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WILLIAM FRANCIS GIAUQUE

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A Biographical Memoir by

KENNETH S. PITZER AND DAVID A. SHIRLEY

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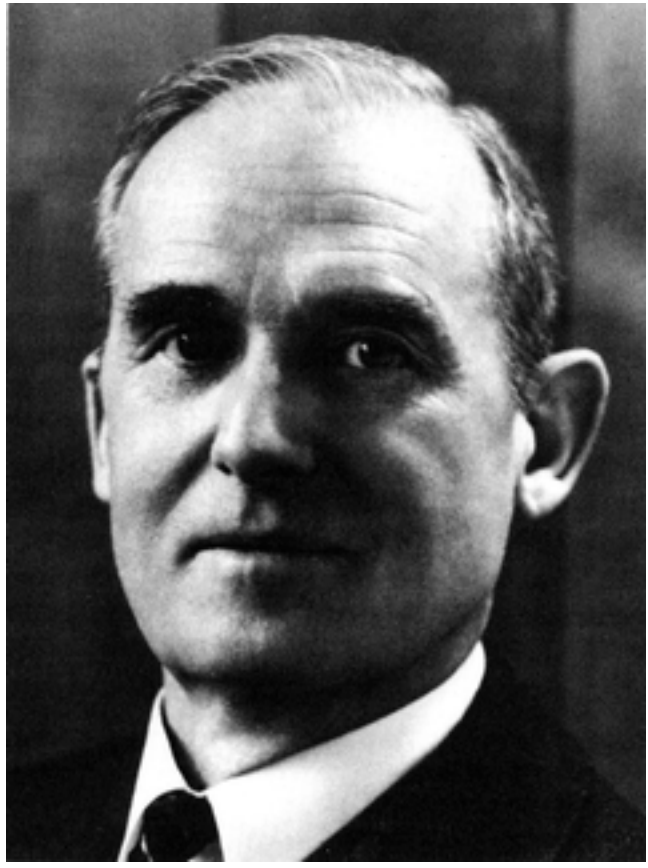

W. F. Giauque

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WILLIAM FRANCIS GIAUQUE

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BY KENNETH S. PITZER AND DAVID A. SHIRLEY

WILLIAM FRANCIS GIAUQUE IS remembered particularly for his discovery of adiabatic demagnetization as a means to reach very low temperatures as well as for his exhaustive and meticulous thermodynamic studies, over a lifetime of research, which utilized the third law of thermodynamics while also developing a large body of evidence for its validity. His "achievements in the field of chemical thermodynamics and especially his work on the behavior of matter at very low temperatures and his closely allied studies of entropy" were cited by the Nobel Committee for Chemistry in the award of the prize in 1949.

Giauque was born May 12, 1895, in Niagara Falls, Ontario, Canada, the eldest of two sons and one daughter of William Tecumseh Giauque and Isabella Jane (Duncan) Giauque. His father was an American citizen, and thus William Francis Giauque was able to adopt American citizenship although born in Canada. Neither of Giauque's parents completed a formal high school education, but both were convinced of the value of education. His father was a skilled carpenter and cabinetmaker and was adept at mechanical procedures in general. He was employed variously as a weighmaster and station agent for the Michigan Central Railroad.

Giauque's mother was skilled in sewing and tailoring and worked in those occupations on occasion.

His father died when Giauque was thirteen, leaving the family with meager financial resources that had to be supplemented from part-time and summer jobs by all members. Among these jobs was part-time seamstress work by the mother for the family of Dr. John Woods Beckman, assigned to Niagara Falls by his employer, American Cyanamid Company. This connection had a pivotal role in William Francis Giauque's later education and career.

To his mother's consternation, Giauque made a youthful, headstrong decision upon entering high school that he would prepare for gainful employment as soon as possible; he elected the two-year business course rather than the five-year college-preparatory course. Unable to change Giauque's mind and distraught that he would forego a college education because of financial pressure, Mrs. Giauque enlisted the help of Mrs. (Gertrude Wheeler) Beckman. Giauque often described to his students the long walk he took with Mrs. Beckman in the course of which she contrasted for him the experience of her brothers. One had foregone a college education; a second, Charles Stetson Wheeler, graduated from the University of California with the class of 1884, had a highly successful career as an attorney, and served as a regent of the university from 1902 to 1907 (and later from 1911 to 1923). Giauque switched to the college-preparatory curriculum, with electrical engineering as his goal. His search for employment upon graduation from high school led Giauque, by chance, to the Hooker Electrochemical Company, in Niagara Falls, New York, where his new fascination with chemistry changed his career goal from electrical to chemical engineering. His supervisor, Mr. Burr H. Ritter, assisted this change by answering his questions about chemistry whether they were related to the work or not,

and he fully supported Giauque's decision to leave Hooker after two years to continue his education.

Mr. Ritter also promptly and permanently changed Giauque's nickname from Frank to Bill, at least among chemists, to avoid confusion with another employee. The thought of his having a nickname assigned by someone else would have amazed his students, who knew him in later years as "Giauque" and addressed him as "Professor Giauque." They realized that he was called Frank by his family and Bill by his peers, but his stern demeanor and his practice of always addressing *them* by their last names, unadorned by modifiers, discouraged experimentation along these lines on their part.

Again the Beckmans were to play a key role in determining Giauque's future direction. While Giauque worked at Hooker, Dr. Beckman, himself an electrochemical engineer with American Cyanamid, had been transferred to Berkeley. When Giauque's mother wrote to Mrs. Beckman of Giauque's decision to enter chemical engineering, Mrs. Beckman wrote back about her husband's admiration for the work that G. N. Lewis and his colleagues, J. H. Hildebrand, W. C. Bray, and others, were doing at the University of California. Giauque had been considering the Massachusetts Institute of Technology and Rensselaer Polytechnic Institute, but Lewis's scientific reputation, the pleasant climate, and the fact that there was no tuition, even for out-of-state students, at that time and only a total of $10 per semester in fees combined to persuade him to move to Berkeley in August 1916 and enroll at the University of California.

Giauque thus began an association with the College of Chemistry, University of California, that lasted for the remaining sixty-six years of his life, as undergraduate, graduate student, faculty member, and professor emeritus, unin-

terrupted by sabbatical leaves and with few trips made for any purpose except to receive major awards. He also persuaded his family to move to Berkeley in 1919 when his brother and sister were ready to enter the university.

Motivated in part by the need to support himself through part-time work throughout his student years, Giauque led a life style even as an undergraduate that was orderly in the extreme. He neither smoked nor drank alcoholic beverages, by preference. Although while in high school he rarely passed up an opportunity to play basketball, as an undergraduate time constraints limited his participation in sports to the boxing team during his freshman year. He also decided at an early age to read no more fiction, regarding time thus spent as wasted.

As an undergraduate Giauque continued his interest in engineering as well as chemistry, and he received very substantial engineering training that served him well in planning and carrying out his later scientific work. However, the faculty assembled by G. N. Lewis soon stimulated his primary interest toward fundamental research. During his senior year Giauque pursued low-temperature research on the third law of thermodynamics under the direction of G. E. Gibson—research that was to evolve into his life's work.

After graduation in 1920 with a B.S. in chemistry (with highest honors), Giauque was awarded a university fellowship to continue his education, earning a Ph.D. in chemistry in 1922, with a minor in physics. His thesis research, also supervised by G. E. Gibson, was on the heat capacity of glycerol. It showed that the third law of thermodynamics cannot be applied directly to the disordered systems known as glasses. In later life, Giauque liked to point out to his students the four-year gap between the publication of his thesis work in 1923 and his next publication, as proof by example that a large number of early publications are not

essential for an academic career with tenure, if one's senior colleagues have enough patience.

Giauque was informed by G. N. Lewis early in 1922 that he would be offered a faculty appointment upon completion of his Ph.D. work, and he weighed this offer for several months before accepting. He had planned to apply the fundamental science that he had learned to engineering problems, and he also had done no teaching in his two-year tenure as a graduate student, having been able to devote all his available time to his studies for the first time since entering college. The excellent research atmosphere in the College of Chemistry prevailed and Giauque accepted the offer, although his interest in engineering persisted throughout his career and was often expressed by his tendency to do research on a pilot-plant scale. He designed and supervised the construction of the heavy equipment for the liquefaction of both hydrogen and helium, as well as for the production of the high, uniform magnetic fields needed for his research. He was registered as a professional engineer in the state of California.

During his graduate studies and in his early days as a faculty member, Giauque interacted extensively with Raymond T. Birge of the physics department. He thus acquired an understanding of the applicability of quantum statistics to the calculation of thermodynamic quantities, in particular calculation of the absolute entropy of any gas of diatomic molecules from spectroscopic data. Giauque realized that this would provide an absolute reference with which he could compare calorimetric values of entropy, thus achieving a more definitive test of the third law of thermodynamics than had previously been possible.

His study of the spectra of diatomic molecules led to the discovery of the isotopes of oxygen. While the spectra of ^{16}O–^{16}O gave a calculated entropy in agreement with the

calorimetric measurements, some faint lines in the oxygen spectrum remained unexplained. With typical thoroughness, he explored several possibilities, concluding finally that an isotopic molecule ^{16}O–^{18}O would exhibit the unexplained lines. The world authority on isotopes, Aston, had studied oxygen with a mass spectrograph. He asserted that only ^{16}O existed and thus that oxygen was an ideal atomic weight reference. Undaunted by Aston's authority, Giauque calculated the frequencies expected for the ^{16}O–^{18}O molecule and found agreement with the unexplained faint lines. However, his calculations predicted a number of additional lines that were not included in the data reported by Dieke and Babcock, whose spectra he was using. These authors had not reported faint lines that did not lie close to strong ones, believing that they were not associated with oxygen. At Giauque's request, Babcock provided the unreported lines, most of which agreed with Giauque's predictions. Further study identified the ^{17}O isotope as well. The discovery of the oxygen isotopes provided the first clear proof that molecules retain zero-point vibrational energy at absolute zero temperature. It also revealed that physicists and chemists had unknowingly been using different atomic weight scales, a situation that persisted until the ^{12}C scale was adopted in 1961.

Giauque's discovery of adiabatic demagnetization was a consequence of his broad scientific interests as well as his keen and innovative mind. In the fall of 1924 another young colleague, Nelson W. Taylor, invited Giauque to join him in developing a seminar on magnetism, which Taylor was studying. Giauque agreed to present anything he could learn about the relationships of thermodynamics with magnetism. After following several lines of investigation in which the small effect of magnetism on total energy led to uninteresting results, Giauque came across a report from Leiden on

the low-temperature magnetic susceptibility of $Gd_2(SO_4)_3 \cdot 8H_2O$. Because of the eightfold spin degeneracy of the Gd^{+3} ion, a large residual entropy remained in this salt, in the absence of a magnetic field, even at very low temperatures. Applying the thermodynamic equations that he had just developed, Giauque found that readily available magnetic fields could remove very substantial amounts of entropy from this or similar systems at very low but currently accessible temperatures. Given his engineering training, it was natural for him to associate entropy changes with heat engines and refrigerating machines, and adiabatic demagnetization became obvious to him as a means for achieving lower temperatures than those available by the conventional use of cryogenic liquids.

Giauque shared his idea for magnetic cooling, conceived late in 1924, freely with his colleagues and with visitors to Berkeley from European laboratories, and he published it in 1927, but over eight years passed before Giauque and MacDougall, his student, carried out the first adiabatic demagnetization experiment in March 1933. The Berkeley laboratory was ill equipped to conduct the experiment when it was conceived, lacking a helium liquefier and an air-core magnet, which would be required for meaningful measurements of the final low temperatures reached upon demagnetization. Characteristically, Giauque set out on a long-range program to develop the necessary equipment. Although he had the support of G. N. Lewis and W. M. Latimer, who favored him in the allocation of scarce resources, there was very little money available for research. Colleagues at better-funded low-temperature laboratories in Europe could have carried out the experiment earlier, but perhaps they lacked Giauque's conviction. It was in 1933 that all of the equipment was completed and Giauque's first demagnetization experiment yielded 0.25 K.

In addition to lesser honors, Giauque was elected to the National Academy of Sciences in 1936 and to the American Philosophical Society in 1940. He received the Nobel Prize in chemistry in 1949.

Muriel Francis Ashley, who earned a B.S. in chemistry at the University of California in 1922, had been a longtime friend of both Giauque's sister and mother, but it was only after she returned to Berkeley for her graduate work in physics that he displayed any interest in her. On the day that she filed her Ph.D. thesis in 1932 she and Giauque were married. The union produced two sons, William Francis Ashley Giauque and Robert David Ashley Giauque, and four grandchildren. Muriel became an accomplished botanist, specializing in fern spores collected for her by a worldwide network of friends. Although characteristically reserved in direct praise, Giauque was clearly very proud of her accomplishments. When the Giauques traveled to Stockholm for his Nobel award, she received almost comparable attention from her botanist friends. Giauque's students remember pleasant Thanksgiving dinners at the Giauque home, with Muriel as cook and Frank (as she called him) as raconteur, with a keen sense of humor. The stories he most enjoyed telling were those in which the joke was on him. She predeceased him by eight months, on July 28, 1981.

Although adiabatic demagnetization was a dramatic discovery, Giauque's primary interest was in entropy and the third law of thermodynamics, which he explored by meticulously accurate absolute measurements: in this context, magnetic cooling was a means to an end. He eschewed making approximate measurements and insisted on a target accuracy of a tenth of 1%, a tall order for thermodynamic data. He envisioned building a 10-Tesla iron-free magnet large enough to produce a uniform magnetic field over a volume of 100 cubic centimeters or more, with an iron-free envi-

ronment over a 10-meter diameter. This project took over two more decades, reaching completion only in 1959, with the successful operation of a multiple-layer solenoid of 3/4-inch by 1/4-inch copper conductor carrying 10,000 amperes of current and dissipating 7 megawatts of power. Giauque insisted that magnetic samples be accurately ellipsoidal, and he required that all calorimetric measurements, magnetic or not, be made by direct-current methods. Standard cells from the National Bureau of Standards were delivered first to his laboratory, where they were treated with great respect. They were released to the college only when the next shipment of standard cells arrived. After the Low-Temperature Laboratory (later the Giauque Laboratory) was completed in 1954, and the first 10-Tesla magnet was finished in 1959, Giauque and his colleagues proceeded with magnetic and thermodynamic studies of paramagnetic compounds as he had originally intended forty years earlier. Many of his later publications report careful and accurate data on these compounds, setting an enviable standard for future workers.

Giauque's research interests were not restricted to magnetic systems or to very low temperatures. Early in his career he measured the heat capacities and heats of transition of the halogen acids from very low temperatures upward. With his careful measurements the excitations of degrees of freedom "frozen in" at very low temperatures (e.g., molecular rotation) were identified as sharp anomalies in the heat capacity. In other molecular systems, accurate heat capacity measurements allowed him to identify random molecular orientations that showed up as residual entropies, such as $S = R\ln 2$ for the carbon monoxide molecule, which could be oriented as C-O or O-C. The structure of ordinary ice was of special interest in this regard. Giauque expected a molecular rotation degree of freedom, while Linus Pauling

proposed a tetrahedral structure for the oxygen atoms, connected by random hydrogen bonds, leading to a residual entropy $S = R\ln 3/2$. Giauque and Stout confirmed this value experimentally, supporting Pauling's model. Giauque used this example to convince his students of the need for careful measurement as well as the superiority of fact over speculation.

In addition to his interest in magnetic salts and simple molecules that illustrated statistical thermodynamic principles, Giauque made substantial contributions to instrumentation and experimental techniques. He helped to refine low-temperature scales throughout his career. He wrote an amusing parable in *Nature* in 1939 as a plea to use a single fixed point in defining the size of the degree in the absolute temperature scale. He also studied the chemically very important and difficult systems of sulfuric acid and sodium hydroxide over a period of years from 1950, using low-temperature calorimetry and other thermodynamic measurements to establish the properties of these complicated and corrosive materials.

Giauque's conservatism was legendary. He always appeared at the university dressed in an iron-gray tweed suit. He recounted that one day in 1924 he had sought clothing appropriate for a young faculty member and had a tailor make him a suit. He bought the suit and the bolt of cloth from which it was made, and over the years he always owned two identical suits. Whenever a jacket or pair of trousers showed enough wear, he had another made from that material, which lasted for over twenty years.

He did not learn to drive an automobile and did not own one until after receiving the Nobel Prize in 1949. He lived only seven blocks from the Berkeley campus and walked each way, except in his later years. Then he suffered from arthritis, and his wife Muriel drove him to work and back.

His conservatism was expressed in many ways in the laboratory. Giauque required that permanent metal joints be hard soldered, then covered with soft solder to ensure vacuum tightness. For many years his students used "ball-vee" vacuum-tight seals to hold sample chambers in place. Both surfaces in these seals were made of clean stainless steel, and a torque wrench was used to create a vacuum-tight seal without deforming the steel. It was through these and other meticulous but very difficult techniques that Giauque and his students were able to make precise absolute measurements.

Giauque's immunity to social fads had its counterpart in his scientific work. Although well versed in statistical mechanics, he was comfortable with the more empirical perspective of thermodynamics when he felt the situation warranted it. He also enjoyed the role of iconoclast when he felt that a colleague's approach didn't deliver all that it advertised. He jokingly referred to unusual g-factors as the "activity coefficients of magnetism," and he was very unenthusiastic about the ease with which the concept of spin temperature was adopted and applied to assign negative temperatures to systems with inverted populations, without also demonstrating the requisite rapid internal "thermal" equilibrium.

Giauque taught his research students to be the most demanding critics of their own data, reasoning that once published their work would then stand the test of time. He conveyed to them many of the practical aspects of experimental science, such as the improvement in accuracy on integrating, and loss on differentiating, a data set; the unreliability of the first point in a heat-capacity run because of hysteresis; and the advantages and pitfalls of least-squares fitting procedures. A dominant personality himself, Giauque not only tolerated but respected students who dis-

agreed with him, and he was especially pleased when they could prove their point.

The constancy of Giauque's commitment to classroom teaching was no less remarkable than his dedication to research. Starting with his appointment as instructor in 1922, he taught a discussion laboratory section of the freshman chemistry class in every semester for thirty-four consecutive years. In 1926 G. N. Lewis assigned him the responsibility for teaching the college's course in advanced physical chemistry, taken mainly by graduate students. Giauque taught that course every spring semester thereafter until his nominal retirement in June 1962. His classroom style was to lecture while using the blackboard to solve problems and prove points. His tests were problem based, and the problems were designed to test the students' understanding in depth. Over the years old problems recurred in somewhat altered forms, and students adopted the strategy of studying collections of problems that Giauque had used in previous years. Giauque must have regarded this as a good way to learn the material. In 1943 he also assumed the responsibility for a section of chemical thermodynamics for graduate and undergraduate honors students, which he taught every fall semester through 1960. While eschewing administrative posts in the university, he unstintingly gave his time in helping students, serving as adviser for undergraduates in the College of Letters and Science who wished to major in chemistry throughout the period 1945-60.

Giauque loved his work and made it the dominant part of his life, commenting on many occasions that he didn't need vacations because he spent the whole year doing what he enjoyed most. His legacy is that of one of the later major figures in the development of chemical thermodynamics, specifically regarding the influence of atomic and molecular structure on entropy and the third law of thermody-

namics. His work will long endure in the textbooks. His influence on colleagues and students, though largely unrecorded, will also endure.

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