of all-pervading radiation. He remarked that no one had tried drastic shielding—say, in an underground vault —of a radioactive element. I had the feeling then that what I was hearing was the expression of the last stand of a retreating skeptic. He gave no indication that he himself would try any experiment with radioactive material. This was not strange, as he and his students had never immersed themselves in a knowledge of the techniques used in studying radioactivity.

The question arises, why did Richards ever become involved in the study of the atomic weight of lead of radioactive origin? The answer is given in a footnote on page 1330 of the Richards-Lembert paper (*4*). It reads in part as follows.

> Mr. Max E. Lembert Dipl. Ing. a pupil of Dr. Fajans was sent by him and the Technische Hochschule of Karlsruhe with the support of Professor Bredig to Harvard especially for this purpose. Sir William Ramsay, also, at about the same time had urged on behalf of Dr. Soddy that the atomic weight of radioactive lead should be studied in the Wolcott Gibbs Memorial Laboratory. It is needless to say that the opportunity was welcomed; indeed, the matter would have been taken up here before except for fear of trespassing upon a field which might properly be considered as belonging to the proposers of the theory.

If one asks further why Bredig, Fajans, Sir William Ramsay, and Soddy all turned to Richards, the answer is that he was the acknowledged international authority on atomic weight determinations. Indeed, he had occupied that position since the turn of the century. Some might be inclined to say that Richards' contribution to the development of the periodic table lay not in his part in the story of determining the atomic weight of lead from radioactive sources but in his long series of publications dealing with atomic weights [see (*6*)]. Therefore, it is appropriate that I conclude my remarks by presenting Richards' own summary of his study of atomic weights.

Richards' Summary of His Study

I am able to quote from an unpublished manuscript because of the happy circumstance that I married Richards' daughter. Written in the third person about 1914, the document starts as follows.

> The scientific work of Theodore W. Richards may be divided for convenience into five categories more or less closely interrelated. The first of these categories includes the study of atomic weights, the second, the investigation of various problems concerning chemical equilibrium, the third, original work upon chemical thermodynamics both practical and theoretical, the fourth, the study of various problems in electrochemistry, and the fifth both practical and theoretical work concerning the significance of atomic compressibility and the changes exhibited by atomic volumes under varying conditions.

Since we are concerned here with the periodic table, I shall present only the first section of Richards' own account of his life work.

> During the past twenty-six years Richards has been directly concerned in the study of the atomic weights of twenty elements, and some of his pupils at Harvard have independently studied ten more. Thus far no one has been able to show that any one of the investigations concerning these thirty elements is seriously in error, and the results of all have been accepted as the best heretofore published by the International Committee on Atomic Weights, which has no Harvard representative upon it. The elements investigated under the immediate direction of Richards or with his own hands are as follows: oxygen, copper, barium, strontium, zinc, magnesium, nickel, cobalt, iron, uranium, calcium, caesium, chlorine, bromine, silver, sodium, potassium, nitrogen, sulphur, and lithium.
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> The determination of the ratio of oxygen to hydrogen was taken up in collaboration with J. P. Cooke in 1886. They weighed hydrogen directly in large glass globes, and after having burnt it with copper oxide, determined the weight of water. The outcome gave a result for hydrogen [see (*7*)] only 0.0004 different from the value 1.0078 now generally accepted. This was the first direct determination showing that the ratio of hydrogen to oxygen is distinctly less than 1 is to 16, and the error in the result was one-half as large as the error that was previously considered as the best.
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> The behavior of copper oxide led Richards to suspect that the atomic weight of copper accepted at that time was in error, and accordingly he commenced an investigation of this element which lasted four years. He discovered that oxides of metals prepared from the nitrate always contain included gases, a circumstance which he found to vitiate the earlier work not only upon the atomic weight of copper but also those of a number of other elements. He showed also that the copper sulphate had much greater tendency to retain water than had been attributed to it, and by means of a number of new methods obtained a series of consistent results for the atomic weight of copper. The relation of copper to silver, of copper to bromine, and of copper to sulphuric acid were all determined with care, and all yielded essentially the same new value, thus leaving no doubt that the old value for copper was nearly one-half a percent too low.
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> The anomalous behavior of barium sulphate led Richards then to study the atomic weight of barium; both barium chloride and barium bromide were analyzed taking care to drive off all the water without decomposing the salts. Much time was spent upon the preparation of pure silver and every step of the analysis was tested taking great heed especially of the solubility of silver chloride. The result showed that barium was previously almost as unexact as copper. In this case as in the other not only were new results obtained but also the reasons for the deviations in the old ones were made clear.
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> Strontium, magnesium, zinc, nickel, cobalt, iron, uranium, and caesium were then taken up in succession, being studied by somewhat similar methods with the help of the experience gained in the earlier researches. In some of these Richards had the assistance of pupils. He was able to show that the old results on zinc and magnesium were in error because of the retention of gases on the oxides, and that most of the other values also had been vitiated by chemical imperfections in the methods employed. Richards not only employed and revised the old methods but devised new ones in the course of this work.
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> The investigation upon caesium marked the end of the first period of his investigations concerning atomic weights—the time during which the work of Stas had been considered impeccable. In 1904 the investigation of a large number of specimens of sodium bromide while verifying Stas's atomic weight for bromine seemed to indicate that his value for sodium was distinctly too high. Because the sodium bromide underwent transition from the dihydrate to the anhydrous salt at a perfectly definite point, it was evidently very pure. Hence its verdict could not be ignored and a new study of the atomic weight of sodium was undertaken. This investigation began a new period in Richards's work in which he was able to show the errors into which Stas had unwittingly fallen. He proved without question that not only was Stas's value for sodium too high but his value for chlorine was too low, and both of these conclusions have been verified by the subsequent work of others. Because Richards had previously chiefly used bromides, this discovery of the error in chlorine was not made during his earlier researches.
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> The discovery of error in two of Stas's most accurately determined results led to the natural suspicion that others also might need revision. Accordingly three determinations of potassium, of sulphur, and of nitrogen were undertaken with the help of able assistants, the last of the three investigations being conducted partly at the University of Berlin during the term of his exchange professorship there. Potassium chloride and bromide were both analyzed with all the care used in the case of sodium. Sulphur was approached by a new method involving the conversion of silver sulphate into the chloride, and nitrogen was attacked both by the synthesis of silver nitrate and by the analysis of ammonium chloride. The work on silver nitrate was in some ways the most convincing of all, because in this case it was possible to prove that the salt was essentially free from water, by decomposing it and passing the products of decomposition, suitably treated, through a phosphorus pentoxide tube. No more concordant results have ever been secured in the Harvard Laboratory than the six successive experiments by which the silver was converted into silver nitrate

—the extreme variation between the results being less than one-thousandth of a percent. If any error existed in them, it was an error of amazing constancy.

The most recent finished problem with which he has been concerned was a study of the atomic weights of lithium, and silver. Not only was the ratio of lithium chloride to silver determined but also its ratio to silver chloride and besides this by a new method the amount of lithium chloride contained in lithium perchlorate was carefully determined. The ratio of silver to oxygen was thus directly obtained by this equation.

$$\frac{Ag}{LiCl} \times \frac{LiCl}{LiClO_4 - LiCl} = \frac{Ag}{O_4}$$

This was entirely a new procedure and for many reasons seems to give one of the very best means of determining the atomic weight of silver. Incidentally the atomic weight of lithium was found to be almost a whole percent less than that obtained by Stas. This seems to have been Stas's most grievous error, and came to pass only because all the defects in his process accumulated on the head of this lightest of all the metals.

Richards has himself said that "the secret of success in the study of atomic weights lies in carefully choosing the particular substances and processes employed, and in checking every operation by parallel experiments so that every unknown chemical and physical error will gradually be ferreted out of its hiding place. The most important causes of inaccuracy are: the solubility of precipitates and of the material of containing vessels; the occlusion of foreign substances by solids, and especially the presence of retained moisture in almost everything. Each of these disturbing circumstances varies with each individual case. Far more depends upon the intelligent choice of the conditions of experiment than upon the mere mechanical execution of the operations, although that too is important." In carrying out these suggestions he has brought into play all the powerful aid furnished by the new science of physical chemistry which has thrown so much light upon the mechanism of the establishment of chemical equilibrium. He has always heeded the advice given in the paragraph above, especially the series of errors caused by the unsuspected presence of water in the salts to be weighed. With this in mind there was evolved in the course of this work a remarkably simple device for driving off every trace of water from any salt, and then enclosing this salt in a bottle without exposure for an instant to the outside air so that it could be weighed without risk of attracting moisture. This device greatly helped his work as did also the nephelometer, an instrument for detecting minute traces of suspended precipitate by means of the light reflected by them. Both of these instruments were original with him. He has always pointed out very emphatically that the chemical difficulties in work of this kind greatly exceed the physical ones. The operation of weighing is far more easily controlled than the solubility of precipitates and the retention of foreign substances in the material to be weighed. For this reason he has preferred to use rather small quantities of material and to prepare these in a state of undoubted purity. As he has pointed out, there is no object in weighing 100 grams of material even to within 5 milligrams, if it contains as much as 0.01 percent of impurity. A much better result can be obtained by weighing 10 grams to within 0.1 of a milligram, provided that the material itself contains no more than 0.001 percent of impurity.

A few additions to Richards' own account of his atomic weight determinations may be in order. They concern the early age at which he started his scientific career. He prepared for college at home under his mother's guidance and entered the sophomore class at Haverford College at the age of 14. There he studied chemistry under Lyman B. Hall, graduating in 1885. He then entered Harvard College as a senior, receiving the A.B. degree summa cum laude in 1886. His investigation of the atomic weight of oxygen with Josiah Parsons Cooke provided material for his thesis for the Ph.D. degree, which he received 2 years later. A year's study in Europe was followed by a teaching appointment in the chemistry department at Harvard.

Richards' Contribution

From 1890 on, a flow of papers recorded Richards' successful attacks on the atomic weights, first, of copper and then of one element after another. Before 1895, when he was 27, he was the sole author of more than ten papers. By the time he was 33, he and his students had revised the atomic weights of nine elements. As a young man he must have been a prodigious worker, with a confidence in himself as an investigator which enabled him to use his energies effectively. He early demonstrated that he knew what it meant for a chemist to take infinite pains. He set a standard for accuracy which may be counted his permanent contribution to the development of early 20th-century science. The award of the Nobel prize in chemistry for the year 1913 was a recognition of the significance of the totality of his labors. Of these, a major part was his contribution to the building of the definitive periodic table of the elements.

References and Notes

1. K. Fajans, *Phys. Z.* **14**, 136 (1913).
2. ———, *Ber. Deut. Chem. Ges.* **46**, 422 (1913).
3. F. Soddy, *Chemistry of the Radio-elements*: Part II, *The Radio-elements and the Periodic Law* (Longmans Green, London, 1914).
4. T. W. Richards and M. E. Lembert, *J. Amer. Chem. Soc.* **36**, 1329 (1914).
5. "The atomic weight of lead of radioactive origin," *Science* **39**, 831 (1914).
6. H. Hartley, *J. Chem. Soc.* **1930**, 1937 (1930).
7. The value was 1.0082.
8. I am greatly indebted to Professor Fajans for calling my attention to the article by Oswald V. Anders on "The place of isotopes in the periodic table" [*J. Chem. Educ.* **41**, 522 (1964)] and for his kindness in providing information to answer a number of questions about the years 1913 and 1914.