WILLIAM GILBERT MIXTER (1846-1936): A YALE CHEMIST WHO DESERVES TO BE REMEMBERED

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Introduction

My great-aunt, Hilda Groening, was a pharmacist who graduated from the Melbourne College of Pharmacy in 1918 (1). The family pharmacy, where she worked with her father and mother, both qualified pharmacists, was not far from my home and it was there that I had my first exposure to chemicals and set out on the road to a career in chemistry. They were known, as pharmacists still are in Australia, as "chemists," and the shop was a "chemist shop." It was a traditional pharmacy, with globes of colored water in the window, and an extensive stock of *materia medica*. Patients were encouraged to bring their own bottles for what was often dispensed as "The Mixture." Growing up in the 1940s, I was able to explore the organics, like liquorice root, and the inorganics like sulphur (always with a "ph"), copper sulphate, and Condy's crystals and to play with the machine that squeezed corks down so they would fit into the customers' bottles.

Although in the early twentieth century Australia was more closely linked to Britain than to America, the chemistry textbook that Hilda used in her training was an American one, *An Elementary Textbook of Chemistry* by W. G. Mixter (2). It is not clear whether this text was prescribed by the College or simply purchased by Hilda, but since Mixter's book is not held in any Australian academic or public library it is likely that it was not one that a generation of students purchased. Texts from an eclectic range of authors—but not including Mixter—were set for students at the nearby University of Melbourne's chemistry school (3, 4) but there was a flourishing market for technical books in the city.

Mixter's was my first chemistry book and I still have it. My evident interest in the subject was the reason that my parents brought me a chemistry set for my twelfth birthday. I soon accumulated other chemistry texts from second-hand shops. Later in life, when I became interested in the history of chemistry, I began to wonder about my first book: who was Mixter? and what he had contributed to the development of chemistry, apart from his textbook? Mixter was too late on the scene to be listed by Silliman (5) as a leading American chemist post-1845, his oeuvre amounting to only five articles by then. He was subsequently active in teaching and productive in research publication in a long career that I believe merits re-examination.

Biography

Obituaries for Mixter provide the outline of his life (6). He was born in 1846 in Dixon, Illinois, to George Mixter (Yale B.A. 1836) and his wife, Susan Elizabeth nee Gilbert. He graduated from Rock Island High School, Illinois, and went on to university study at Yale where he graduated Ph.B. in 1867. Although Yale had introduced the Ph.D. degree in 1860, many candidates took the three-year Bachelor of Philosophy degree, entry to which did not require the Latin that was required for the B.A. (7). His baccalaureate degree was sufficient to gain Mixter an appointment as Assistant in Chemistry which he held for 1868-1870. He served as Instructor in Chemistry 1870-1872 and 1874-1875, the appointment being interrupted by two years spent in Europe, the first as assistant to R. W. Bunsen at the University of Heidelberg, and the second with A. W. von Hofmann at Berlin (8). It was common in the nineteenth century for American and British chemists to study in Germany, where chemical science was most advanced, without necessarily taking out a degree. Advancement in the profession did not always require an advanced degree, preferring study abroad to, for example, nascent Ph.D. programs at Johns Hopkins and Yale.

In 1875, at age 29, Mixter was appointed to a newly created chair of chemistry, and served as Professor until 1913, following which he was Professor Emeritus for 23 years until his death from bronchopneumonia. In 1875 he married Ada Louise Webber, who bore him a son and a daughter, but predeceased him by many years. In 1887 Mixter was awarded an M.A. (Hon) by Yale.

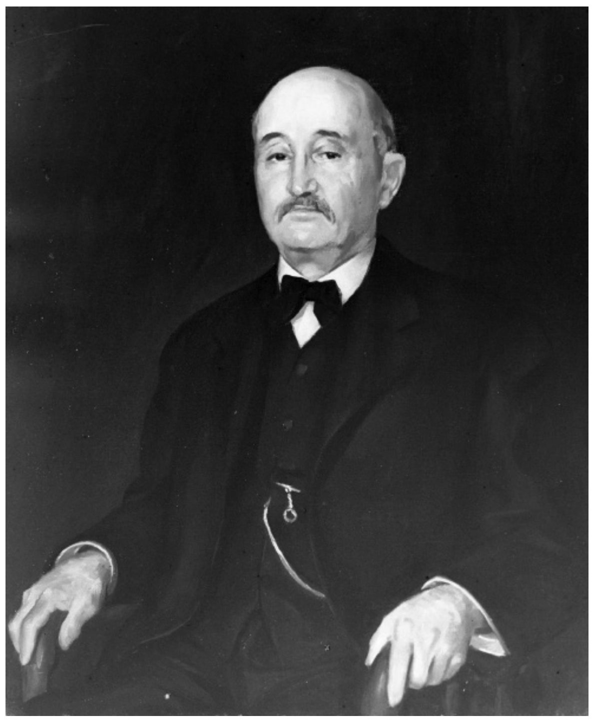

Figure 1*. Portrait of William Gilbert Mixter by Huc-Mazelet Luquiens (1914). Yale University Art Gallery. Gift of George Mixter, Ph.D. 1895 and Mrs. Henry Galpin to the Sheffield Scientific School.*

Mixter (Figure 1) was in charge of freshman chemistry at Yale for 38 years. He was (8)

> more than a disciplinarian, more than a teacher of elementary chemistry. He was broadly and thoroughly trained in the science of chemistry, deeply interested in experimental work, and zealous in carrying on such research work as the time at his disposal would permit.

Upon Mixter's retirement in 1913, Yale's president, A. T. Hadley, wrote in his annual report that (9)

> He was one of those men whom we could least afford to lose—eminent as an investigator, unremitting in his devotion as a teacher, and ideal in his relation as a man to his colleagues and to his students. I do not know which we shall most miss; his advice, his teaching, or his example.

Mixter's Published Research

Mixter published 33 single-author papers in the *American Journal of Science* which was founded by Benjamin Silliman Sr. in 1818, 19 in the *American Chemical Journal* founded in 1879 by Ira Remsen, two in the *Journal of the American Chemical Society* and two, arising from his work in Germany in the early 1870s, in European chemical journals. He divided his attention between organic chemistry, largely published in Remsen's journal, and thermochemistry, in the *American Journal of Science*.

His first publication concerned two silicate minerals found in a New Jersey mine (10). Willemite was a zinc silicate, $SiO_2 \cdot 2ZnO$, which owed its yellow or green color to a manganese impurity. Tephroite was the analogous manganese silicate, $SiO_2 \cdot 2MnO$, containing some zinc. Mineral chemistry and mineralogy were prominent in the work of the Sheffield School at Yale, influenced by Benjamin Silliman (1779-1865), his son, Benjamin Jr. (1816-1885), his son-in-law and successor James Dwight Dana (1813-1895) and Dana's son, Edward Salisbury (1849-1935).

Mixter's second publication (11) demonstrated a method for the estimation of sulfur in various materials by burning them in oxygen, passing the combustion mixture over platinum gauze, exposure to bromine in hydrochloric acid to promote oxidation to SO_3, absorption in water, and finally precipitation of barium sulfate. Coal, iron pyrites, crude sulfur, carbon disulfide, and wool were the materials studied. Oxygen for use in the assay was generated from potassium chlorate or potassium chlorate reacted with manganese dioxide, the latter being found to be contaminated with sulfur and thus requiring a blank determination. Sulfur-vulcanized rubber was avoided at critical parts of the apparatus. Concluding his paper, Mixter thanks Professors Samuel William Johnson, who taught agricultural chemistry at Yale 1857-1875, and the professor of analytical chemistry, Oscar Dana Allen, for assistance and suggestions.

The abstractor for the *Chemical News* (12) noted that it was not possible to understand Mixter's work without seeing the woodcut in which the apparatus was depicted, whereupon the journal reproduced the whole of the paper in a subsequent issue (13). Almost a decade later, Mixter returned to the analysis of sulfur, this time in gas streams, and suggested refinements in the methods employed by him and other chemists (14, 15).

Although abstracted in the *American Journal of Science* (16), Mixter's next paper, on specific heats of three elements, was actually published with his collaborator, E. S. Dana, in Justus Liebig's *Annalen* (17). The authors note that the determinations were carried out in Heidelberg, in the laboratory of Robert Bunsen, whom they thank for support and encouragement. Thermochemistry was to become a major activity for Mixter, but his exposure to organic chemistry in Berlin (18) kindled an interest in a second field of research in which he was to publish extensively. Three papers in the *American Journal of Science* and one in the *American Chemical Journal* in 1877-1879 described the preparation of silver ammine sulfates and nitrates from aliphatic and aromatic amines, and an accompanying paper from Dana described the crystal habit of hydrated and anhydrous forms of one of Mixter's compounds (19). Before the days of X-ray diffraction, of course, "crystallography" consisted of the classification of gross crystal habit and measurement of the interfacial angles.

Between 1879 and 1893 Mixter did not publish in the *American Journal of Science*, but instead sent his manuscripts to Remsen's *American Chemical Journal* and it was there that the bulk of his organic chemistry (16 papers) was published. Six of these papers, all dealing with the chemistry of acyl-anilides (1886 to 1889), were published with his graduate student co-authors, Thomas Burr Osborne, Conrad Henry Matthiessen, Joseph Osterman Dyer, Frank Otto Walther, Charles Percy Willcox, and Felix Kleeberg. Most took the Ph.B. degree and subsequently took medical or law degrees at other universities. The outstanding career was that of Osborne (1859-1929) who took the Ph.D. degree in 1885 and was assistant in analytical chemistry in the Sheffield School 1883-1886. For forty two years he was employed as a biochemist at the Connecticut Agricultural Experiment Station where his investigations concentrated on vegetable proteins, but he was also the co-discoverer of vitamin A (20).

Resuming publication in the *American Journal of Science*, Mixter published two papers on what he called "electrosynthesis." He reported on the products of reactions between gases that were exposed to electrical discharge in the kind of apparatus used to generate ozone from oxygen, which he described first as a "feeble alternate discharge" and later as a "glow discharge" between the glass walls of a eudiometer surrounded by a water jacket. The reactions took place at temperatures far below those where the gaseous molecules would dissociate. In the first experiments (21), water and dry carbon monoxide ("carbonic oxide") reacted slowly to form carbon dioxide. Methane, ethane, ethylene and acetylene, exposed to oxygen were wholly or partly converted to carbon dioxide and water. In a second paper (22) Mixter reported that oxygen and hydrogen combined to form water, while a mixture of oxygen and ammonia formed ammonium nitrite that was deposited as white coating on the walls of the apparatus.

After the turn of the century, Mixter embarked on a series of researches with gases and gaseous mixtures, in the first of which (23) he explored the thermal decomposition of acetylene and other "endothermic gases"—cyanogen and nitrous and nitric oxides. Turning to explosions of mixtures containing oxygen (24), he found that below certain pressures the reactions were not self-propagating, the reason for which, he hypothesized was the "infrequency of impacts of molecules having velocity or internal energy adequate for chemical union." Such a view places Mixter in the mainstream of physical chemistry where the kinetic theory of gases was developed (25), and although his approach was non-mathematical, it may have benefitted from the presence, "working in splendid isolation at Yale University" (26) of J. Willard Gibbs (27). Further investigating the explosion of acetylene-oxygen mixtures, Mixter noted the presence of acetylene in the mixture after the reaction and ascribed this not to residual, unconsumed acetylene but to subsequent re-synthesis, in support of which he reported also the presence of a compound of carbon and nitrogen that had been formed in the eudiometer (28). He then showed that hydrocyanic acid was formed during explosive reaction of acetylene and ammonia (29).

Mixter then commenced a series of researches on heats of reaction and heats of formation of metal oxides. The oxidant was sodium oxide (sodium peroxide), which enabled him to conduct oxidations that were not accessible with molecular oxygen and to calculate results based on the known heat of formation of sodium peroxide for cases where other methods such as heat of neutralization were not applicable (30). In the following paper (31) of what turned out to be a series of 18 papers over the next 17 years, he announced his aim "to determine if the position in the Periodic System and the magnitude of the atomic weight of the element have a marked influence on" the heats of such reactions. This proposal was examined in a detailed review (32) of his own and other researchers' results—notably those collated by Julius Thomsen (1826-1909) (33). He observed that within sub-groups there was good linearity between atomic weight and heat of oxidation, and that anomalies might be due to errors in experimental results that called for further investigation. He also urged attention to the thermochemistry of rare elements.

His final thermochemical paper (34) was an overview of reactions involving sodium peroxide, "the only way known for finding the heat of oxidation of elements which do not burn in oxygen and which form oxides insoluble in acids." In it, he described his experimental methods in great detail, and noted that "the sterling silver bomb weighed when made 472 grams and after eight years' use 465 grams. The loss is due to corrosion, especially by sulfur, and to polishing."

While the bulk of Mixter's publication after 1895 was in the *American Journal of Science*, he published two papers in the *Journal of the American Chemical Society* and the chemistry described in them was quite different from those of his major series on organic chemistry, gaseous reactions, and inorganic thermochemistry. The first of these "outliers" (35) concerned a translucent ruby-red deposit formed on a gold electrode during electrolysis experiments, which Mixter showed to have arisen from oxidation of the metal. In the presence of appropriate solutes, auric hydroxide, potassium hydrogen aurate, basic auric sulfate, and a fulminate could also be formed. The second paper (36) described a qualitative test for carbon developed by his late colleague, Professor S. L. Penfield (37). The test consisted of fusion of the test sample with lead chromate in a narrow hard-glass tube, and placement of a drop of barium hydroxide solution further along the tube where it could intercept any carbon dioxide emitted by the fusion mixture. Meticulous as ever, Mixter noted that the test was "so delicate that lead chromate that has been exposed to the air in preparation will react for carbon from dust in the air." To judge from its absence from Feigl's compilation (38), the Penfield test was not widely adopted.

Mixter's Textbook

Mixter's textbook (See Ref. 2) was first published in 1888, with successive editions incorporating revisions in 1889, 1890, 1893, and the fifth and final edition in 1897. Following digitization by the Library of Congress it is available on-line (39), and has recently been republished in paperback. The unsigned review published in the *American Journal of Science* was complimentary, briefly summarizing the contents and noting that it "presents the general facts and principles of the science under a succinct form and a sensible arrangement well adapted for its purpose" and that "the volume is handsomely printed and the illustrations are excellent" (40). Another friendly review appeared in *Scientific American* (41), saying that the book gave "a very complete view of the bases of the science of inorganic chemistry" and praising the illustrations. A less complimentary account appeared in *Chemical News* (42), where the reviewer pointed to "one feature of distinction from the almost endless array of chemical manuals—it is based on the periodic classification" but qualified this praise with "Strangely enough we can find in it no mention of the originator of this system, Mr. Newlands!"

Mixter's professorial colleague Charles S. Hastings (43) contributed the sections on the Physics of Chemistry (pages 1-45) and Spectral Analysis (pages 90-94). His major section covered fundamental concepts including units, forms of matter and use of the balance, temperature and heat, and devoted 12 pages to each of crystallography and gases (pressure, volume, laws, kinetic theory, diffusion, gas density). The spectroscopy section drew on the work of Bunsen and Kirchhoff, Hastings having attended the lectures of Kirchhoff in Heidelberg in 1874.

Mixter began his chemistry section with a list of the 68 elements recognized up to the year 1888, together with their atomic weights. Mixter acknowledged the existence of other forms of the periodic classification, but chose to reproduce Mendelejeff's [*sic*] so-called "vertical table" of the kind first published in 1869, with the periods appearing in columns, while the groups run horizontally across the page, rather than the now more familiar "horizontal" version of 1871 (44).

The main text begins with hydrogen, and then come the elements and their compounds in their Groups, in the order VII, I, VI, II, V, III, IV and VIII. The reason for this idiosyncratic order allows Mixter to cover, in a particular group, only those compounds which an element forms with elements in previous groups. This cumulative approach is enriched by occasional inter-Group essays, devoted to valence; bases, acids and salts; atomic theory; and the periodic law. In the penultimate essay Mixter takes a stance on the question "do atoms exist," noting that "the atomic theory is in accord with all facts and laws of physical and chemical science" and must be "regarded as established … until facts are discovered which are clearly at variance" with it.

Perhaps acknowledging that his arrangement of material is unusual, Mixter advises students to use the index (11 pages) and adds that they may wish "to look up the properties of many substances before studying them systematically." He also recommends to such students that they might wish to "refer to larger works such as Roscoe and Schorlemmer's *Treatise on Chemistry*, and Watts' *Dictionary of Chemistry*, for in doing so "will early form the invaluable habit of using the literature of chemistry."

For purposes of comparison I have chosen the presentation of material in a contemporary text, *Watts' Manual of Chemistry* (45). When Tilden took over publication of this classic, his first edition included over 100 pages of the physics "which properly precedes the study of chemistry," but in his second edition, faced with the need for even greater coverage of physics at the expense of pages that could be devoted to chemistry, he greatly abbreviated this. Like Mixter, Tilden intersperses the sections on groups of elements with chapters on chemical affinity and combination, crystalline form, spectral analysis, and atomic theory including the periodic classification. The organization of the main body of material is quite different, however. He begins with non-metallic elements, covering hydrogen and the halogens (including their hydrides and oxyacids), oxygen and the sulfur/selenium/tellurium group, carbon and silicon, and nitrogen/phosphorus/arsenic. Although there are fewer illustrations, Tilden's coverage of the chemistry is more extensive than that in Mixter's elementary text and it is clearly written for more advanced students. He dealt with the chemistry of metals in groups such as alkalis and alkaline earths, and those headed (typified) by magnesium, lead, copper, iron, chromium, tin, antimony and platinum. In most of these, the group includes what we now regard as main group elements and those members of sub-groups with similar combining power.

Concluding Remarks

As the reviewer for the *Chemical News* observed, rather tetchily, the nineteenth century saw "an almost endless array of chemical manuals" many of which are still to be found in second-hand bookshops, for sale through the internet, and in some cases accessible electronically in digital format. Mixter's textbook is not remarked on these days although it must have enjoyed considerable esteem because it ran to five editions. Nor is his research cited, probably due to advances in thermochemical methods that have produced better data.

Dying in his ninetieth year, Mixter had long outlived most of his contemporaries although he was remembered at Yale (46) and there were brief but generous obituaries (47, 48), in which it was stated that "his data in branches of thermal chemistry have become international standards." He is mentioned in biographical compilations (49, 50) and in lists of American chemists who worked with Robert Bunsen. In one of these (51), he is listed among a "few of the better known chemists of the U.S.A.," but this was insufficient recognition to gain this innovative and productive chemists a lasting place in the pantheon, and he does not appear in either of Miles and Gould's volumes on American Chemists and Chemical Engineers (52).

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