History of Science

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Theodore William Richards: Apostle of Atomic Weights and Nobel Prize Winner in 1914

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The atomic weights ... are certainly concerned in determining the composition of every compound substance in the heavens above, on the earth beneath, or in the waters under the earth. Every protein in each muscle of our body, every drop of liquid in the ocean, every stone on the mountain top bears within itself the stamp of the influence of this profoundly significant and impressive series of numbers.

T. W. Richards[1]

Figure 1. Postage stamps honoring devotees of atomic weights (pictures taken from the Internet): Dalton (top left), Avogadro (top right), Mendeleev (bottom left), and Richards (bottom right). Curiously, the building depicted on the 1974 stamp commemorating the 1914 Nobel Prize for Richards is the Widener Library (opened in 1915), not the Gibbs Laboratory built in 1912 for Richards.

1. Atomic Weights

Early in the 19th century, John Dalton (1776–1844) compiled the first table of relative atomic weights. He had adopted the ancient notion that matter is comprised of atoms: indivisible, tiny, and myriad. From atomic weights, combined with density data, Dalton aimed to determine both the relative masses and sizes of atoms.[2] The previous century had provided two major legacies for quantitative chemistry: conservation of matter in reactions and the concept of definite proportions of elements in chemical compounds, both neatly explained by the atomic theory. However, to derive relative atomic weights solely by chemical analysis required knowledge of the correct formulas of the compounds compared. That gave rise to a half-century of confusion and controversy.[3] Ironically, chemists had rejected or ignored an approach presented in 1811 by an Italian physicist, Amedeo Avogadro (1776–1856). He applied a hypothesis, consistent with the atomic theory, that under similar conditions, equal volumes of all gases contain equal numbers of molecules. Thereby, he determined from experimental data on gas reactions the molecular weights of gases and thus obtained their molecular formulas.[4] Belated appreciation of Avogadro's work, fostered by a Congress held in Karlsruhe, Germany, in 1860, proved important in attaining a consistent basis for atomic weights. Beyond their practical utility, atomic weights soon after took a leading role in the discovery of the periodic table of elements by Dmitri Mendeleev (1834–1907) and Julius Lothar Meyer (1830–1895) around 1869.

Figure 2. Richards in his laboratory, about 1905 (from Schlesinger Library, Radcliffe Institute, Harvard University).

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Theodore William Richards (1868–1928) was born about one year before the periodic table emerged (Figure 1).[5–9] By then, reliable atomic weights of modest accuracy had been obtained for around 60 elements. Richards (Figure 2) was destined to redetermine the atomic weights for about 25 of those elements and train others who redid most of the rest. His meticulous techniques resulted in "a degree of accuracy never before attained", as emphasized in the presentation statement for the 1914 Nobel Prize in Chemistry.[10] Not mentioned in that statement was the most dramatic episode of Richards' career. In 1913–1914, he supervised work by Max Lembert (1891–1925), a visiting German postdoctoral fellow, sent to Richards expressly to determine whether the atomic weight of ordinary lead differed markedly from that of lead from radioactive minerals.[11] The difference indeed proved to be large, about a whole mass unit. That provided compelling evidence for the theory of isotopes boldly proposed by Frederick Soddy (1877–1956), a young physicist, and by Kasimir Fajans (1887–1975), the even younger mentor of Lembert.

Nobel celebrations were suspended during the World War, and Richards did not deliver a manuscript for his acceptance lecture until December, 1919.[12] His closing paragraphs emphasized the "great theoretical interest" of the existence of isotopes, which "give us … new ideas as to the ultimate nature of the elements … [and] perhaps the most certain clue as to their origin and history". In November 1919, Frances Aston (1877–1945) had resolved and measured the weights of isotopes of neon by means of mass spectrometry, a method superior to chemical analysis in scope and accuracy. During the next few years, Aston measured over 200 isotopes.[13] Atomic weights, for most of the elements, thus were seen to be averages over several isotopes. That meant the atomic weights were less fundamental than previously thought. Yet they acquired a new significance, as Richards noted. He had found for several elements that the atomic weights did not differ for samples from different sources, such as iron from terrestrial ores and from meteors. That indicated the constancy of the isotopic proportions, a basic fact later widely confirmed, of abiding importance for theories of the origin of the elements.

This essay follows Richards from his precocious youth to becoming a celebrated chemist. It is a remarkable, largely idyllic story. All the more striking are some unhappy episodes. Visiting those is consistent with Richards' dedication in striving to foresee likely sources of error and how to avoid them.

2. Precocious Youth

Theodore was a precocious youngster, fortunate to have extraordinary parents who shaped his character and fostered his career.[7,8] Born on 31 January 1868 in Germantown, a suburb of Philadelphia, Pennsylvania, Theodore was the third son and fifth child of William Trost Richards and Anna Matlack Richards. Although largely self-taught as an artist, William Richards had prospered as a marine and landscape painter. Anna Matlack was a poet, from a Quaker family that "looked askance" when she had dared to marry an artist. Anna, dissatisfied with the local schools that had been attended by her older children, decided to teach her younger children herself. So Theodore never went to school until he was ready to go to college. His home education was intense and included drawing and music. It was further enhanced when in 1878 the family went to Europe for two years, chiefly residing in England. There his Christmas present in 1880 was a large box containing chemicals and an apparatus for 200 experiments. His interest in chemistry blossomed so quickly that on returning to Philadelphia the next year, he was allowed to attend chemical lectures and given special instruction in qualitative analysis at the University of Pennsylvania. He also printed on a hand-press a collection of his mother's sonnets, which he sold as a booklet, using the proceeds to fit up a small laboratory at home. At the early age of 14, he entered Haverford College, not as a freshman, but as a sophomore. He graduated with a Bachelor of Science in 1885, at the head of his class.

At Haverford, Theodore had decided to become a chemist. He had also been strongly attracted by astronomy, but felt his eyesight was too defective for an astronomer. Years earlier, during summer sojourns at Newport, Rhode Island, the Richards family had come to know Josiah Cooke (1827–1894), Professor of Chemistry at Harvard. Cooke advised that Theodore come to Harvard College, entering as a senior specializing in chemistry. That required that Theodore pass an entrance examination in Greek. His mother promptly learned Greek and, in six weeks during the summer, taught it to her son. Thus, in 1886 Theodore received a second Bachelor's degree, summa cum laude, with highest honors in Chemistry from Harvard.

He went on to graduate studies, undertaking research with Cooke to redetermine the ratio of the atomic weights of oxygen and hydrogen. The motivation stemmed from a hypothesis proposed in 1815 by William Prout (1785–1850): that the atomic weights of the elements should be integral multiples of the atomic weight of hydrogen. Cooke wanted to see whether the ratio was actually 16 to 1. The project involved reacting hydrogen gas with copper oxide to form water, and required very careful quantitative analysis. The O/H ratio obtained by Richards was 15.869 ± 0.0017, well below the Prout hypothesis.[14] With this work as his doctoral thesis, Richards received his Ph.D. in 1888, at the age of 20.

3. Consummate Chemist

Richards was rewarded with a fellowship to study in Europe for a year. In the winter semester, he worked at Göttingen, doing analytical experiments; in the spring and summer, he made peripatetic visits to most of the important laboratories in Germany, Switzerland, France, and England. Richards then returned to Harvard, becoming an instructor and later assistant professor, teaching analytical chemistry (Figure 3). He resumed research on atomic weights, *not merely because I felt more competent in that direction … but also because atomic weights seemed to be one of the primal mysteries … silent witnesses of the very beginning of the*

Figure 3. Students from Chemistry 4, the analytical chemistry course taught by Richards (standing in the middle of the back row), in 1892 (from Harvard University Archives: HUP (21b) in Richards file).

universe, and the half-hidden, half-disclosed symmetry of the periodic system of the elements.[7] As he later described in his Nobel Lecture, his success in attaining exceptional accuracy came from careful planning in advance as well as painstaking execution. A key step was the choice of the compound or reaction to study, with close attention to possible impurities and side reactions. Also important were checking every operation by parallel experiments and techniques he developed to avoid occlusions and residual moisture.

In 1895, Cooke died and Harvard asked Richards to undertake teaching physical chemistry. He was sent off to Europe again to study this new field with great German chemists: Wilhelm Ostwald (1853–1932) at Leipzig and Walther Nernst (1864–1941) at Göttingen. On his return, Richards launched a wide-ranging course of lectures that he taught for the rest of his career: *Elementary Theoretical and Physical Chemistry*. His research was likewise intense and enterprising. While still centered on atomic weights, its scope soon grew to include electrochemistry, thermodynamics, and compressibility of chemical compounds. In 1901, his colleagues and likely Richards himself were amazed when he was offered a chair at Göttingen as a full professor (Figure 4). In that era, it was a tremendous, unprecedented honor for a young American assistant professor. Yet Richards opted to continue at Harvard. President C. W. Eliot (1834–1926) made him a full professor, and also pledged, if and when funds could be raised, to construct a new research laboratory for Richards. That promise was finally fulfilled in 1912, when the Wolcott Gibbs Memorial Laboratory was built. Among a host of other honors[7–9] awarded to Richards, in 1925 an endowed professorship at Harvard was named for him.

Beyond atomic weights, Richards studied a wide variety of properties. He made a major contribution by inventing the adiabatic calorimeter, in which the flow of heat to or from the outside was greatly reduced by surrounding the calorimeter by a jacket whose temperature was kept equal to the internal temperature. With his students, he published 60 papers on

Figure 4. Richards in about 1900, then 32 years old (from Harvard University Archives: HUP (21b) in Richards file).

precise measurements of heats of reactions and heat capacities of many substances. Particularly important were the data obtained on heats of neutralization of various pairs of strong acids and bases.

In electrochemistry, another important series of papers tested the generality and exactness of the laws of electrolysis discovered by Michael Faraday (1791–1867). The amount of material deposited was found to be proportional to the electric current and the equivalent weight of the material, to high accuracy over a wide range of temperatures, solvents, and materials, including molten salts. Richards also conducted a long series of measurements of the EMF of electrochemical cells, useful for extracting thermodynamic Gibbs energy data. Again, he devised means that much improved accuracy. His first graduate student to work on electrochemical cells was Gilbert Newton Lewis (1875–1946). After a postdoctoral year with Ostwald at Leipzig, Lewis became a faculty member at Harvard and at MIT, then in 1912 moved to Berkeley where he built a great center of physical chemistry.[15]

From about 1901 on, Richards was enamoured of a simplistic theory of compressible atoms with which he sought to correlate many phenomena. He undertook many experiments suggested by the theory and developed new apparatus for measuring compressibilities of the elements and their compounds, in solid or liquid states. Happily, he found that compressibility was a periodic function of the atomic weight of the elements, closely related to their atomic volume (Figure 5). Richards overreached, however. He asserted that his theory gave "entirely new insights" into properties ranging from ductility, surface tension, and the critical point, to several "peculiar relations of material and light", and

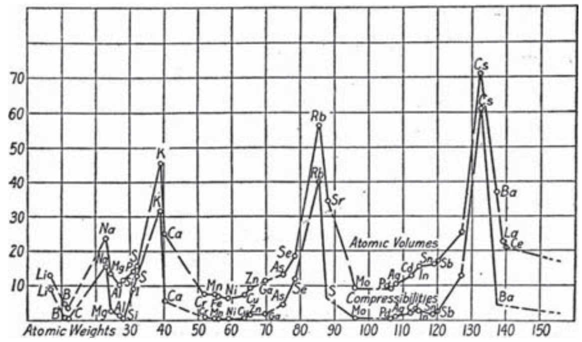

Figure 5. Plot of atomic compressibilities and volumes versus atomic weights (from Ref. [7]).

chemical bonding. Confronted by too many variables, his efforts to cast the theory in mathematical form failed.[16]

When promoted to full professor of physical chemistry, Richards gave up teaching analytical chemistry, but took on giving a full course of lectures for undergraduates. As a privilege, he asked to continue teaching in addition the more theoretical and historical half-course that he had initiated, taken mostly by graduate students. For him, eager pursuit of research did not conflict with teaching tasks, which "he thoroughly enjoyed because he did them well".[8] After the call to Göttingen, he was nominally exempted at Harvard from administrative duties, which he did not relish. Nonetheless, from 1903 to 1911 he served as Chairman of the Division of Chemistry, with "conscientious attention to detail and far vision for the future".[6] Richards never availed himself of the privilege of taking a half-year sabbatical at full salary. During term time, he wanted to maintain contact with his graduate students, whose experiments he followed almost daily.

4. Contrasting Perspectives

What follows is adorned with quotes from Richards and his close colleagues. These offer more vivid and genuine perspectives on his life and career than can be conveyed by paraphrasing. His character and personality was much admired. Richards described his guiding principles as "kindliness and common sense". Colleagues praised him as having "many lovable qualities: his perfect modesty and simplicity, his courtesy, his unselfishness, his good company and humor".[7] Also hailed was his "extraordinary experimental skill, ingenuity, critical judgment, and his unsurpassed standards of scientific integrity".[1] A creed stated by Richards was often quoted: *First and foremost, I should emphasize the overwhelming importance of perfect sincerity and truth: one must purge oneself of the very human tendency to look only at the favorable aspects of his work … Each step should be questioned … then, patience, patience, patience! Only by persistent, unremitting labor can a lasting outcome be reached.*[1,6,7]

Richards was also deeply devoted to his family. In 1896, he married Miriam Stuart Thayer, daughter of a professor at the Harvard Divinity School. Her "appreciation for his work was extraordinarily sympathetic". Thanks to the generosity of his father, Richards was able to build a house not far from the Harvard College yard. The couple had three children: their daughter Grace Thayer became the wife of James Bryant Conant (1893–1978), professor of chemistry and later President of Harvard, their son William Theodore became a chemistry professor at Princeton, and their son Greenough became an architect. As respite from arduous science, summer months were reserved for long family vacations, often at Mt. Desert Island in Maine. Although the health of both Richards and his wife was somewhat precarious, they enjoyed outdoor sports. For years, part of the summer was spent on their cruising yawl. Richards was a good tennis player in his younger years, then became "one of the earlier devotees of golf in America [which] he never gave up".[6]

Likewise noted was Richard's close attention to his research students during the academic terms. He was said "invariably" to bring *encouragement and inspiration, either through his enthusiasm or by crucial suggestions … and rouse the students to new levels of carefulness and thoroughness.*[6] Another perspective was expressed by Richards; in a letter written in 1916, he said: *In my experience, assistants who are not carefully superintended may be worse than none … The less brilliant ones often fail to understand the force of one's suggestions, and the more brilliant ones often strike out on blind paths of their own if not carefully watched.*[16]

That attitude led to conflicts with Gilbert Lewis, his most brilliant student. During his postdoctoral year in Germany, Lewis sent Richards a draft paper presenting his concept of fugacity. He was dismayed when Richards responded, proposing an addition, supplied by him, saying that Lewis had adopted Richards' idea of *outward tendency*, derived from the atomic compressibility theory. That put Lewis in a difficult position, both because he would be returning to Harvard and because fugacity had nothing to do with *outward tendency*. He answered by making clear that fugacity was his idea, but added a diplomatic footnote rather than Richards' suggestion. Richards accepted that, but Lewis remained resentful.[15] When soon after, he was assisting Richards with the physical chemistry course, Lewis had begun developing his ideas about atoms and chemical bonds arrayed with electron pairs. He got no encouragement from Richards, who disparaged such talk as "Twaddle … a very crude method of representing certain known facts".[16] Richards had long cautioned that the atomic theory of Dalton and the molecular-kinetic concepts built upon it were merely unproven hypotheses. Into the first decade of the 20th century, that view was still adamantly shared by Ostwald along with Mendeleev[17] and many other chemists. For Richards it seemed especially odd, considering his new pursuit of the compressible-atom theory.

Actually, Richards' preoccupation with the compressibility theory led him very close to discovering the Third Law of Thermodyamics in 1902. He compiled data on the temperature dependence of the change in both the Gibbs energy and the enthalpy for various reactions. Richards noted definite trends with decreasing temperature: e.g., ΔG and ΔH were headed toward each other, with slopes of opposite sign approaching zero. Within a few years, from much more such data extending to far lower temperature, Nernst had established the generality of those trends and hence the Third Law.[18] For chemistry, its great importance is that it enables determining chemical equilibrium for reactions just from thermal properties of the reactant and product molecules.

Scrutiny of Richards' papers on thermodynamics and the compressible atom has revealed that he was handicapped by a weak grasp of elementary calculus. He seems not to have recognized the significance of his nascent data for the Third Law.[15,16] Later, however, he felt his observations in 1902 "are without question the basis of Nernst's subsequent mathematical treatment".[8] Richards complained bitterly that he had not received due credit.[15] Although he recognized mathematics was a useful tool, he did not consider it important in the training of chemists.[19] In private letters, he often disparaged scientists whom he felt dressed up unproven ideas with mathematics. Notably, in a letter in 1923 to his friend Svante Arrhenius (1859–1927), he even questioned the Nobel Prizes awarded shortly before to Albert Einstein and Niels Bohr.[16] After acknowledging that they were "very brilliant" and "their hypotheses are highly ingenious", Richards wrote: *I can not help thinking, however, that it remains to be proved whether or not the hypothesis of either is consistent with reality … Any good mathematician can put on frills according to the most recent mathematical fashion, but the result is unsatisfactory if the figure inside is a doll stuffed by human hands, and not a real being of fresh and blood*. Yet, in 1924 Richards nominated Gilbert Lewis, who had the mastery of calculus and thermodynamic concepts that Richards lacked, for the Nobel Prize.

Nearly 50 years after Richards' death, his son-in-law, J. B. Conant, concluded his memoir[8] with a poignant reflection: *The habit of attempting to foresee all possible contingencies, which was basic to his success as a scientific investigator, placed a heavy strain on his life as a husband and father. To worry about the smallest detail was to be a painstaking chemist … To carry over to daily life the same attitude condemned the scientist to a total life of anxiety. As he approached sixty, it became apparent to his close relatives that the nervous load Richards had been carrying for years was too much. Yet, he continued his lectures and went to his laboratory on his regular schedule until within a few days of his death*, on 2 April 1928.

5. Richards' Legacy

"The light which formerly radiated from Europe to America is now brilliantly reflected back again." Thus spoke Carl Grabe, the President of the German Chemical Society, in 1907, commending the remarkable quality and scope of Richards' work.[7] Richards at Harvard and Arthur A. Noyes (1866–1936) at MIT are justly considered the patriarchs of physical chemistry in America.[20] Today, a large fraction of chemists pursuing the many branches of the field can trace their academic ancestry back to Richards or Noyes. That outshines the hard-won experimental results amassed by Richards, although in fact many of his thermodynamic and electrochemical data still abide in tables that are widely used. In contrast, there looms the enigma of his stubborn courtship of the compressible-atom theory. He violated his creed of caution about hypotheses, by failing to purge himself of the human tendency to overvalue his theory while overlooking other explanations for the correlations that he observed. In doing so, he neglected the profound advances in atomic theory taking place in the first decades of the 20th century. Despite the emphasis on history in his courses, he was nearly oblivious to the dramatic gestation of quantum mechanics. This aspect of Richards' legacy is a cautionary tale.

Conant recalled[21] that as late as 1921 Richards had said he was *far from convinced that any element ever spontaneously disintegrated … what was observed might be due to the action of some all-pervading radiation*. Conant regarded that as the "last stand of a retreating skeptic". Yet, should we not muster some empathy? What for Richards was the "primal mystery" of atomic weights, might nowadays be considered a "fantastic reality".[22] Last year, the Nobel Prize for Physics celebrated the theory confirming how matter acquires mass, at least the ordinary matter that we can observe. A press release, titled "Here at Last!" described how "Everything from flowers to … planets" (including atoms) acquires mass "from contact with an invisible field that fills up all space", the Higgs boson field.[23] Experimental confirmation of the theory took 40 years and the labor of 10000 physicists!

T. W. Richards closed his Nobel Lecture[12] with this benediction: *Each generation builds upon the results of its predecessors … In years to come, let us hope that yet finer means of research and yet deeper chemical knowledge may make possible further improvements, yielding for mankind a more profound and far-reaching knowledge of the secrets of the wonderful Universe in which our lot is cast.*

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[1] T. W. Richards, quoted by G. S. Forbes, *J. Chem. Educ.* **1932**, *9*, 452.
[2] W. H. Brock, *The Norton History of Chemistry*, Norton, New York, **1992**.
[3] A. J. Ihde, *Science* **1969**, *164*, 647; A. J. Ihde, *Development of Modern Chemistry*, Harper & Row, New York, **1964**.
[4] Avogadro's analysis of experimental data on gas reactions revealed that hydrogen, oxygen, nitrogen, and halogen gases were diatomic molecules, water was H_2O, and ammonia NH_3. Although aware of Avogradro's results, Dalton clung to his "rule of greatest simplicity", maintaining that gases were atomic, water was OH, and ammonia NH.
[5] This essay is drawn chiefly from memoirs by Richards' contemporaries: G. S. Forbes,[1] G. P. Baxter,[6] H. Hartley[7] and J. B. Conant,[8] as well as from Richards' own summary of his research up to 1914 (written in third person) and publication list, both included in Ref. [8]. Also consulted to check some details were the comprehensive Ph.D. thesis of S. J. Kopperl[9] and Richards' diaries and personal correspondence available in the Harvard University Archives.
[6] G. P. Baxter, *Science* **1928**, *68*, 333.
[7] Theodore William Richards Memorial Lecture: H. Hartley, *J. Chem. Soc.* **1930**, 1937.
[8] J. B. Conant, *Natl. Acad. Sci.* **1974**, *44*, 251. This biographical Memoir of Theodore William Richards is also available at http://www.nasonline.org/publications/biographical-memoirs/memoir-pdfs/richards-theodore-w.pdf.

[9] S. J. Kopperl, *The Scientific Work of Theodore William Richards*, Ph.D. Thesis, University of Wisconsin, **1970** (available from University Microfilms, Inc., Ann Arbor, Michigan); see also S. J. Kopperl, *J. Chem. Educ.* **1983**, *60*, 738.
[10] The Royal Swedish Academy of Sciences did not announce the 1914 prize until November, 1915; see H. G. Söderbaum, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1914/present.html.
[11] T. W. Richards, M. E. Lembert, *J. Am. Chem. Soc.* **1914**, *36*, 1329.
[12] T. W. Richards, *Nobel Lecture*, **1919** (see http://www.nobelprize.{org/nobel_prizes/chemistry/laureates/1914/richards-lecture.html). Richards never delivered his lecture personally in Stockholm; he intended to do so on a trip in 1922 but was thwarted by a family illness.
[13] F. W. Aston, *Mass Spectra and Isotopes*, Edward Arnold, London, **1942**.
[14] J. P. Cooke, T. W. Richards, *J. Am. Chem. Soc.* **1888**, *10*, 81. Ironically, however, the result initially reported by Crooke and Richards was 15.953 ± 0.0017, seemingly supporting the Prout prediction. An important correction, pointed out by Lord Rayleigh, had to be made for the contraction of the bulb containing the hydrogen when it was evacuated. Likely this early experience fostered Richards' meticulous scrutiny of possible sources of error in all his later work.
[15] P. Coffey, *Cathedrals of Science*: *The Personalities and Rivalries That Made Modern Chemistry*, Oxford University Press, **2008**, pp. 48–51, 78–80, and 157–158.
[16] J. W. Servos, *Physical Chemistry from Ostwald to Pauling*, Princeton University Press, **1990**, p. 81 and 118.
[17] M. D. Gordin, *Dmitrii Mendeleev and the Shadow of the Periodic Table*, Basic Books, New York, **2004**, pp. 24–25.
[18] D. K. Barkan, *Walther Nernst and the Transition to Modern Physical Science*, Cambridge University Press, **1999**.
[19] As an undergraduate in 1925, J. Robert Oppenheimer took Richards' course in physical chemistry, but came away feeling it was "a very meager hick course … tentative and timid; Richards was afraid of even rudimentary mathematics". Quoted in Ref. [16].
[20] E. B. Wilson, Jr., *Proc. Welch Foundation* **1977**, *20*, 106. Edgar Bright Wilson, Jr. (1908–1992), my Ph.D. mentor, was a leading architect of chemical physics and quantum chemistry; he held the T. W. Richards chair at Harvard for 30 years.
[21] J. B. Conant, *Science* **1970**, *168*, 425.
[22] F. Wilczek, *Fantastic Realities*, World Scientific, Singapore, **2006**, pp. 57–80. Despite the reluctance noted by Conant, later Richards concluded that "beyond reasonable doubt" spontaneous disintegration of radium occurs and "the theory of atomic disintegration seems to be well supported." See p. 22 and 25 in T.W. Richards, *Chem. Rev.* **1924**, *1*, 1–40.
[23] L. Randall, *Higgs Discovery*: *The Power of Empty Space*, HarperCollins, New York, **2013**.