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Radium for Beauty and Profit

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CITATION FOR CHEMICAL BREAKTHROUGH AWARD: MENDELEEV'S PERIODIC SYSTEM OF THE ELEMENTS

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In 2012, the Division of the History of Chemistry (HIST) of the American Chemical Society's Citation for Chemical Breakthrough award was given to St. Petersburg State University for Dmitrii Mendeleev's publication "Ueber die Beziehungen der Eigenschaften zu den Atomgewichgten der Elemente" (1, 2), which introduced was is now known as the Periodic Table of the Elements to readers in western Europe. One key element of the Citation award requires that the paper honored be the breakthrough paper, but exactly what that demands is left to the reviewers to judge (3). Historically, the breakthrough paper has not always been the first paper in which the breakthrough is announced, but is rather the most influential paper—the one that had the greatest impact in the scientific community, and thus was far more than an interesting innovation but rather a true scientific "breakthrough" (4). In the case of Mendeleev's Table, there are six reasonable candidates for the breakthrough publication:

- Mendeleev's Osnovy Khimii [Elements of Chemistry], which was published in February, 1869 (5), and particularly the periodic arrangement of the elements contained therein;
- the German abstract of the same section of *Osnovy Khimii*, published in the *Zeitschrift für Chemie* also published in 1869 (2);

- the 1869 paper in the Zhurnal Russkago Fiziko-Khimicheskago Obshchestva, actually presented to the Academy by Mendeleev's friend, Nikolai Aleksandrovich Menshutkin, in which the relevant section of the Osnovy was described (6);
- the 1871 paper (7) in the *Zhurnal*, in which the case for the periodic system is laid out much more clearly, with the full predictions of the existence and properties of the three as-yet-undiscovered elements, eka-boron (scandium), eka-aluminum (gallium) and eka-silicon (germanium), and which included corrections to the earlier paper;
- the 1872 paper (8) in the Supplement to *Liebigs Annalen der Chemie*, which is a German translation of the 1871 *Zhurnal* paper; and
- Mendeleev's 1871 paper (9) in the *Berichte der deutschen chemischen Gesellschaft*, in which he answers questions about his periodic system raised by other authors, Lothar Meyer among them.

If we examine each of the journal articles in turn, beginning with the 1869 *Zhurnal* paper (which contained essentially the same periodic table as that proposed in the *Osnovy Khimii*), we see the gradual evolution of the periodic table to the final form proposed by Mendeleev. In the 1869 paper, Mendeleev had already begun the

process that was to make his the dominant name in the development of the periodic system. In the Zhurnal paper, Mendeleev went to great lengths to show the logic by which he had arrived at his system of the elements, which is shown in Figure 1. It already contained the two major intuitive leaps that have come to characterize his periodic system: First, four missing elements (scandium, predicted atomic weight 45; gallium, predicted atomic weight 68; germanium, predicted atomic weight 70; and hafnium—the one usually forgotten—predicted atomic weight 180) are already specified by placeholders (question marks) with appropriate approximate atomic masses; and second, tellurium and iodine have been placed where their chemical properties require, making the chemistry of an element the dominant factor in determining its place in the Table. One should note that Mendeleev's decision appears to be predicated, in part, on the possibility that the atomic weight of tellurium is in error.

However, the table also contains errors that were later corrected: Gold is placed in Group IIIA, and lead in Group IIA presumably based on the Au (III) oxidation state, which is much more common than the Au (I) oxidation state, and the Pb (II) oxidation state, which is much more prevalent than the Pb (IV) oxidation state. Thallium, on the other hand, is placed in Group IA for the same reasons. It is interesting to note that Mendeleev placed these elements in positions now occupied by radioactive elements unknown at the time. Incorrect atomic weights also played their part: the atomic weights of uranium (116 instead of 238), thorium (118 instead of 232) and indium (75.6 instead of 114.8) are all incorrect, and led to errors in placement.

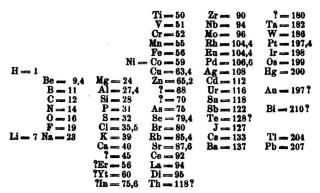


Figure 1. The periodic system of the elements as it appeared in Mendeleev's 1869 article in the Zeitschrift für Chemie. It is essentially the same as the table that appeared in the Zhurnal Russkago Fiziko-Khimicheskago Obshchestva earlier the same year.

The 1869 *Zhurnal* paper is clearly the heart and soul of the periodic system, but since it was published in Russian, its circulation would not have raised it to the level of being the breakthrough paper. This was fulfilled by the 1869 German abstract, in the *Zeitschrift*, with its wider circulation, and more diverse readership.

The 1871 paper in the *Berichte* is a polemical response to comments by others made on the basis of the German abstract, instead of the full paper, as is clear from the opening sentence: "Since the observations of HH. Gerstl, Blomstrand, Lothar Meyer, and Baumhauer on the subject of my proposed system of elements are made on the basis of the Referate***) of the full paper published in Russian, allow me to add some explanation." In the footnote referred to in this sentence, Mendeleev then sets out the chronology of his papers on his Periodic System of the Elements. The fact that Mendeleev's claims had already attracted such attention from German-reading chemists certainly bolsters the credentials of the Zeitschrift paper to be the breakthrough paper. Other than that, the Berichte paper itself contains no new information, but is largely a defense of Mendeleev's claims to priority over those of Odling and Meyer.

The remaining two papers, the 1871 publication in the Zhurnal, and its 1872 translation into German, published in the Supplement to the Annalen are both much more substantial papers than the original 1869 publication. The Zhurnal paper is over twice as long as the original, and, in dramatic contrast to the brevity of the two-page summary in the Zeitschrift, the Annalen paper was substantial: in its 96 pages, it contained a detailed development of the concepts underlying the periodic law, setting out explicitly the predicted properties of the three elements that gave credibility to his system as they were discovered: eka-boron (Sc), eka-aluminum (Ga) and eka-silicon (Ge). Mendeleev's thinking is set out in this paper in a highly logical fashion, and his arguments are both powerful and persuasive. At the same time, a number of errors in the original paper were corrected: the correct atomic weights for indium, uranium and thorium led to their placement being changed, as also happened for thallium, gold and lead, all of which were moved to their correct locations in the Table. Mendeleev did, however, pull back from his prediction of the existence of a new element below zirconium, and he replaced his predicted hafnium with lanthanum—the placement of the rare earth elements was problematic for Mendeleev in both forms of his periodic table, and was not cleared up until the work of Henry Gwyn Jeffries Moseley (10).

As intimated above, deciding which of these candidates is the breakthrough paper becomes a subjective call, made somewhat more so by the fact that three of them are in Russian, and all appeared before the corresponding German versions. Thus, if simple precedence in time is the determining factor, the 1869 Zhurnal paper should get the accolade. But, during the nineteenth century, German was the most authoritative language in science. Almost all Russian chemists could read and write German and French, and many (but not Mendeleev) could also read and write English. The reciprocal situation did not, however, hold: relatively few western European chemists could read Russian, a situation that still obtains today. Thus, because the first published paper detailing what later became known as the Periodic Law is written in Russian, which would undoubtedly have much reduced its impact outside of Russia.

A good example of the impact of this difference in language on the reception of a publication is provided by the Wolff-Kishner reduction. The first paper describing the decomposition of hydrazones by base was published-in Russian-by Nikolai Matveevich Kizhner in March, 1911, in the Zhurnal Russkago Fiziko-Khimicheskago Obshchestva (11); some eighteen months later, at the end of 1912, essentially the same reaction was published—in German—by Ludwig Wolff in Liebigs Annalen (12), without reference to Kizhner's earlier work. Kizhner's paper had also been abstracted, in German, into the Zeitschrift für Chemie, which is where Mendeleev's 1869 paper was also abstracted; the fact that Wolff did not refer to Kizhner's earlier work suggests that Wolff did not regularly read the Zeitschrift, and is probably indicative that the influence of this journal in western European chemistry had waned by that time. The effect of the language of publication, means that the reaction is known today in the west as the Wolff-Kishner reduction rather than the Kizhner-Wolff reduction (as it is known in Russia) because Wolff's paper, in German, was much more widely read by western chemists than Kizhner's, in Russian. This situation, also, may provide yet another example of where the "breakthrough" paper may not be the first paper published on the subject.

There appears to be little disagreement that the origins of Mendeleev's periodic table can be traced to his 1869 textbook *Osnovy Khimii*, and that during the writing of this treatise he came to the conviction that the periodicity he had observed was, in fact, both real, and useful. As is taught in many introductory chemistry textbooks, it was Mendeleev's leap of faith that there were elements not yet discovered, and his prediction

of their existence and their properties—spectacularly confirmed as his predicted elements were discovered, one by one—that separated his predictions from those of Lothar Meyer (13) and John Alexander Reina Newlands (14). However, Mendeleev's textbook was written in Russian, and this reduces its claim to be the breakthrough publication for the concept of periodicity. Likewise, the 1869 publication in the Zhurnal likely had insufficient impact to qualify as the breakthrough paper. In fact, it has been argued by Gordin (15) that, at that point in time, Mendeleev himself had not grasped the epoch-making nature of his discovery, since he had his friend, Nikolai Aleksandrovich Menshutkin (1842-1907), deliver the paper to the Russian Physical-Chemical Society while he, himself, was inspecting cheese factories outside Moscow. Of course, one can also place the interpretation on events that Mendeleev did, in fact, fully realize the importance of his Periodic System, and chose to have his friend present the paper rather than delay its presentation until he could do so in person.

In similar fashion, Mendeleev's 1870 paper in the *Zhurnal* possesses all the hallmarks of the breakthrough paper—it clearly defines the underlying science, corrects some earlier mistakes, and makes the predictions that, when confirmed later, placed the periodic table of the elements on course to become one of the most widely-recognized scientific icons of modern times. But ... it was written in Russian, and that means that its dissemination in western Europe was limited. The language of publication thus becomes an automatic disqualifier for a paper to become the "breakthrough paper."

This analysis leaves us with the two German publications as the possibilities for the breakthrough paper. The earlier of the two is the brief, two-page abstract of the 1869 Zhurnal paper, and it appeared the same year in the Zeitschrift für Chemie. This journal had had a checkered history from its founding by Richard August Carl Emil Erlenmeyer, through its heyday when the editors were R. Fittig H. Hübner (both in Göttingen) and Friedrich Konrad Beilstein (Fëdor Fëdorovich Beil'shtein; like Mendelejeff, in St. Petersburg), to re-emergence in various guises over the next century and a half. Early on, it became an important western outlet for Russian chemists to publish original research papers — Butlerov published his version of structural theory (16) in the Zeitschrift at Erlenmeyer's urging—but this journal's influence fluctuated over time. Nevertheless, its abstracts of papers appearing in Russian became an important part of the dissemination of these papers to a wider audience. At the time that Mendeleev's paper was abstracted by the Zeitschrift, one of the editors was Beilstein, who had become Professor of Chemistry, and Mendeleev's successor at the St. Petersburg Technological Institute, in 1865; Beilstein was a strong advocate of having his Russian colleagues publish their papers directly in the Zeitschrift. However, as noted above, despite the wider readership of the Zeitschrift by comparison with the Zhurnal, the question remains as to whether or not this paper satisfies the high-impact criterion.

For me, the answer to this question was provided by the 1871 paper in the Berichte (9), which was discussed above. In this polemical paper, Mendeleev addresses the questions raised by western chemists. To my mind, this adds unequivocal support to the claim of the 1869 Zeitschrift paper to be the breakthrough paper, since it had clearly attracted the attention of chemists, among them Lothar Meyer, who had been working on a similar arrangement of the elements. It is doubtful that a chemist of Meyer's standing would have commented on a paper in the Zeitschrift at this time had that paper not been, in his eyes, important enough to warrant comment. Whatever his reasons, Meyer's response, and those of his contemporaries in the west, clearly mark Mendeleev's paper in the Zeitschrift as a breakthrough development. But is it the breakthrough paper?

Which brings us to the 1872 paper in the Supplement to Justus Liebigs Annalen der Chemie (8). This paper, too, was a German translation (by Felix Wreden, or Feliks Romanovich Vreden, d. 1878) of the paper (7) that had already appeared in the Zhurnal, and the difficulty it presents is in terms of deciding whether it is a much stronger candidate for the breakthrough paper than the Zeitschrift paper. Certainly, Justus Liebigs Annalen der Chemie was the most established, and influential chemical journal in Europe by the middle of the nineteenth century, and papers published in it were both widely read and influential.

But the question remains, does the 1872 full paper deserve to be the award-winning paper? Despite its greater detail, and fewer errors, it appears that by the end of the nineteenth century, chemists had decided that Mendeleev's 1869 paper in the *Zeitschrift* should be the one credited with the discovery. Thus, although references to the 1872 paper continued, the periodic table itself was dated to 1869, which suggests that Mendeleev's contemporaries and their immediate successors made the decision that the 1869 *Zeitschrift* paper was the breakthrough publication. The reasons for this preference, particularly in light of the persistent references to the 1872 paper, are not clear.

It is interesting to examine how Mendeleev's Table is referred to around the turn of the twentieth century, by which time its validity had been established beyond doubt. In his 1913 textbook, "A New Era in Chemistry," (17) devoted to the rise of physical chemistry, Harry C. Jones makes the statement, "A generalization that fits the facts much better, was the periodic system of the Russian, Mendeléeff, and the German, Lothar Meyer. Mendeléeff in 1869¹ published his now famous periodic table of the elements, and Lothar Meyer discussed his arrangement of the elements, which was essentially the same as that of Mendeléeff, in 1870.2" It is interesting that the reference to Mendeleev's work here was not the Zeitschrift paper of 1869, but the Annalen Supplement paper of 1872, even though precedence was given to the 1869 date. In his 1911 "Theoretical Chemistry," (18) Nernst also uses 1869 as the date of origin of the Periodic Table, but he couples the names of Meyer and Mendeleev, and draws most of his material from Meyer's work.

In conclusion, based on the criteria for the award, and—an admittedly subjective—judgment of the available literature, I came to the conclusion that the 1869 *Zeitschrift* paper should be the one honored. This recommendation was accepted (see Figure 2), and the award plaque was formally presented on October 31, 2013 (Figure 3).

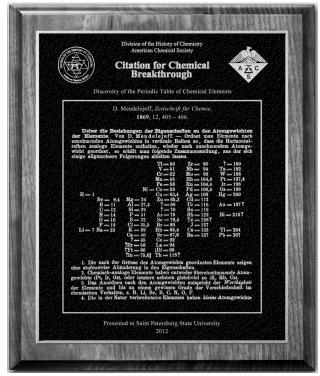


Figure 2. The plaque of the Citation for Chemical Breakthrough award to St. Petersburg State University.



Figure 3. The unveiling of the plaque of the Citation for Chemical Breakthrough award to St. Petersburg State University, adjacent to the statue of Mendeleev in the main hall of the historic Twelve Collegia building by the author (representing HIST, l) and Professor Sergey Sergeevich Ermakov (Vice-Dean of Chemistry, SPBU, r). Photograph courtesy of St. Petersburg State University.

References and Notes

- The transliteration from the Cyrillic alphabet presents a recurring problem for western writers, translators and publishers referring to Russian authors and articles. The exact transliteration used will depend on the writer, and on the language into which the article or name is translated or transliterated. In this paper, I have adhered to my previous practice of transliterating the Cyrillic using the BGN/PCGN romanization system for Russian as the most intuitive for English speakers. In this system, the name of the subject chemist becomes Mendeleev. In the German language publications, the transliteration, Mendelejeff, was used by Mendeleev himself as rendering the pronunciation of his name by German readers the closest to the Russian, but some early English transliterations (e.g. in the 1911 Encyclopaedia Britannica), his name is rendered as "Mendeléeff."
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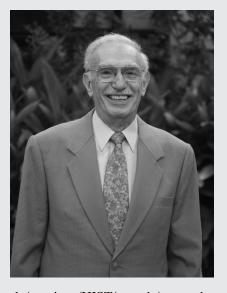
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About the Author

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Bulletin for the History of Chemistry Outstanding Paper Award for 2013

The Division of the History of Chemistry of the American Chemical Society is pleased to announce Professor Stephen J. Weininger as the winner of its 2013 Outstanding Paper Award. His paper, entitled "Chemistry for the 'Industrial Classes': Laboratory Instruction, Mass Education and Women's Experience in Mid-Western Land-Grant Colleges, 1870-1914", appeared in the Bulletin for the History of Chemistry, **2013**, 38(2), 97-108. On July 2, 1862, in the midst of the Civil War, President Abraham Lincoln signed the Land-Grant Colleges Act, commonly known as the Morrill Act after its principal sponsor. The Act's mission statement ensured that, because of their perceived centrality to agriculture, chemistry and other natural sciences would have a predominant place in the curriculum. Weininger's paper tracks each state's divergent ambitions by focusing on course curricula and catalog rhetoric relating to qualitative and quantitative analysis, bedrock courses for numerous majors that provided students with marketable skills. This paper is



available for all to read at the HIST website: http://www.scs.illinois.edu/~mainzv/HIST/awards/paper.php

The 2013 winner, Stephen J. Weininger, was educated at Brooklyn College, CUNY and the University of Pennsylvania, where he received his Ph.D. in 1964. In 1965 he joined the Chemistry Department at the Worcester Polytechnic Institute and became Professor of Chemistry Emeritus in 2005. A former Chair of the HIST Division, he has published extensively in the areas of the history of physical organic chemistry, thermodynamics and chemical representation. Seeing the vital connection between chemistry and culture, he co-founded the Society for Literature and Science (SLS) in 1985, served as its president from 1987-89, and has given numerous talks in this area.

The Outstanding Paper Award is presented to the author of the best paper published in the *Bulletin* for the History of Chemistry during the previous three years, including the award year. The 2013 award is for a paper published in 2011, 2012, and 2013.

DECORATING WITH EXPLOSIVES: THE USE OF AURUM FULMINANS AS A PURPLE PIGMENT

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Supplemental Material

Introduction

The polychrome decoration of terracotta and glazed earthenware using metal oxides was already known since early antiquity, and the decoration of porcelain with overglaze enamels had begun in China during the early Ming Dynasty (1368-1644). A full palette of colors including red, green, yellow, turquoise, violet and black had been developed and was in widespread use by the Chenghua era (1464-1487).

The Meissen Manufactory, despite its initial success as Europe's first hard-paste-porcelain manufactory, had substantial difficulties with overglaze polychrome decoration during the first decade of its existence (1). In his famous Memorandum to the King, of March 28, 1709, Johann Friedrich Böttger (1682-1719) had promised, among other technical advances, the production of "the good white porcelain with the finest of glazes and all the proper painting..." (2). Despite some crude steps taken in that direction (3), the promise of "all the proper painting" was never fully realized during Böttger's lifetime. The Manufactory Commission often expressed its displeasure over the state of the art. So it was with great pride and considerable relief that Manufactory Inspector (4) Johann Melchior Steinbrück (1673-1723) could announce in his 1717 report on the state of the Manufactory the invention of a decorating technique for porcelain (5):

Therefore one should not doubt that one will gradu-

ally discover whatever is still missing [in technology] and introduce it. Just as a short while ago a truly new way of decorating called Mother-of-Pearl or Opal glaze (even though it of course is not a glaze) was applied onto white porcelain, to which it imparts a new and very beautiful appearance.

This new decoration gave the white surface of porcelain a pink to violet lustrous tint with a sometimes mottled and cloudy appearance and later came to be known as Böttger luster. Only a handful of objects from the Böttger period (1710-1719) decorated in this fashion exist today, six (three cups and their associated saucers) are on display at the State Porcelain Collections in Dresden and a cup and saucer are kept in storage at the Metropolitan Museum of Art in New York City. In a subsequent memorandum written in 1719 Steinbrück provides a little more background about the invention (6):

...the Mother-of-Pearl glaze also stems from Böttger, and he taught it to Mehlhorn and Funcke and allowed them to experiment at his expense (as the glaze is made of gold)...

We are told for the first time that gold is a main ingredient of this new decoration. Also, in Steinbrück's view Böttger was the inventor, though he also mentions Böttger's coworker Johann George Mehlhorn and acknowledges the participation of George Funcke. Funcke was listed as master goldsmith and enameller in the Dresden municipal archives (*Ratsarchiv*) from 1692 until 1726. He joined Böttger's circle of close coworkers

in 1710 and was listed as a Meissen employee until May 1713. During this time he was involved in the gilding and early enamel decoration of Böttger porcelain with a rather limited palette of colors. Thereafter he worked as an independent contractor paid piecemeal for his decorative work. Given Böttger's inability to develop reliable polychrome decoration in house, the Manufactory management began viewing reliance on an outside contractor with considerable trepidation. Following Steinbrück's concerns about the confidentiality of trade secrets, Funcke was forced to enter an exclusive contract with Meissen, involving eight types of decoration, encompassing pretty much everything that Meissen offered for sale. Number eight on the list was decoration with mother-of-pearl glaze (Böttger luster) (7).

Our knowledge of Funcke's work comes mainly from periodic memoranda filed by Steinbrück who was also Böttger's brother-in-law and whom he served with great loyalty and devotion. In these memoranda, Funcke is consistently depicted merely as a competent technician following Böttger's instructions. But Funcke was also an accomplished goldsmith with experience in the enameling of gold and silver. Many scholars have therefore suggested that Funcke has not received sufficient credit for his contributions to the development of porcelain decoration. The chemical origins of the "Böttger luster" discussed in this paper will point to a more pivotal role for Funcke in the invention of this decorative technique.

No explicit recipes for Böttger luster dating to the actual Böttger period are known today. The earliest known formal documentation of this process had to await the arrival of that most celebrated porcelain painter of all, Johann Gregorius Höroldt.

The Arrival of Johann Gregorius Höroldt

Böttger died on March 13, 1719, after a protracted illness. In anticipation of Böttger's imminent death Augustus (at that time King of Poland as well as Prince Elector of Saxony) had made arrangements to salvage as much of Böttger's library of books, laboratory notebooks, manufactory-related business documents as possible and any samples of experimental ceramic materials (8). Böttger was under oath to document his research and according to his closest associates kept detailed notes of his work. Nevertheless, no documents describing his experiments after 1708 are known to exist today.

During the rest of 1719 the Manufactory Commission tried to secure the continuation of the business.

Part of that was to protect intellectual property against the incursions of the emerging competition in Vienna. Samuel Stöltzel (1685-1737), one of Böttger's closest associates, and in possession of the *Arcanum*, (the closely guarded secret formula for making porcelain), had defected to the newly founded Vienna Manufactory of Claudius Innocentius du Paquier just two months prior to Böttger's death. Stöltzel's betrayal of the *Arcanum* accelerated the emergence of a second, competing porcelain manufactory in Europe. Fearful of losing its position of monopoly, on June 17, 1719, Meissen signed a contract with Funcke stipulating that he could not sell privately Meissen porcelain decorated in his shop (9).

According to the Saxon State Archives, Funcke was on record as having expertise in the painting of porcelain with the colors black, green, purple, deep purple, blue and red, by employing the same techniques he applied to the enameling on gold and silver (10). Funcke had perfected the techniques of gilding porcelain and stoneware. In contrast, the quality of Funcke's overglaze enamels on porcelain lacked the crispness and vibrancy of color the Meissen Manufactory was destined to achieve within less than a decade after Böttger's death. The turning point came with the arrival of Johann Gregorius Höroldt (1696-1775) on May 16, 1720, a pivotal event that forever changed Meissen's fortunes.

Little is known about Höroldt's early life, prior to his joining the Meissen Manufactory. He was born in Jena in 1696 as the son of a tailor and was probably trained as a draftsman, engraver, or enameller. It is known that in 1718 he was working as a carpet painter in Strasbourg and moved that year to Vienna to continue in the same line of work. Once in Vienna, he quickly established contact with the newly founded Du Paquier Manufactory, probably through the intermediation of Christoph Hunger, an earlier Meissen defector. It was there that Höroldt met and befriended Stöltzel. When a disillusioned Stöltzel decided to return to Meissen, he brought Höroldt with him as some sort of a trophy to mollify the powers that be since defection from Meissen was a serious offense. Höroldt was introduced simply as "an established and well-trained artistic painter."

Thanks to his diligence and artistic talents, within a few years Höroldt became the undisputed leader in the area of porcelain decoration. Nevertheless, as far as the preparation of pigments is concerned he initially depended almost entirely on Stöltzel and David Köhler (1683-1723), another of Böttger's associates (11). One could hardly expect Höroldt to immediately distinguish himself in pigment technology. Within a decade, how-

ever, he was able to integrate the disparate knowledge of individual arcanists into a coherent whole, thus generating an adequately broad palette of colors. Progress did not come easily since Höroldt did not have a workplace within the Manufactory until 1722.

Initially Höroldt worked as an independent contractor with his own staff of painters and was paid by the piece. A series of embezzlements and shady deals under Meissen Manufactory director Carl Heinrich Graf von Hoym were uncovered at the beginning of April 1731. This event led to the demand by the Manufactory Commission to document the intellectual property of the manufactory. On April 12, four leather-bound notebooks with parchment pages were distributed to key people, namely, Samuel Stöltzel, Johann Andreas Hoppe, Johann Georg Schubert and Höroldt to write down "sämtliche Wissenschaften", i.e. their entire knowledge of the manufacturing process. Stöltzel, Hoppe and Schubert had their documentation completed by May 1 of that year. Höroldt did not start writing until Christmas of that year.

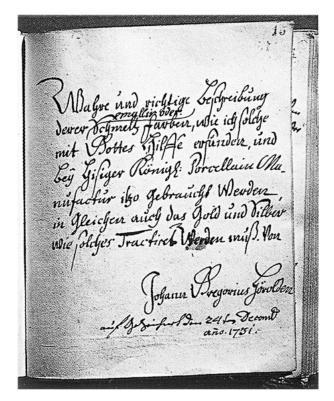


Figure 1. Cover page of Höroldt's book of recipes. The full title is "True and correct description of the enamel or melt colorants that I have invented with the help of God and which are in use in this the Royal Porcelain Manufactory and also the Gold and Silver and how they should be treated, Johann Gregorius Höroldt, entered on the 24th of December of the year 1731"

An overview of the Höroldt recipes from a technological point of view has been published by Seyyfarth (12) and in somewhat more detail by Mields (13). Neither paper gives complete transcripts of the procedures. Höroldt's handwritten book consists of 19 chapters on color and flux recipes, and one chapter on ovens and the firing of painted porcelain (14).

The front page of Höroldt's book of recipes is shown in Figure 1. The text is always on the right side of the notebook. The left side is reserved for notes and clarifications. The chemical operations and processes employed by Höroldt give us a unique insight into the laboratory practices of the period. They can be summarized as follows:

- 1. All starting materials were first calcined at a temperature corresponding to the bisque firing step in the production of porcelain (a temperature scale expressed in degrees was unknown at the time, the actual temperature range for bisque firing is thought to have been 900-1000 °C).
- 2. Mechanical processing (grinding) of the raw materials included quenching from high temperatures for the initial break-up of the ores (for example quartz) as delivered, coarse grinding in iron or brass mortars (with consideration given to which mortar material would introduce the least amount of interfering impurities), separation of particles by size using sieves made of hair, and further grinding. Flotation was also used as an alternative method for the separation of particles by size. Agate mortars were used for fine grinding. Compounding of the powdered ingredients was carried out in dry form.
- 3. Chemical processing included roasting, decomposition using alkalis or acids, and precipitation. The filtering of precipitates was known, but seldom used; decantation was instead the method of choice. Sand baths were used for mild heating and solvent removal.
- 4. Oxidation of metals and alloys like Cu, Pb, Sn, and brass by heating them in air (converting them into what was termed metal ash followed procedures developed previously by potters. The health hazards of vapors released in some of these processes were pointed out.

Höroldt's Recipe for Böttger Luster and its Origins in Alchemy and Early 17th Century Chemistry

Chapter 11 on "How the Mother-of-Pearl or Copper Color is Made" (Figure 2) is the first and only known detailed recipe for Böttger luster. The recipe is six pages long (odd numbered pages 111-121) plus one page (120) containing a brief footnote. We have transcribed and translated the entire chapter. Facsimiles of the handwritten pages, and a modern German transcript and English translation by the author are available as Supplemental Material on the *Bulletin* website. An outline of the recipe is given below:

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Figure 2. Facsimile of the first page of chapter 11 from Höroldt's book of recipes, describing the preparation of the mother-of-pearl or copper color (i.e. Böttger luster). A complete transcript of the text and English translation of the chapter are available as Supplemental Material.

- 1. Bring a gold ducat to red heat, cut it and dissolve it in aqua regia.
- 2. Neutralize the solution by slowly adding *oleum tartari* (concentrated aqueous potassium carbonate) until bubble formation stops and let it stand for a day and dilute it with a pot of hot water.
 - 3. Decant the supernatant and heat to almost dryness
- 4. A warning is given against the explosive nature of the thoroughly dried precipitate that can lead to injury.
- 5. Mix the yellow precipitate 2:1 with lead silicate flux in an agate mortar; to paint apply it as thinly as possible.

6. Prepare *oleum tartari* by calcination of potassium tartrate and dissolve it in the least amount of water possible, remove the insoluble impurities using a filter made of blotting paper.

The footnote on page 120 explains the reasons for preheating the gold coin: "Easier to cut and dissolves faster."

Upon reading the above a chemist should immediately ask the question: "How can this procedure lead to an explosive compound?" The answer to this question can be found in the earliest reported recipe for this material as it appears in the work of the alchemist(s) who wrote under the pseudonym Basil Valentine.

The author of the Valentine corpus represents himself as a Benedictine monk from Rhineland. The first five books, ostensibly by Basil Valentine, were published by Johann Thölde (1565-ca.1614). Thölde was a chemist, part-owner of the salt mines in Frankenhausen am Kyffhäuser (Thuringia), and member of the city's Chamber of Councilors (Rathskämmerer). He claimed to be in possession of the original Valentine manuscripts. No evidence for a person by the name of Basil Valentine exists prior to the publication of the manuscripts by Thölde who probably is the real author of most of the content. The books were written no earlier than 1590 and reflect the ideas of Paracelsus. Thölde also published the work on antimony of another Paracelcist, Alexander von Suchten (1520-1575). A thorough refutation of both the existence of a 15th century monk by the name of Basil Valentine and of the early date for the Valentine corpus claimed by Thölde (which, if true, would have predated the work of Paracelsus (1493-1541)) was given by Stillman (15). More recently, Principe (16) has given an extensive analysis of the Valentine corpus in The Secrets of Alchemy. A particular point brought up by Principe is Valentine's attempt at detoxification of antimony by using the Paracelsian principle of Scheidung (meaning separation of properties rather than components), a point to which we shall return shortly.

In his longest book, *The Last Will and Testament*, Valentine gives a recipe for an explosive gold compound. A facsimile of the passage describing the preparation of this explosive "gold calx" (*Goldkalck* in the original German text) taken from the first English edition of the book (17) is reproduced in Figure 3. The Valentine procedure, outline below, is essentially identical to Höroldt's recipe for Böttger luster, which it predates by at least a century, with one key piece of information in the first step not mentioned by Höroldt.

- 1. Prepare aqua regia by dissolving 8 lot (4 ounces) of *sal armoniac* (ammonium chloride) in one pound of good strong *aqua fortis* (nitric acid).
 - 2. Dissolve thin gold foils in aqua regia.
- 3. Neutralize solution with concentrated potassium carbonate
- 4. Wash precipitate up to twelve times with water followed by decantation.
- 5. Decant the supernatant and allow the precipitate to dry but not over fire.
- 6. Warning that the least amount of heat ignites the powder leading to great damage.
- 7. Its fulminating quality can be removed by boiling it in strong vinegar for 24 hours, "dulcifying" it i.e. dilut-

ing it with water (presumably until the taste is no longer objectionable) and drying it. The blood red powder can be driven *per alembicum* and can be converted to gold by means of coagulation.

In step one we learn that Valentine makes aqua regia by using a mixture of nitric acid and ammonium chloride, not hydrochloric acid (as modern chemists would do), a point about which Höroldt is silent. Actually this formulation for aqua regia using ammonium chloride is given already by Georgius Agricola (1494-1555) in *De Re Metallica* (18). As we shall see in the next section the presence of ammonium ions is essential to the formation of this explosive precipitate.

The naming of this material during the first quarter of the 17th century was still in flux. In his *Tyrocinium Chymicum* (first published in 1610) iatrochemist Jean

Of Sulphur of Sol.

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to proceed in, and to bring each into its certain frate and order.

Take the Philosophick Sulphur, which in order is the second principle, and is extracted with the spirit of Mercury, pour it on the white body of the King, digest it for a month in a gentle Balny, then fix it in ashes, and at last in sand, that the brown powder may appear, then melt it with a sluxing powder made of Saturn, then will it be malleable and fair Gold, as it was formerly, in colour and vertue nothing desective.

But note, the Salt must not be taken from the Solar body, of which I made mention formerly, in a repition of the XII. Key, where you may read of it. There may be prepared yet in another manner a transparent Vitriol, from Gold in the following manner.

Take good Aqua Regis made with Sal armoniae. one pound, id est, dissolve four ounces of Salmiac in Aquafort, then you have a strong Aqua Regis, distill and rectifie it often over the helmet, let no feces stay behind, let all that ascends be transparent. Then take thinly beaten Gold rolls, cast tormerly through Antimmy, put them into a body, pour on it Aqua Regis, let it dissolve as much as it will, or as you can diffolve in it : having diffolved all the Gold, pour into some Oyl of Tartar, or Salt of Tartar dissolved in fountain water, till it begins to hifs, having done hifsing, then pour in again of the Oyl, do it so long that all the dissolved Gold be fall'n to the bottome, and nothing more of it precipitate, and the Agna Regis (Lar up. This being done, then cant off the Aqua Regis from the Gold calx, edulcorate it with common water, eight, ten, or twelve times : the Gold calx 186 Of Sulphur of Sol.

being well fetled, cant off that water, and dry the Gold calx in the air, where the Sun doth not shine, do it not over a fire, for as soon as it feeleth the leaft heat it kindleth, and great damage is done, for it would fly away forcibly, that no man could flay it. This powder being ready alfo, then take strong Vinegar, pour it on, boil it continually over the fire in a good quantity of Vinegar, full stirring it, that it may not stick unto the bottome, for xxiv. hours together, then the fulminating quality is taken from it: be careful you do not endanger your felt: cant off that Vinegar, dulcine the powder, and dry it. This powder may be driven per alembieum without any corronve, bloud-red, transparent and fair, which is strange, and uniteth willingly with the spirit of wine, and by means of coagulation may be brought to a Spiar body.

Do not speak much of it to the vulgar: if you receive any benefit by and from my plain and open information, be thus minded, to keep these mysteries secret still to thy dying day, and make no shew of it, else thou art naked and lyest open to the Devils temptations in all thy ways: therefore pray give attention to what I shall tell thee, for I will impart unto thee this Areasum also, and entrust thee upon thy conscience with it.

Take good spirit of wine being brought to the highest degree, let fail into it some drops of spirit of Tartar, then take thy Gold powder, put to it three times as much of the best and subtilest common slowers of sulphur, grind these together, set it on a stat pan under a muste, give to it a gentle fire, let the Gold powder be in a glowing heat, put it thus glowing into the spirit or wine,

cant

Figure 3. Passage describing Valentine's procedure for making gold calx (later known as aurum fulminans) taken from Ref. 17.

Beguin (1550–1620) gives a recipe identical to that of Basil Valentine (19). A footnote on p. 293 of the 6th edition that appeared in 1625 states: "The Germans say das Schlaggoldt, in Latin [it is called] aurum fulminans because it gives forth a very sharp sound like thunder as it explodes. [Oswald] Kroll calls it aurum volatile" (20). To complicate matters further, in the text itself Beguin uses the term "Ceraunochryson" derived from the Greek keraunos (thunderbolt) and cruson (golden). Also in the German literature after the middle of the 19th century one typically encounters the word "Knallgold." At the present time, however, the term used most commonly is aurum fulminans and that is what we shall use throughout the remainder of this paper.

What is Aurum Fulminans?

At this point a brief review of the chemistry of *aurum fulminans* would be useful for the purposes of the subsequent discussion. The name *aurum fulminans* and the shock-sensitive nature of this material might lead one to believe that it is simply gold fulminate (AuCNO) a salt of fulminic acid (HCNO). This is definitely not the case. The reaction of gold with aqua regia yields AuCl₃. In neutral to slightly alkaline media mild reducing agents convert Au(III) to Au(I). The formation of AuOH from Au(III) and hydrogen sulfite ion, for example, is a well-known reaction (21).

$$Au^{3+} + HSO_3^- + 2H_2O \rightarrow$$

 $HSO_4^- + 3H^+ + AuOH \text{ (dark violet precipitate)}$

Ammonia can also act as a mild reducing agent and when reacted with Au³⁺ yields the highly explosive compound gold(I) hydrazide which indeed is *aurum fulminans*.

$$Au^{3+} + 2NH_3 \rightarrow AuNHNH_2 + 3H^+$$

It should now be evident why aqua regia prepared in the historical manner is so important to the success of this synthesis. Already during the early 17th century several authors pointed out that using sodium chloride rather than ammonium chloride as the source of chloride ions in aqua regia does not lead to an explosive product. In fact Rudolf Glauber (1604-1670) observes that using *spiritus urinae* (probably ammonium carbonate) instead of *oleum tartari* for the neutralization/precipitation step leads to a better explosive (22) (presumably by improving the reaction yield).

The detoxification of antimony discussed by Principe and mentioned in the previous section is not the only instance when Valentine entertains the possibility of selectively removing an undesirable property from a material. Valentine describes how heating aurum fulminans in vinegar under constant stirring for 24 hours (!) yields a "bloud-red" product that is not explosive. This product can be converted to gold through the process of "coagulation." We have not performed actual replication experiments as part of our research. We speculate that the "removal" of the fulminating property observed by Valentine involves decomposition of gold hydrazide. The "bloud red" color could be caused by finely divided gold in suspension or, if an iron implement was used for stirring, it could be due to the formation of iron acetate as in the case of antimony. While the removal of the undesirable fulminating property through chemical means is illusory, surprisingly the suppression of uncontrolled fulminations by physical means proved feasible, as we shall see in the next section.

The Use of *Aurum Fulminans* in the Decorative Arts

Aurum fulminans is a highly unstable compound that is recorded on numerous occasions as having caused substantial physical damage and even a few casualties. Could such a material have found any use in the decorative arts of the 17th and 18th centuries, particularly in a manufactory setting such as Meissen? In this section we shall present archival evidence showing that aurum fulminans was indeed commonly used by jewelers and enamelers long before the time of Höroldt and Böttger, and conclude by reexamining the role of the goldsmith Georg Funcke in the invention of Böttger luster.

The purple color or lustrous coppery tone of Böttger luster should not be confused with another gold-based deep-red to purple colorant known as the Purple of Cassius, though both owe their color to the formation of metallic gold nanoparticles. In the case of the Purple of Cassius, the nanoparticles are precipitated by the addition of stannous chloride to AuCl₃ and are stabilized by the colloidal hydrated SnO₂ ("stannic acid") produced during the redox reaction. The Purple of Cassius was well known, widely used in the production of ruby glass and as enamel color on ceramics and is still in use today. Its colloidal nature was determined by Richard Zsigmondy (1865-1929). The study became part of the body of work for which Zsigmondy was awarded the 1925 Nobel Prize in Chemistry. An excellent review of the history of the

Purple of Cassius was published by Hunt (23). The preparation of the Purple of Cassius and its application to porcelain painting are described separately, in chapter 10 of Höroldt's book of recipes (14). By contrast, no Sn is detected in Böttger luster by X-ray fluorescence (24). As we shall see, the finely divided gold is produced by the thermal decomposition of aurum fulminans.

The earliest detailed account of the physical and chemical properties of *aurum fulminans* was given by Torbern Bergman (1735-1784) in his *Opuscula Physica et Chemica* first published in 1780. Bergman was professor of chemistry and mineralogy at the University of Uppsala, a member of the Royal Swedish Academy of Sciences and Fellow of the Royal Society of London. He was a proponent of the phlogiston theory and a follower of Johann Joachim Becher (1635-1682/85) and Georg Ernst Stahl (1660-1734). The *Opuscula* (Essays) comprise six volumes and are a collection of Bergman's scientific papers and memoirs. Dissertation XVII (25) titled "Of the Fulminating Calx of Gold" describes

...experiments, which are partly new, and partly such as have been described by others but carefully revised and corrected...

In the opening paragraph of the first section Bergman informs us that he undertakes the study of this material in the belief that an understanding of the various phenomena associated with its explosive nature:

Historical Introduction

Although the wonderful fulminating property of gold was known at least in the 15th century, it has not been yet examined by the philosophers so as to determine the cause of the prodigious noise and stupendous explosive force; yet in this explosion there occur phænomena highly worthy of attention-phænomena whixh not only indicate very singular properties, but are of such a kind that the causes of them, well understood, must certainly throw great light upon the theory of chemistry.

Dissertation XVII consists of 14 sections, and an in-depth critique of the rather lengthy essay is outside the scope of the present paper (26). Bergman does make several observations relevant to our topic, and we shall restrict our discussion to these salient points.

In the *Historical Introduction* Bergman recognizes Basil Valentine as the "perhaps first who has clearly described the method of communicating this property to gold" though the opening paragraph implies that he has fallen for Thölde's hoax of an early 15th century authorship. Quite telling are his quotes of Georg Ernst Stahl (1660-1734) and Robert Dossie (1717-1777):

The celebrated Stahl says, that *aurum fulminans*, treated with sulphur, as hereafter described, *is used as a pigment by goldsmiths and enamellers* [emphasis added by the author]. Dossie mentions this as a valuable secret.

Here we have a significant first clue to the use of this material as a pigment. A further clue as to how *aurum fulminans* might have been handled safely comes in section IV titled "*Means by which the fulminating property may be destroyed*":

...by the addition of a dry substance of any sort provided it be well pulverized, and intimately mixed with the *aurum fulminans* by trituration, so that the particles of the latter may be separated as much as possible.

Dossie provides a more detailed account of the use of *aurum fulminans* as an artist's material in *The Handmaid* to the Arts, a book first published in 1758, roughly two decades before the *Opuscula* (27). The book, dedicated "to the Noblemen and Gentlemen Members of the Society for the Encouragement of Arts, Manufactures, and Commerce" has been described as "by far the best treatise on the practice of the industrial arts" (28). It consists of three Parts each divided into several chapters, which are in turn subdivided into sections. Chapter IX deals with enamel painting and in Section III of that chapter he deals with the colorants themselves. About the use of *aurum fulminans* he writes (29):

When a red color is wanted which verges greatly on the purple, a precipitation of the gold should be made by means of any fixt alkaline salt. Which may be thus done.

Dossie then proceeds to outline the same procedure as Valentine and follows it with the remarks:

The powder thus produced is called *aurum fulmi-nans*, from its quality of exploding when exposed to a moderate heat: which must therefore be carefully guarded against in the use of it, by keeping it out of the reach of any such heat till it be mixed with the flux for enameling.

Thus addition of the flux makes the handling of the material safer, an observation that, as we have already seen, Bergman was able to generalize to all admixed powders.

A reference to the use of *aurum fulminans* in the decorative arts prior to the time of Böttger and Funcke can be found in a little book, *Sol Sine Veste* (*Gold without Vestments*) by Johann Christian Orschall. Very little is known about Orschall's biography (30). He was trained in alchemy and the art of amalgamation (used in the mining

of gold and silver) by Johann Heinrich Rudolf in Dresden. In 1684 he was appointed Inspector-General of Mines to Landgrave Carl of Hessen-Kassel because of his promise to greatly improve the yields of the mines at Frankenberg, a task in which he failed and was terminated from his position in 1687. His book was published the year of his appointment, describing the Purple of Cassius one year before the appearance of Cassius' (the younger's) own book, *De Auro* in 1685 (31). Orschall's primary concern in this book was to devise ways to decompose gold into its constituent parts such that it could not be reconstituted, a key step in the quest for transmutation. He describes thirty experiments, two of which are relevant to our topic. As part of experiment 26 Orschall observes (32):

...I would like to concern myself [with the question] whether the beautiful red comes from gold or whether the salts have something to do with it. What motivates me to raise this question is the gold purple used a lot for painting, which the goldsmiths use to paint glass enamels, the preparation of which is much too well known and not necessary to repeat here, except to remark that it is aurum fulminans...

He then proceeds to recount an explosion he experienced while working with *aurum fulminans* that completely destroyed his expensive jasper mortar and burned him in the face. This somehow brings him to his 27th experiment (33):

...I have observed this as my 27th experiment, if I want to know whether my gold purple will turn out well I take some of it before it is mixed with flux, hold it to the light [flame] and the stronger and more [loudly] it explodes the more beautiful it will be afterwards...

The sources quoted so far suggest that by the middle of the 17th century goldsmiths were routinely using *aurum fulminans* as a purple colorant in enameling.

Concluding Remarks: Implications for the History of Art

In this paper we have examined the history of a gold compound with, as Bergman wrote, "singular properties" concentrating on its practical use as a colorant in the decorative arts. The evidence assembled from various sources has implication for the history of art, especially the history of early 18th century European porcelain.

Meissen historians have suggested periodically, Lübke as recently as 2004 (34), that *aurum fulminans* is too unstable to be used in ceramics decoration and that the recipe is, somehow, an attempt at misdirection by Höroldt motivated by his penchant for secrecy. This view is fueled in part by the attempts of early 20th century Meissen historians and the Manufactory itself to shroud this technique in secrecy and mystique. The present work should lay to rest any speculation that *aurum fulminans* was actually never used.

More significantly, the documents examined here should elevate the role the goldsmith Funcke played, in the original invention of Böttger luster. Walcha (11) suggests that in his search for usable overglaze colors, Böttger probably sought the advice of goldsmiths who knew how to fire low melting silicate-based colorants on noble metals in a variety of ways. Funcke, a wellestablished Dresden enameller prior to his association with Böttger was undoubtedly familiar with the use and safe handling of aurum fulminans. Enamellers used low melting fluxes unsuitable for porcelain painting, possibly one of the reasons why Böttger could not adopt their formulations for his purposes. The use of inappropriate fluxes may be the cause for the mottled appearance of the decoration on pre-1720 objects. While the fluxes used by Höroldt have been amply described and their composition studied by non-destructive techniques like X-ray fluorescence on numerous occasions, this author is not aware of comparable measurements on objects decorated by Funcke. This essay might hopefully provide the impetus for further research in this area. With the additional insights about how aurum fulminans was used in enameling one could also entertain laboratory replication experiments to better understand the details of the procedures used to apply Böttger luster on Meissen porcelain. Replication of historic materials and processes is an increasingly important research tool for a deeper understanding of materials science issues in cultural heritage objects.

Finally while the use of *aurum fulminans* appears to have been discontinued in Meissen after 1735 (35), it persisted considerably longer as a decorative technique in Great Britain. Thus in *The Botanic Garden*, an unusual book published in 1791, combining poetry and technology in an attempt to popularize the science of the day, Erasmus Darwin, grandfather of Charles, wrote (36):

The fine bright purples or rose colours which we see on china cups, are not producible with any other material except gold; manganese indeed gives a purple, but of a very different kind.

[Darwin goes on to discuss using the Purple of Cassius]...

I am informed that some of our best artists prefer aurum fulminans, mixing it before it has become dry, with the white composition or enamel flux; when once it is divided by the other matter, it is ground with great safety, and without the least danger of explosion whether moist or dry. The colour is remarkably improved and brought forth by long grinding, which accordingly makes an essential circumstance in the process.

Acknowledgment

We would like to thank the Staatliche Porzellan-Manufaktur Meissen GmbH - Historische Sammlungen for facsimiles of the pages from the Höroldt Recipe book.

Supplemental Material

A color photograph of a Meissen cup and saucer decorated with Böttger luster, courtesy of the Metropolitan Museum of Art, as well as facsimiles of the handwritten pages of Höroldt's recipe and a modern German transcript and English translation by the author, can be found in the Supplemental Material for the *Bulletin for the History of Chemistry* at the journal's website,

www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

References and Notes

- 1. The process of making porcelain was a closely guarded Chinese trade secret until the reinvention of the basic formulation by Johann Friedrich Böttger, Ehrenfried Walther von Tschirnhaus (1651-1708), and their assistants, the so-called Contubernium, sometime in late 1707 and definitely by the beginning of 1708. Augustus the Strong, Prince Elector of Saxony and King of Poland, signed a decree stating the intention of founding a porcelain manufactory on Jan. 24, 1710. The actual manufactory was founded in the city of Meißen on June 6 of the same year, and is still in operation today. See for example, N. Zumbulyadis, "Böttger's Eureka!: New Insights into the European Reinvention of Porcelain," *Bull. Hist. Chem.*, 2010, 35, 24-32.
- "das guthe weisse Porcellain samt der allerfeinsten Glasur und allem zubehörigen Mahlwerck..." Staatsarchiv Dresden, Loc. 1339, vol. I Johann Friedrich Böttigern und deßen Manufacturen betr., 1707-1719.
- 3. Zimmermann depicts a pair of beakers with primitive polychrome enameling, one glazed the other unglazed, presented by Böttger to Augustus the Strong in 1710. See E. Zimmermann, *Die Erfindung und Frühzeit des Meissner Porzellans*, Druck und Verlag von Georg Reimer, Berlin, 1908, Figure 70, p 169.
- 4. The Manufactory Inspector was roughly equivalent to the chief operating officer of a modern day corporation.

- Similarly, the Manufactory Commission was akin to today's board of directors.
- 5. Menzhausen, Johann Melchior Steinbrück Bericht über die Porzellanmanufaktur Meissen von den Anfängen bis zum Jahre 1717; Kommentar, Transkription und Glossar, Edition Leipzig, 1982, p. 228. "...dahero nicht zuzweifeln, man werde das übrige, so noch fehlet, ebenfalls nach und nach finden, und herbÿe bringen. Wie denn vor kurtzen würklich eine neüe Arth von embellissement, so man Perlen Mutter- oder Opal-Glasur nennet, (: ob es wohl keine Glasur ist:) auf das weiße porcelain gebracht worden, so demselben ein neües und sehr schönes Ansehen giebet."
- 6. J. M. Steinbrück, Meissen Manufactory Archives, Dec. 30, 1719, cited by R. Rückert, "Biographische Daten der Meißner Manufakturisten des 18. Jahrhunderts", Bayerisches Nationalmuseum, München, 1990, 146-147. "...Perl-Mutterglasur so auch von Böttgern herrühret, der solche Mehlhorn und Funcke gelehret, und auf seine Kosten (weil sie aus Golde bestehet) experimentiren lassen..."
- Rückert ref. 6. See also I. Menzhausen, "Das rothe und das weiße Porcellain" in "Johann Friedrich Böttger; Die Erfindung des europäischen Porzellans" R. Sonnemann and E. Wächtler, Eds., Büchergilde Gutenberg, 1982, 298-299.
- 8. Ref. 3 (Zimmermann), Ch. VII, pp 244-271.
- 9. Ref. 7 (Menzhausen), p 299.
- 10. Ref. 3 (Zimmermann), p 172.
- 11. For an account of Höroldt's first year in Meissen see O. Walcha, "Höroldts erstes Arbeitsjahr," *Mitteilungsblatt der Keramikfreunde der Schweiz, Nr. 47*, **1959**, 28-31.
- 12. R. Seyyfarth, "Johann Gregor Höroldt als Chemiker und Techniker," *Mitteilungsblatt der Keramik Freunde der Schweiz*, **1957**, 22-25.
- M. Mields, "Die Entwicklung der Aufglasurpalette des europäischen Hartporzellans bis 1731 mit besonderer Berücksichtigung der Arbeiten von Johann Gregorius Höroldt," Keramische Zeitschrift, Nr. 8, 1963, 15, 453-450
- 14. The chapters as listed by Mields (ref. 13) are:
 - 1. Fluxes
 - 2. Red pigments
 - 3. Brown pigments
 - 4. Black pigments with Manganese
 - 5. Yellow pigments
 - 6. Green and bluish-green
 - 7. Blue (including wet chemistry for the preparation of pure cobalt compounds)
 - 8. Optical black (as mixture of pigments)
 - 9. Precipitation of silver
 - 10. Preparation of the purple color (this procedure is essentially identical to the preparation of the Purple of Cassius and used tin (II) to precipitate nanoparticles of metallic gold which vary from red to purple to blue depending on size).
 - 11. Mother-of-pearl or copper luster (=Böttger luster)

- 12. Dissolution and precipitation of gold
- 13. Japanese yellow
- 14. Flux for sea-green (Celadon)
- 15. East Asian (overglaze) blue
- 16. Old Japanese purple
- 17. Flux using potash
- 18. The application of overglaze ground colors
- 19. Oven and firing of enameled goods
- 20. Brown highlighting
- J. M. Stillman, "Basil Valentine: A Seventeenth–Century Hoax," *The Popular Science Monthly*, 1912, 81, 591-600.
 E. O. von Lippmann suggests that chemists in the 17th century already knew that Thölde was the real author of the Valentine corpus, see E. O. von Lippmann, *Entstehung und Ausbreitung der Alchemie*, Vol. 1 Verlag von Julius Springer, Berlin, 1919, 640.
- L. M. Principe, *The Secrets of Alchemy*, The University of Chicago Press, Chicago and London, 2013, 137-158.
- 17. B. Valentine, *Last Will and Testament of Basil Valentine, Monke of the Order of St. Bennet*, Edward Brewster, London, 1671, 185-186. The frontispiece points out "Never before Published in English," and "are to be sold at the sign of the *Crane* in St. Pauls Church-yard."
- 18. G. Agricola, *De Re Metallica*, translated from the first Latin edition of 1556 by H. C. Hoover and L. H. Hoover, New York, Dover Publications, Inc., 1950, 441. On p 354 of the same book the translators indicate that aqua regia was known prior to 1400 AD. According to some scholars the knowledge goes back to the Jabirian Corpus (the writings of the 8th century Islamic alchemist Jabr ibn-Hayyam), while others point to an Italian origin around 1300 AD, see for example, E. O. von Lippmann, *Entstehung und Ausbreitung der Alchemie*, Vol. 1 Verlag von Julius Springer, Berlin, 1919, 487-488.
- 19. J. Beguin, *Tyrocinium Chymicum E Naturae Fonte et Manuali Experientia Depromptum*, Workshop of Christophorus Glückradt, 1625, 292-295.
- 20. Ref. 19, p 293. "Germanicis dicitur das Schlaggoldt Latinis aurum fulminans, id est, quod instar fulminis dissiliendo fragorem acutissimum edit: Crollio vero vocatur aurum volatile." Beguin here is referring to Basilica Chymica by Oswald Kroll (1563-1609), first published in 1608 (see for example p 297 of the 1610 edition).
- 21. See for example, A. F. Holleman and E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter & Co., Berlin, 1964, 476-478.
- 22. R. Glauber, De Purgatorio Philosophorum oder von dem Fegefewer der Weisen, Johan Waesberge, Amsterdam, 1668, 38, (note old German spelling of Fegefeuer in the title). Angelus Sala writing in the first half of the 17th century mentions that aurum fulminans cannot be prepared if hydrochloric acid is used to make aqua regia instead of ammonium chloride.
- 23. L. B. Hunt, "Gold based glass and enamel colours," *Endeavour, New Series*, **1981**, *5*, 61-67. Hunt points out that already in 1857 Michael Faraday in his Bakerian Lecture to the Royal Society casually remarked that "I believe the

- Purple of Cassius to be essentially finely divided gold associated with more or less of oxide of tin." M. Faraday, "Experimental Relations of Gold (and other Metals) to Light," *Phil. Trans. R. Soc. Lond.*, **1857**, *147*, 145-181. It appears that the same conclusion was reached by Pierre Joseph Macquer in his *Dictionnaire de chymie* eighty years earlier as reported by T. P. Hanusa (abstract, HIST 3, 246th ACS National Meeting, Indianapolis, IN, 2013).
- 24. D. Lübke, "Böttger-Lüster," Keramos, 2004, 185, 13-22. Lübke reports that fourteen porcelain objects decorated with Böttger luster and dating to 1723-1730 were examined by Alfons Stiegelschmitt of the University of Erlangen using X-ray fluorescence. No tin was detected in any of them.
- 25. T. Bergman, *Physical and Chemical Essays* (translated by E. Cullen from the original Latin *Opuscula Physica et Chemica*), J. Murray, London, 1784, vol. 2, 134-164.
- 26. Bergman reports several other noteworthy observations and experimental results that may be of interest to the chemistry historian. In section II he writes "the necessity of employing volatile alkali (i.e. ammonia) in this operation was but little regarded until the present century." He confirms that the precipitate is yellow. Bergman, known for his contributions to the techniques of gravimetric analysis, also reproduces Becher's earlier result that gold calx thoroughly washed and dried exceeds the weight of the gold employed by 1/5 implying a calx to original gold weight ratio of 1.2. This is a remarkably accurate result for the times, when compared to the exact ratio of 1.16 based on the hydrazide structure. In section III he examines the physical and chemical properties of the material, interesting for our purposes is the observation that "When carefully and gradually exploded in a glass phial, it leaves a purple soot." The final section XIV titled "The Phenomenon of Fulmination Explained" (5 pages long) gives a phlogistic interpretation of the phenomenon and should be of interest to scholars of the phlogiston theory.
- 27. R. Dossie, "The Handmaid to the Arts," Nourse, London, 1763.
- 28. For a detailed, two-part biographical essay on Dossie and his work see F. W. Gibbs, "Robert Dossie (1717-1777) and the Society of Arts," *Ann. Sci.*, **1951**, 7, 149-172; F. W. Gibbs, "Robert Dossie (1717-1777)," *Ann. Sci.*, **1953**, 9, 191-193.
- 29. Ref. 27, p 257.
- F. W. Strieder, Grundlagen zu einer Hessischen Gelehrten und Schriftsteller Geschichte vol. 10, Griesbach Kassel, 1795, 107-110. K. C. Schmieder, Geschichte der Alchemie, Verlag der Buchhandlung des Waisenhauses, Halle, 1832, 454.
- 31. Ref. 23, p 63.
- 32. J. C. Orschall, *Sol Sine Veste*, Augsburg, 1684, (p 66 of the 1742 edition). "...mich nicht unbillig bekümmern ob dann diese schöne Rothe gewiß und eigentlich vom Gold herrühre oder ob etwan die Salia nicht etwas darbey thun möchten. Dieses nun zu erwegen, bewegt mich das schon zu viel mahlen gemelte Gold // Purpur, damit die

- Goldschmiede auf ihr Amulir-Glaß zu mahlen pflegen, dessen Bereitung als zu wohl bekannt, und hier nicht unnöthig zu wiederhohlen, ausser zu melden daß es ein Aurum Fulminans seye...."
- 33. Ref. 32, p 68. "... wann ich wissen will ob mein Gold//
 Purpur schön wird so nehme ich etwas darvon und ehe es mit Fluß versetzet wird halte es in ein Licht und je stärker und mehrer es knallet je schöner es hernacher wird..."
- 34. Ref. 24. Lübke makes a particularly strong statement on p 14 with the ironic remark that in Meissen, nobody has ever reported regular explosions during porcelain firing, "Nirgends wird überliefert, dass es beim Brennen regelmäßig zu Explosionen kam."
- 35. The reasons for the discontinuation of Böttger luster have never been spelled out in company documents. The most likely explanation is that this type of decoration fell out of favor with the customers who found opulent gilding more to their taste. So the decision probably reflects rational resource allocation.
- E. Darwin, *The Botanic Garden*, London, 1791, 184, see Note XXI on Enamels.

stadt, in Germany, and his Ph.D. in Physical Chemistry from Columbia University in 1974. In March 1976 he joined the Eastman Kodak Research Laboratories where he worked as a research scientist until his retirement in June 2005. He is the author of over sixty scientific publications focusing on the application of solid-state nuclear magnetic resonance to problems in materials science. Dr. Zumbulyadis is also a collector of 18th century German porcelain and since his retirement, he is active as an independent scholar in the area of ceramic history. His general research interests include topics at the intersection of the history of chemistry and the history of art. He has written several articles published in art historical journals and has lectured on the subject at major museums and universities. He is currently working on the application of solid-state NMR methods to the characterization and conservation of cultural heritage objects jointly with the Metropolitan Museum of Art, the University of Delaware, and most recently the Rochester Institute of Technology.

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The Partington Prize 2014

The Society for the History of Alchemy and Chemistry is delighted to announce that the 2014 Partington Prize has been awarded to Evan Hepler-Smith (Princeton University), for his article "Just as the Structural Formula Does': Names, Diagrams, and the Structure of Organic Chemistry at the 1892 Geneva Nomenclature Congress."

SHAC is also pleased to announce that Joel Klein (Indiana University, Bloomington) has been highly commended for his essay, "Daniel Sennert, the Philosophical Hen, and the Epistolary Quest for a (Nearly-)Universal Medicine." Both essays will be published in the Society's journal, Ambix.

The Partington Prize was established in memory of Professor James Riddick Partington, the Society's first Chairman. It is awarded every three years for an original and unpublished essay on any aspect of the history of alchemy or chemistry. The prize consists of five hundred pounds (£500).

The Partington Prize and certificate of commendation will be presented at a ceremony at the History of Science Society Annual Meeting, held this year from 6-9 November 2014 in Chicago. Further details will be available nearer the time.

Congratulations to our winners!

ON THE HISTORY OF PRUSSIAN BLUE: THOMAS EVERITT (1805-1845) AND EVERITT'S SALT

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Introduction

Recently, we reported several aspects of the history of the blue pigment, Prussian Blue (1). The reduced form of Prussian Blue is a white powder that is frequently called Everitt's salt. In this article, through a short biography of this white powder's namesake, English chemist Thomas Everitt, we examine how this substance came to be known as Everitt's salt.

Everitt's Salt: Ferrous Ferrocyanide

Ferrous ferrocyanide, or iron(II) hexacyanoferrate(II), is the fully reduced form of Prussian Blue. The substance is also known by alternative names, such as Prussian White, Berlin White or, historically, Williamsons's salt (2) or white prussiate of iron. The name Everitt's salt has been used for more than 170 years and is still used today (3).

Ferrous ferrocyanide is formed by precipitation upon mixing an aqueous solution of hexacyanoferrate(II) with a solution of iron(II) salt(s). Everitt's salt can also be produced by reducing Prussian Blue either by using a reducing compound or by electrochemical means. Alternatively, Prussian Blue (iron(III) hexacyanoferrate(II), ferric ferrocyanide) can be prepared through the oxidation of Everitt's salt. Air oxidizes ferrous ferrocyanide rapidly to create Prussian Blue. The reversible electrochemical redox reaction between the uncolored Everitt's

salt and the deep blue colored Prussian Blue is the basis for the use of Prussian Blue as an electrochromic material (4). The reduction of Prussian Blue to Everitt's salt by certain reducing substances is one cause of the sometimes observed fading of its blue color in paintings (5). Everitt's salt is also temporarily formed by photochemical reduction when cyanotype photographs are overexposed to light (6). In the modern production process for the pigment Prussian Blue, Everitt's salt is formed as an intermediate product. In this industry, the pasty mixture of white ferrous ferrocyanide with water is often called white paste (7). The paste is oxidized using hydrogen peroxide, alkali metal chlorate or dichromate to create the end product of Prussian Blue.

The key publication by Thomas Everitt (1805-1845), which led to the name Everitt's salt, was written in December 1834 and published in February 1835 in *The London and Edinburgh Philosophical Magazine and Journal of Science* (8) under the title "On the Reaction which takes place when Ferrocyanuret of Potassium is distilled with dilute Sulfuric Acid; with some Facts relative to Hydrocyanic Acid and its preparation of uniform strength." In this article (see Figure 1), Everitt describes his experiments to prepare dilute aqueous solutions of hydrocyanic acid for medical and chemical purposes. His goal was to provide a method to reproduce dilute aqueous solutions of hydrocyanic acid with a defined concentration.

XV. On the Reaction which takes place when Ferrocyanuret of Potassium is distilled with dilute Sulphuric Acid; with some Facts relative to Hydrocyanic Acid and its preparation of uniform strength. By Thomas Everitt, Esq., Professor of Chemistry to the Medico-Botanical Society, &c.*

(1.) A S the decomposition of the ferrocyanuret of potassium by means of sulphuric acid is likely to become the only method by which hydrocyanic acid will be prepared for chemical and medical purposes, on account of the cheap rate at which this salt is now to be had chemically pure; and as in all operations of this sort the more exactly we adhere to the proportions indicated by an accurate knowledge of the na-

• Communicated by the Author.

Third Series. Vol. 6. No. 32. Feb. 1835.

Figure 1. The title and the first lines of Thomas Everitt's article from 1835 (8), which led to the name of Everitt's salt for the reduced colorless form of Prussian Blue.

The background of this research was the use of such solutions for medical purposes in the 19^{th} century (9). As hydrocyanic acid is highly poisonous, overdosing could lead to dangerous or even deadly accidents. Everitt had bought and analyzed medicinal hydrocyanic acid from several producers in London that were purported to have a consistent concentration of hydrocyanic acid ("Scheele's strength" = 5%), but he found that the concentration varied between 1.4 and 5.8%.

According to Everitt's method, yellow potassium ferrocyanide dissolved in water is distilled after the addition of dilute sulfuric acid (approximately 20%). This procedure leads to the production of hydrocyanic acid, which escapes as a gas. Everitt reports that, during the reaction, a yellow insoluble salt is formed. He also reports that potassium bisulfate stays dissolved in the solution. The reaction performed by Everitt can be written as:

The insoluble salt reported by Everitt is indeed ferrous ferrocyanide (K₂Fe^{II}Fe^{II}(CN)₆). Everitt also reports that this yellow salt can be converted to Prussian Blue. However, he remarks that "the theory of the subsequent conversion of the salt into Prussian blue by moistening it with dilute sulphuric acid and exposing it to air is consequently unknown." He then speculates that potassium "is dissolved out" and that "the action of oxygen is essential to the change." This oxidation of ferrous ferrocyanide to Prussian Blue can be written as:

$$4 \text{ K}_2\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6 + 4 \text{ H}_2\text{SO}_4 + \text{O}_2 \Rightarrow$$

 $4 \text{ KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6 + 4 \text{ KHSO}_4 + 2 \text{ H}_2\text{O}$ [2]

Ironically, Thomas Everitt was not the first person who prepared and described ferrous ferrocyanide. He

even states in his article, "I am well aware that in the 46th volume of the *Annales de Chimie et de Physique*, p. 77, M. Gay Lussac states that a white salt is produced during this reaction."

In fact, ferrous ferrocyanide is an uncolored compound with a white appearance when in the form of a powder—not yellow, as described by Everitt. It is possible that Everitt's yellow salt was contaminated with a different yellow compound.

Gay-Lussac's (10) article with observations on Prussian Blue was published in 1831 (11). In this paper, he describes, among other things, the same experiment that Everitt performed four years later and reports the precipitation of a white powder ("poudre blanche").

Other scientists of the time also produced a white substance upon repeating Everitt's experiments. For example, Jonathan Pereira (12) wrote in 1839: "The salt here called biferrocyanide of potassium is termed, by Mr. Everitt, the *yellow salt*. I have prepared it with the greatest care, but have always found it to be white. Gay Lussac also says it is white. By exposure to the air it becomes blue" (13).

Colorless ferrous ferrocyanide was also prepared prior to the 1830s by methods other than those described by Gay-Lussac and Everitt. These alternative methods were the chemical reduction of Prussian Blue and the direct precipitation through the use of ferrocyanide and a ferrous salt. These methods were described in detail in 1797 by the French chemist Proust (14), who called ferrous ferrocyanide the white prussiate ("Prussiate blanc") (15). The reducing agent employed by Proust was hydrogen sulfide.

The term "Everitt's salt" appears for the first time in a chemistry textbook written by the Irish chemist Robert Kane (1809-1890) and published in 1842 (16). Thus, although Everitt was not the first chemist to prepare and describe ferrous ferrocyanide, and although he erroneously described it as a yellow instead of a white powder, the substance was nevertheless named after him.

This raises the question why ferrous ferrocyanide was called Everitt's salt and not Proust's or Gay-Lussac's salt? We believe the cause is the following: The name Everitt's salt was first used in English language textbooks and scientific articles probably because the authors were much more familiar with English language scientific articles then with foreign language ones. In the English scientific literature Everitt was indeed the first to describe ferrous ferrocyanide.

Who was Thomas Everitt?

Scant and not completely correct biographical information on Thomas Everitt can be found in two obituaries from the 1840s (17, 18). The following biography is based on these obituaries and on some additional materials collected from various other sources, including genealogical sources and contemporary journals and magazines.

Thomas Everitt was born in Caister next Yarmouth (today Caister on Sea), Norfolk, England, on August 12, 1805 (19). His christening is recorded as having occurred on September 15, 1805 (20). His parents, the farmer George Everitt (1761-1850) and Jane Everitt née Clowes (1767-1853), married in Caister on October 5, 1790. For more than 40 years, George Everitt was the tenant of the Caister Castle estate. Caister Castle (21), a 15th century moated fortress, currently houses a motor museum. Even in George Everitt's time it was mentioned that "the greater part of Caister castle is a picturesque ruin" (22). Figure 2 shows this castle as it looked in 1799. In 1847, George Everitt is described as "a truly patriarchal farmer, the father of eleven and the grand-father of forty-seven children" (22).



Figure 2. View of Caister Castle, drawn by Thomas Hearne (1744-1817), engraved by William Byrne (1743-1805), published in 1799. Caister Castle was the home of the Everitt family.

Everitt studied at the universities of Glasgow, Paris and Göttingen (Germany). In both of the above-mentioned obituaries, it is stated that he received his chemical education "principally in the schools of Germany" (18), or, more precisely, "in Göttingen in the laboratory of Professor Friedrich Stromeyer (23)" (17).

It can be proven that Everitt studied chemistry at the University of Göttingen for approximately one year from November 1828 (24) until September 1829 (25) so that he could study under Stromeyer for two terms. During this time, Stromeyer gave lectures on "theoretical chemistry with the necessary experiments" six hours a week, from Monday to Saturday, always starting at 9 am. Practical exercises in the "academic laboratorium" were held on Mondays and Wednesdays from 1 to 3 pm (26).

No information on Everitt's studies in Glasgow and Paris could be found; only the fact that he studied there before he came to Göttingen could be established (24). In Göttingen, Everitt finished his university education in Chemistry, but did not acquire a Ph.D.

It is not known when exactly Everitt came back to England, where he began a career as a public teacher of chemistry in London. Most of his teaching took place in various medical schools, which flourished in London during the first half of the 19th century. These medical schools often offered courses in chemistry. First, we find him in the fall of 1830 as a chemistry teacher in the Theatre of Medicine and Chemistry (27), No. 1, Dean Street, Borough (28), also called Grainger's School. He also taught a course on chemical manipulation in the same institution "to gentlemen wishing to study this science more especially, in the laboratory connected with the Theatre" (29).

In 1831, Everitt became teacher of chemistry to the pupils at the Little Windmill Street School of Medicine in London (30), introduced by Dr. George G. Sigmond (31). Together with two colleagues (Jewel (32) and Sigmond), he also lectured on Forensic Medicine at this institution (33). In addition, he continued to be an active teacher at Grainger's School, his first professional station in London, then called the "Theatre of Anatomy and Medicine, Webb-street, Maze-Pond, Southwark." Here, he gave lectures on Materia Medica together with a colleague named Dr. Whiting (34). In the following years, including the session of 1834-35, he lectured at two institutions: Materia Medica at Grainger's School in Southwark and Chemistry and Chemical Jurisprudence at Little Windmill Street (35). In the 1834 list of London medical schools, Everitt is listed for the last time as a lecturer in Chemistry and (together with Dr. Sigmond and Dr. Jewel) Medical Jurisprudence at the "Theatre of Anatomy in Little Windmill Street, Golden Square," and also as a lecturer (together with Dr. Whiting) for "Materia Medica, Pharmacy, and Therapeutics" at the "Theatre of Anatomy and Medicine, Webb-street, Maze Pond, Borough" (36). In 1834, Everitt lived in 28, Golden

Square, Soho, London, in the vicinity of Little Windmill Street (8).

Back in England in 1830, Everitt also became an active member in the Medico-Botanical Society (March 9, 1830). On June 22, 1830, he "was elected to fill the office of Professor of Chemistry to the Society" (37). The Medico-Botanical Society (38) was a relatively shortlived scholarly society, founded 1821 by John Frost (39) in London and lasting only until 1852. In this society, which held regular meetings, Everitt delivered presentations on the work of different chemists, but also presented samples of his own work. For instance, he reported on the detection and analysis of hydrocyanic acid (in 1830), on opium (in 1831), on the mode of obtaining oxalic acid from the vegetable kingdom (in 1833), on the work of French and German chemists with iodine (in 1833), on the chemical composition and comparative strength of medical hydrocyanic acid (in 1835), on tests for arsenic and on the presence of arsenic in several new types of candles (in 1837) and on his analytical procedure to detect opium in the stomach of humans (in 1839). Additionally, Everitt gave public presentations at the Western Literary Institution (on recent discoveries of Faraday in electrochemistry in 1837) and at the Royal Institution (on Liebig's method of analyzing organic bodies in 1839).

In 1835, a school of medicine was established at the Middlesex Hospital. On June 8, 1835, Everitt was named the chair of Chemistry. When the school of medicine opened on October 1, 1835, Everitt was a member of the staff as lecturer in Chemistry (40). To take this position, he ended his employment at the Little Windmill Street School, but did not end his second lectureship at Grainger's School in Borough until after the 1837-38 session.

Everitt's employment at the Middlesex Hospital was his primary occupation during his short lifetime. The job included not only the lectureship, but also a position as the head of the hospital's laboratory. In this position, he performed many analytical tasks for the hospital and for other clients. During his career, Everitt was generally known as "an accomplished analyst" (17).

Everitt was involved in the resolution of two poison scandals of his time. The first scandal became known as "Death in the candle" (41). On a June evening in 1837, Everitt prepared to retire. After blowing out a candle, he smelled garlic. As a chemist, he knew that this scent could be caused by arsenic. The candle was of a new type, a so-called "composition candle" (42). Everitt decided to analyze the candle and others which were sold in London

at the time. After analyzing several of these new candles and finding arsenic in each of them, Everitt reported his findings in a lecture before the Medico-Botanical Society on June 28, 1837. In October 1837, the Westminster Medical Society (43) established a special Committee on Arsenicated Candles. Three chemists, including Everitt, performed experiments with composition candles to detect arsenic and to determine its concentration and level of danger. In December 1837, a final report from this committee was presented before the society and published (44). This report proved the existence of arsenic in the candles and the danger of the fumes when burning these candles. Thereafter, arsenicated candles were no longer produced or sold in England.

The second scandal concerned a new invention called Harper and Joyce's stove, which was promoted by, among others, the leading English chemist of the day, William T. Brande (45). This stove, which should require no chimney and should only be used with a special socalled "prepared fuel," was constructed in a manner so that all combustion products remained in the rooms in which the heating device was installed. According to the inventors, this process should not be dangerous because of the new "prepared fuel." Everitt was frequently consulted by medical colleagues and his pupils, who wanted his professional opinion about the nature of the "prepared fuel" and on the combustion products of Harper and Joyce's new heating-boxes. Therefore, he began a thorough investigation of the stove, the "prepared fuel" and the combustion products.

On April 21, 1838 Everitt presented his findings before a well-attended meeting of the Westminster Medical Society (46). Everitt demonstrated that the new "prepared fuel" was simply high-quality charcoal and that the combustion product was mainly "carbonic acid gas." Everitt concluded in his presentation that the statement of the inventors that "if their prepared fuel be used no deleterious gas or vapour is produced, is incorrect" and that "in no case ought these boxes to be used for heating dwelling rooms, unless provision be made for carrying off the products of combustion." Although some of these stoves continued to be sold, Everitt's presentation certainly slowed down the commercial success of this device. However, it took several more years and the deaths of several victims before Harper and Joyce's patent stove was equipped with a pipe (47), which in turn led to the loss of the asserted advantage of this invention.

On August 1, 1838, Everitt married Mary Ann Bicknell (1817-1858) in St. Matthews, Brixton, county of Surrey (today in the London Borough of Lambeth) (19).

In 1839, the Everitt family lived in 6, Torrington Square, Bloomsbury (today in the London Borough of Camden).

In 1839, Thomas Everitt became a corresponding member of the scholarly society Naturforschende Gesell-schaft in Basel, Switzerland (founded in 1817 and still existing today). This membership was perhaps promoted by Christian Friedrich Schönbein (48), who performed several experiments together with William R. Grove (49) in Everitt's laboratory in the Middlesex Hospital the same year. Everitt's laboratory in the Middlesex Hospital seems to have been well equipped, especially for low temperature experiments, because Grove and Schönbein conducted experiments on the behavior of ammonium amalgam at a low temperature. This work was only published by Schönbein (50) and Grove (51), not by Everitt. However, both scientists mentioned the help and kindness of Everitt in their publications.

After two years with only one lecturing position, Everitt became lecturer in Chemistry at the College for Civil Engineers in Putney (52), a private institution in the vicinity of London. This institution opened on May 1, 1840, and Everitt is listed among its 12 professors (53). Therefore, in the early 1840's, he again held the position of Chemistry lecturer at two different institutions. In 1842, the Governor General of Canada asked Michael Faraday to recommend a suitable English candidate for the Professorship of Chemistry at the University of Toronto, Upper Canada. The second of the candidates Faraday asked was Everitt, but he declined the position (54).

Everitt was also among the founding members of the Chemical Society of London (founded February 23, 1841) and was an active member of its first Council (55). The Jubilee Album that was prepared for the celebration of 50 years of existence of the Chemical Society in 1891 contains Everitt's signature (56). In a meeting of the Chemical Society on February 17, 1845, it was recommended that Everitt should retire as a council member (57). At this time, he was already gravely ill.

In 1843, eight years after beginning his career at the Middlesex Hospital, it was reported that "the chair of chemistry was vacated in consequence of ill health, at the close of the session 1842-43, by Mr. Everitt. Its duties were temporarily performed during the following session by Dr. Bence Jones (58), and in 1844 the appointment was conferred on Dr. Fownes" (59, 60). In September 1843, Everitt is for the last time mentioned as a lecturer in Chemistry for the winter session of the Middlesex Hospital School of Medicine (61), which was scheduled to begin on October 2, 1843, but came to an end that year.

On May 15, 1845, "the apparatus, chemicals, books etc. of Thomas Everitt ..., who from ill health is compelled to relinquish his avocations" were sold at auction (62).

Due to his worsening severe illness, he became an inmate of the Lady Ellis lunatic asylum at Southall Park (63), near London. Thomas Everitt died there on July 26, 1845, in a tragic accident. The details of the accident are reported in a coroner's inquest (64). According to this source, he was "affected with paralysis and had recently been in so debilitated a state as to render occasional ablutions of his entire body necessary. With this view he was put into a bath of about the temperature of ninety degrees between eight and nine o'clock ... and while there received an extensive scald from a sudden" irregular gush of hot water. The cause was a defect in the boiler apparatus, and his death was a consequence of the severe burn he received. Everitt was buried in Norwood Churchyard in Southall. He was survived by his "dear wife Mary Ann" (65) and two children Mary (1839-1918) and Herbert (1840-1931) (66). In 1850, Thomas' widow Mary Ann Everitt née Bicknell married again. Her second husband was Andrew Edgar (1815-1873), a barrister-at-law.

Because he was "an unfrequent contributor to the scientific literature of his time" (17), only a few original scientific articles written by Thomas Everitt can be found. In addition to his paper on the production of hydrocyanic acid (8) in 1835, he also wrote about economical means of procuring pure salts of manganese (67) in the same year, on medicinal Prussic acid (68), on several novelties in a new edition of the London Pharmacopeia (69) in 1837 and on the leaf stalks of garden rhubarb as a source of malic acid (70) in 1843.

Acknowledgments

I thank Dr. Günther Beer from the Museum of Chemistry in Göttingen for providing information on Everitt's stay in Göttingen and on Stromeyer's lectures during this time.

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- 14. Joseph Louis Proust (1754-1826), French chemist who defined the law of definite proportions.
- 15. J. L. Proust, "Recherches sur le Bleu de Prusse," *Ann. chim.*, **1797**, *23*, 85-101.
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- 18. "Mr. Everitt," *The London Medical Directory*, Churchill, London, 1846, 182-183.
- 19. F.A. Crisp, Ed., *Visitation of England and Wales, Volume* 17, privately printed, 1911, 37.
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- 21. The construction of Caister Castle, a moated quadrangle fortress, began in 1432 and was completed around 1446. The construction was commissioned by Sir John Fastolf (1378-1459), an English knight who came to wealth during the Hundred Years' War in France. Caister Castle was one of the first major brick buildings in England. After Fastolf's death, Caister Castle came into the possession of the Paston family, John Paston (1421-1466) being Fastolf's friend, adviser and lawyer. In 1599, the Paston family moved their residence to Oxnead, Norfolk. In 1659, the Pastons sold the Caister Castle estate to a London merchant. Thereafter, the castle came into decay and the Caister Castle estate was rented to farmers.
- 22. "Antiquarian Researches," *Gentleman's Magazine*, **1847** (Sept.), 292-303 (298).
- 23. Friedrich Stromeyer (1776-1835), German chemist, Professor of Chemistry at the University of Göttingen, discoverer of cadmium. For his biography see G. Lockemann and R. E. Oesper, "Friedrich Stromeyer and the History of Chemical Laboratory Instruction," *J. Chem. Educ.*, **1953**, *30*, 202-204.
- 24. G. von Selle, *Die Matrikel der Georg-August-Universität zu Göttingen 1734-1837*, August Lax Verlagsbuchhandlung, Hildesheim, 1937, 284. Here the entry on Nov. 14, 1828 is: "Thomas Everitt, England, chem., ex ac. Glasgow und Paris. V: Rentier in Caister, Norfolk".
- 25. "Verzeichnis der öffentlichen und Privat-Lehrer, der Mitglieder der academischen Behörden und der Studirenden auf der Georg-August-Universität Göttingen auf das halbe Jahr von Ostern 1829 bis Michaelis 1829 bey der Aufzeichnung den 30 May 1829," SUB 8 Hlp, IV, 54/5.

- Here the entry for Everitt is: "Everitt M 28. Norfolk, Chemie, Oppermann 122d, Kurzen".
- Göttingische gelehrte Anzeigen... 1828. 6 Sept. 1828.
 [Vorlesungen WS 1828/1829] 1436 Naturlehre.
- 27. This private medical school was also known as the Theatre of Anatomy and Medicine, or Grainger's School. It was founded in 1819 by Edward Grainger (1797-1824) and continued by his brother Richard Dugard Grainger (1801-1865). The school closed in 1842.
- 28. Today, Borough is an area in the London Borough of Southwark. Dean Street is Webb Street today. Evidently, the street name changed between autumn 1830 and autumn 1831.
- 29. "Hospitals and Schools," The Lancet, 1830, Sept. 25, 15.
- Little Windmill Street School of Medicine was a private medical school founded in 1822 by George Dermott. Little Windmill Street is now part of Lexington Street, Soho, London.
- 31. George Gabriel Sigmond (1794-1847), English physician, son of a dentist from Bath who emigrated from Poland, Licentiate of the Royal College of Physicians beginning in 1826, leading member and Professor of Toxicology of the Medico-Botanical Society.
- 32. George Jewel, surgeon, Member of the Royal College of Surgeons.
- 33. "List of Lecturers at the London Medical Schools, Session 1831-32," *The Lancet*, **1831**, Oct. 1, 13-16.
- 34. John Whiting (?-1873), M.D., Member of the Royal College of Physicians, Physician to the Royal Dispensary.
- 35. "Account of the Metropolitan Hospitals, Medical Schools and Lecturers, for the Session Commencing October 1832," *The Lancet*, **1832**, Sept. 29, 5 and 10.
- 36. "List of Medical and Surgical Schools in London, Session 1833-1834," *London Med. Surg. J.*, **1833**, *4*, 262-278 (271-272).
- 37. "Literary and Scientific Intelligence. The Medico-Botanical Society," *Gentleman's Magazine*, **1830**, (Aug.) 158.
- 38. The Medico-Botanical Society was founded in London in 1821. The Society's objectives were the investigation of the medicinal properties of plants, the study of the materia medica of all countries, and the making of awards for original research on these subjects. The focus of the Society was the collection, cultivation, study and exploitation of medicinal plants. Fellows, including those drawn from the medical professions, attended lectures, submitted reports and awarded annual medals for the encouragement of medical botany. A journal, *The Transactions of the Medico-Botanical Society*, was published between 1829 and 1840 (Volume 1, Part I to IV). After 1845 the activities of the Society declined. It was broken up in 1852 because of a lack of money and support. Its property was sold privately.
- 39. John Frost (1803-1840), founder, spiritus rector and first director of the Medico-Botanical Society of London beginning in 1821. In 1830, he was expelled from the society because of his arrogant behavior and in 1832,

- due to financial liabilities, he fled from England to Paris. Frost died as a physician in Berlin.
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- 41. "Death in the Candle," The Lancet, 1837, July 8, 556.
- 42. J. C. Whorton, *The Arsenic Century: How Victorian Britain Was Poisoned at Home, Work, and Play*, Oxford University Press, Oxford, 2010, 169-171.
- 43. The Westminster Medical Society was founded in 1809 as an adjunct to the Great Windmill Street Medical School. In 1850, the Westminster Medical Society and the Medical Society of London (founded in 1773) merged under the latter's name. This society still exists today.
- 44. Report of the Committee of the Westminster Medical Society on Arsenicated Candles, Ibotsen and Palmer, London, 1837.
- William Thomas Brande (1788-1866), English chemist, Professor of Chemistry at the Royal Institution beginning in 1813.
- "Westminster Medical Society," The Athenaeum, 1838, April 28, 306-307.
- 47. J. Timbs, Ed., *Manual of Domestic Economy*, David Bogue, London, 1847, 14.
- 48. Christian Friedrich Schönbein (1799-1868), German-Swiss chemist, discoverer of ozone, inventor of the fuel cell, beginning in 1835, professor of Chemistry at the University of Basel, Switzerland, friend of William R. Grove.
- 49. William Robert Grove (1811-1896), jurist and scientist from Wales, FRS beginning in 1840, pioneer of the fuel cell technology and inventor of the Grove cell, a nitric acid battery.
- C. F. Schönbein, "Notiz über das Ammonium-amalgam," Ann. Phys. Chem., 1840, 49, 210.
- W. R. Grove, "On Some Electro-Nitrogurets," *Philos. Mag.*, **1841**, *3.Ser. 19*, 97-104.
- 52. The College for Civil Engineers in Putney was established in May 1840. The attending students were architects and surveyors, civil engineers and engineers for the army, navy and colonial service. The school closed in 1852 because of financial difficulties. During this time, Putney was a town near London. Today Putney is a district in the London Borough of Wandsworth.
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- 59. George Fownes (1815-1849), English chemist, studied chemistry from 1837-1839 at the Middlesex Hospital under Thomas Everitt. In 1844, he became Everitt's successor as chemistry lecturer at the Middlesex Hospital. He published a successful textbook on chemistry in 1844.
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- 61. Advertisement, *Provincial Med. J. Retrospect Med. Sci.*, **1843**, *6* (No. 156, Sept. 23), 537.
- Advertisement, The Athenaeum, 1845, May 10, 1845, p. 449.
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A TRANSNATIONAL NETWORK OF CHEMICAL KNOWLEDGE: THE *PREPARADORES* AT THE LISBON POLYTECHNIC SCHOOL IN THE 1860s AND 1870s

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Antonio Augusto de Aguiar (1838-1887) was the main author of the most important research in organic chemistry carried out in Portugal during the 19th century. Despite not attending any research school in Germany, France or Great Britain, Aguiar's most important research papers, on work carried out at the Chemical Laboratory of the Lisbon Polytechnic School, were published in *Berichte der deutschen chemischen Gesellschaft* between 1870 and 1874.

How then did he acquire the knowledge, the inspiration, and the experimental skills necessary for his research? The influence of his older colleague Agostinho Vicente Lourenço (1822-1893), an élève of Adolphe Wurtz (1817-1884), is not alone sufficient to explain the success of Aguiar's research oeuvre; some papers he co-authored with chemists with German surnames, who spent some time in Lisbon. From where did they come, and how did Lourenço and/or Aguiar recruit them? The first was Eduard Lautemann (1836-1868), a disciple of Hermann Kolbe (1818-1884) in Marburg, knowledge of whose biography was, until recently, rather sketchy. So far, chemistry historians have underestimated Lautemann's exceptional skills and originality, because, due to his illness and early death, he was active in research for only about five years. Lautemann left Lisbon for Goa, then in the Portuguese State of India, Lourenço's birthplace, to lecture on physics and chemistry at the Eschola Medico-Chirurgica, from which Lourenço had

graduated. Another co-author was Alexander Georg Bayer (1849-1928) of Bielitz in former Austrian Silesia, who arrived in Lisbon four years after Lautemann, and has until recently evaded almost completely the attention of chemistry historians, in spite of his interesting professional career, patronized by his elder and more famous brother, Karl Joseph Bayer (1847-1904). The Lisbon Polytechnic School employed Lautemann in 1864-65 and Alexander Bayer from 1868 to 1872 as demonstrators in chemistry (preparadores), but between 1864 and 1876, three other chemists trained in Germany also worked as demonstrators at the Lisbon Polytechnic. Bayer and the other three chemists had in common that they were recruited from the teaching laboratory of Carl Remigius Fresenius (1818-1897) in Wiesbaden. Fresenius had been, like Kolbe, an assistant of Justus von Liebig (1803-1873) in Gießen. Fresenius's teaching laboratory in Wiesbaden turned thus out to have been the hub of the network for the transfer of chemical knowledge from the German states to Portugal.

Introduction

The transfer of chemical knowledge from the center of Europe to the periphery during the 19th century has been the object of numerous studies (1). Perhaps the most famous example is the influence of Justus von Liebig's research school in Giessen on the development

of international chemistry (2). The studies mentioned above made it possible to trace the pathways of transfer of chemical knowledge to various countries of the European periphery, where Liebig's former students founded national research schools. Chemistry is a field in which the communication of knowledge through the reading of books, journals and letters is not enough to enable somebody to start successful research activities in the isolation of a distant location. The acquisition of the necessary experimental skills and immersion into innovative ideas could usually be achieved only through personal contact in a teaching laboratory of one of the major research schools (3). Although chemical genealogies should not be over-interpreted, it cannot be denied that for the great majority of those chemists who left a permanent mark on the history of chemistry, there had been contact with a research tradition handed down through generations of chemists, sometimes also of pharmacists and physicians. One should also not overlook in this context that many chemists of the 19th century started their careers as physicians. When such a research tradition did not exist in a given peripheral country, it had to be obtained from abroad.

The purpose of our research was to investigate the ways how, in the 19th century, chemical knowledge, laboratory skills and ideas were transferred to Portugal through the Lisbon Polytechnic School (Eschola Polytechnica de Lisboa). This institution was founded in 1837, originally for preparatory studies of future army officers who would complete their later education in army or navy schools (4). Only much later, the propaedeutic character of the courses at the Lisbon Polytechnic was expanded to encompass candidates to other professional careers such as medicine and secondary teaching. In its first decades, the Lisbon Polytechnic had to struggle against the difficult situation resulting from Portugal being shaken by a succession of civil wars. Once internal peace was established in 1851, a period of economic development and modernization started in Portugal, known as Regeneração (Regeneration), which also became beneficial for the Polytechnic School. The only other institution of comparable importance regarding university chemical teaching was the University of Coimbra. A first approach to the study of an analogous case for Coimbra has recently been presented (5).

As a result of the reception of chemical knowledge from abroad in the Polytechnic School, papers based on research carried out in its laboratory were published in French and German chemistry journals in the 1860s and 1870s. We used these papers as the starting point of our

research, because they were almost the only tangible evidence for the reception in Portugal of new chemical knowledge from abroad; among their authors were chemists with German surnames. The identification of these foreign chemists and the reconstruction of their lives was the obvious first step in a prosopographic approach (6), which seemed to be the only practical way to start uncovering the pathways of chemical knowledge to Lisbon.

It was not possible, however, to follow the same method in the same order as in the studies of influence of Liebig's research school on international chemistry. In that case, the itineraries of the persons carrying chemical knowledge started all at a given center, Liebig's research school, and ended in a number of destinations in other countries, which had to be determined along the development of the investigation. The names of Liebig's disciples were known from a register and those among them who acted as carriers of chemical knowledge were identified by the reappearance of their names as authors of later publications originated at various locations. In the present case, the situation was the opposite: the destination of the pathways of knowledge was given—the Lisbon Polytechnic School-but the geographic locations of their starting points were unknown. Thus, research on the lives of these men had to follow in the opposite direction to that of the flow of knowledge.

Liebig's school could be ruled out as a relevant origin, because the only known Portuguese contact with Giessen was a short visit around 1845 by the chemistry professor of the Polytechnic School, Júlio de Oliveira Pimentel (1809-1884) (7). Pimentel had practiced in E.-M. Péligot's (1811-1890) laboratory at the Conservatoire des Arts et Métiers in Paris, followed by a journey to Belgium and Switzerland, with only a short stop midway in Giessen. Upon his return to Portugal, Pimentel continued to lecture in chemistry but did not publish any significant research. He became, however, quite active as an industrial chemist. He was responsible, at least in part, for the appointments of Antonio Augusto de Aguiar (1838-1887), in 1861, and Agostinho Vicente Lourenço (1822-1893), in 1862, as assistant lecturers of chemistry (8) at the Lisbon Polytechnic. In 1869 Pimentel was appointed by the government Rector of the University of Coimbra, one of a number of high-ranking positions, which he tried to use in order to modernize higher education in Portugal, an endeavor, which was only partially successful, due to the resistance of powerful conservative forces. Late in life he received the title of Viscount of Vila Maior. There was thus no direct relation between Liebig's school and the publications mentioned above.

The transfer of knowledge crossing national boundaries has also to be seen in the context of the rapid development of steamship and railway lines in the mid-19th century. The strong international character of the Giessen school and its spread was only possible through the increasing availability of such means of communication. Portugal was connected to the European railway network only in 1867, but from 1853 on, there was a French steamship line between Lisbon and Bordeaux, which could already be reached by train from Paris. From that date, travel between the central countries of Europe and Lisbon became easier and faster. The stage was thus set for an intensification of transnational exchanges.

Under Lourenço and Aguiar, chemistry at the Polytechnic School rose between 1864 and 1884 to a sufficiently high international standard as to deserve a visit from a prominent foreign chemist: when the author of the famous Handbuch der Organischen Chemie, the German-Russian Friedrich Konrad (or Fjodor Fjodorowitsch) Beilstein (1838-1906) visited Portugal, in 1884, he met Lourenço and Aguiar at the Lisbon Polytechnic (9). Beilstein had become friendly with Lourenço in Heidelberg and Paris in the 1850s, and was introduced to Aguiar on the occasion of this visit. Aguiar is the author of the most important and internationally recognized research in organic chemistry carried out in Portugal during the 19th century (8). Although Lourenço had published a string of relevant papers on organic chemistry from 1859 to 1863 while doing research in the laboratory of Adolphe Wurtz in Paris, once back in Lisbon his publications on the subject did not measure up to his early work. Unlike Lourenço, who had been granted scholarships that enabled him to become a research student in Heidelberg and Paris, his younger colleague Aguiar had never left the country; he was able, however, to publish a series of research papers on organic chemistry in prestigious journals in France and Germany. How could Aguiar have carried out research in the chemistry laboratory of the Lisbon Polytechnic School in complete isolation? Except for a single joint article with Lourenço, based on research carried out and published in Lisbon, the most important part of which cannot be replicated and was never validated by either Wurtz or Beilstein, there are no traces of a scientific connection between the topics addressed by Lourenço's earlier investigations at Wurtz's laboratory in Paris and most of Aguiar's later work. This can be considered as evidence for the absence of a classical master-apprentice link between them. Since the vast majority of biographies of chemists allow for the establishment of scientific genealogies, through which research traditions and laboratory know-how are handed down from one generation to the next, the case of Aguiar looks like a puzzling exception to this pattern.

Can the answer be found in Aguiar's co-authors Lautemann and Bayer? Who were they? Given the still comparatively slow travel and communication conditions of that period in a European country as peripheral as Portugal, an international research network with members sharing experimental results obtained in their respective laboratories and publishing them together, as we have today, is unthinkable. Therefore, both Lautemann and Bayer must have stayed for some time in Lisbon. Not all papers, however, were explicit about the place where research had been carried out, because, at that time, not all journals required that information. Were the topics addressed part of a research program pursued abroad or were they part of a project entirely designed in Lisbon? The present report shows how Aguiar's foreign co-authors were identified, when and from where they came to Portugal, their activities in Lisbon, and where they went after leaving. The itineraries of their scientific lives enable us to find out where, how and why they had been recruited and help us trace the research traditions to which they belonged and that they brought with them to Portugal.

Although the possible reasons why both Lourenço and Aguiar failed to found a Portuguese school of research in organic chemistry were studied earlier (8), the subject still deserves further investigation. The present work may contribute to a better understanding of that problem.

Eduard Lautemann: Marburg – Paris – Lisbon

Eduard (sometimes spelled Édouard) Lautemann was the first of Aguiar's foreign co-authors. As will be presented in detail and discussed below, the first paper ever published by Aguiar, a short communication in 1864, was published jointly with Lautemann in Paris. The subject had no relation to Lourenço's earlier work, thus suggesting the absence of a teacher-student relationship between Lourenço and Aguiar. Since Lourenço had been an élève of Wurtz, and little is known about other international connections of the Lisbon Polytechnic School with foreign chemists, the next step was to look for Lautemann among Wurtz's disciples. The comprehensive work of Ana Carneiro on the research school of Wurtz (10) confirms that Lautemann was indeed an élève of Wurtz around 1862. Another important clue to Lautemann's identity was then found in a biography of Hermann Kolbe, in which Alan Rocke reports on Kolbe's students in Marburg (11):

... Another worker, quite productive, but probably in the "journeyman category," was Eduard Lautemann, about whom little is known. He studied with Kolbe from 1857 to 1861, thereafter serving as assistant. He published his entire œuvre of seventeen papers, some solo and many co-authored, during the period from 1859 to 1865, then traveled to India, began to study medicine and vanished from sight...

A search in the proceedings of the Council meetings of the Lisbon Polytechnic showed that on 8 January 1863, the Council decided to request government permission for a contract with a certain Dr. Lautemann as "preparador" for two years, with a monthly salary of 40,000 reis (12) in addition to covering his travel expenses (13). He worked in the Chemical Laboratory from July 1863 (14) but he must have left the Polytechnic School already by early spring 1864. In December 1864 Lourenço was granted permission of the Council to replace him with another foreign preparador named William Klaas from November 1864 onward, with the same salary (15). Regarding Lautemann's earlier life, the curriculum vitae (16) submitted together with his doctoral thesis at the University of Marburg contains the following information:

- •1836 born in Felsberg near Kassel, father a "parochus" (i.e., pastor of a Lutheran church)
- •1846 sent to school in Eschwege
- •1849 Gymnasium in Hersfeld, but fell ill and had to abandon further studies on medical advice
- •1852? after three years apprenticeship in a pharmacy, moved to Frankenberg for one year and then to Marburg in order to work in Kolbe's laboratory
- •1857 registered at Marburg University as a student of chemistry and
- •1859 of pharmacy
- •1861 Dr. phil. in Marburg

In a letter dated 6 June 1862 to Emil Erlenmeyer (1825-1909) (17), at that time *Privatdozent* at the University of Heidelberg, Lautemann enquired about an advertisement of a vacancy for a chemist at an ultramarine factory, published in Erlenmeyer's *Zeitschrift für Chemie*. This position was, however, no longer available. In the ensuing letters Lautemann admitted that he had to resign at Easter 1862 from his position as assistant of Kolbe, because of his poor health, that he was subsist-

ing on credit, that he was obliged to give up research in pure science and that he was looking instead for a job in industry. Since Erlenmeyer had learned from his friend Lourenço, who was working at that time in the laboratory of Wurtz in Paris, that he was looking for a chemist to be employed by the Lisbon Polytechnic School, he put the two in contact with each other. By mid November Lautemann had already joined Lourenço in Paris. On his way from Marburg to Paris, Lautemann had stopped in Heidelberg in order to show to Erlenmeyer his gratitude and to pick up a case, which he was supposed to take with him to Lisbon. The case was being packed by Peter Desaga (18), mechanic of the University, and contained not only laboratory instruments and glassware, but also reagents supplied by E. Merck, including a collection of alkaloids, as well as books, all of this ordered by Lourenço, who in the meantime was already taking up his new position of *lente substituto* at the Lisbon Polytechnic School. Lautemann followed him in June 1863 (19).

Publications of Eduard Lautemann

Lautemann authored and co-authored around 18 publications, including his doctoral dissertation submitted in 1861 to the University of Marburg (20). The first 14 articles commented on below and published in journals of chemistry between 1859 and 1863 originated also from Kolbe's laboratory at the University of Marburg. None of his subsequent publications could be identified explicitly as originating from Wurtz's laboratory in Paris; however, one cannot exclude the possibility that he added some last details there to articles declared as originating from Marburg and/or carried out some preliminary experiments on work which was published later in collaboration with Aguiar in one of his four further publications stemming from the laboratory of the Lisbon Polytechnic. In order to understand the importance of Lautemann's work in Marburg and its impact on his collaboration with Aguiar, the publications are summarized and commented on in the following paragraphs.

Lautemann's publications from the laboratory of Kolbe in Marburg

In his first article (21) Lautemann signs as the only author. Upon Kolbe's suggestion he refutes with well-designed experiments a criticism of the method of combustion analysis of nitrogen-containing organic compounds. According to that criticism, the heated copper gauze, used to reduce the nitrogen oxides generated in the combustion process, would also reduce part of the carbon dioxide to carbon monoxide and thereby lead to lower

values for the carbon content of the analyzed organic substance than in the absence of the copper.

The next paper published reports a discovery by Lautemann, which in retrospect can be considered as his most important contribution to organic chemistry. That paper was, however, signed by Kolbe alone (22). According to present-day standards, it would not be acceptable for a leader of a research group to publish an article under only his own name, and to admit merely in the body of the text that a junior collaborator (in this case Lautemann) had actually done the work. This article is the first disclosure of the synthesis of salicylic acid from phenol and carbon dioxide (step $2\rightarrow 1$ in Scheme 1, as represented in structural formulae, which Kolbe did not accept).

Lautemann alone, by contrast, signed the next publication according to chronological order (23). He reports the first direct reduction of lactic acid to propionic acid. Lautemann starts by quoting prior work of C. Ulrich, who had already achieved, in Kolbe's laboratory, the same transformation indirectly, thereby establishing a constitutional relationship between both acids. Kolbe challenged Lautemann to search for a way to achieve the same reduction in a single step. In the direct reduction Lautemann used, for the removal of oxygen from lactic acid, either hydroiodic acid, or, with even better results, "phosphorus diiodide" (now known to be P_2I_4) in the presence of a small quantity of water. He understood this reaction, in the framework of Kolbe's "new radical theory," as "substituting directly again the member HO₂ in the lactic acid by hydrogen" (24). One ought to explain to the modern reader, however, that in Kolbe's school the atomic weight of oxygen was reckoned to be 8 instead of 16, and the term "member" was used to designate a sub-group of atoms in the constitutional formula of an organic compound. If one replaces the designation "member HO₂" by "HO group," one can understand that Kolbe's so-called "new radical theory" could be useful and had some predictive capacities, in spite of not counting the number of atoms correctly and not considering the existence of bonds between two atoms as part of its conceptual framework. Lautemann's new method for reducing organic substances proved to be very useful, not only in his later work, but also as a general method in carbohydrate chemistry to the present day.

In the same issue of the *Annalen*, Kolbe published, under his name alone, a medley of five contributions from his laboratory (25), at least four of them based without any doubt on the work of Lautemann. The first contribu-

tion reports the follow-up by Lautemann of the work reported in his first paper (21). He showed that the reduction of carbon dioxide to carbon monoxide, which allegedly led to errors in the determination of the carbon content of nitrogen-containing organic compounds by combustion analysis, was due to the presence of impurities in the copper, which could be avoided. The second contribution deals with the behavior of diphosphorus pentoxide, P₂O₅, designated according to the nomenclature used in Kolbe's school as "wasserfreie Phosphorsäure" (anhydrous phosphoric acid), upon heating with sodium chloride. Instead of obtaining the PO₂Cl and Na₃PO₄ expected by him, POCl₃ was distilled, leaving behind a residue of Na₂O (26). The third contribution is about an improved method of preparing ethyl iodide from ethyl alcohol. The fourth one describes an improved experimental procedure to obtain lactic acid from a mixture of saccharose, tartaric acid, milk and cheese. Except for the fifth contribution, there can be no doubt that most contributions in this medley are based on Lautemann's work. It is difficult to judge whether such patriarchal ways of handling matters of co-authorship were common practice in that period, or rather a particular trait of Kolbe's character. We are inclined to consider that it reveals Kolbe's belief in strongly differentiated hierarchies, and speculate that this belief may have also contributed to Kolbe's refusal of Kekulé's views (27), according to which there was no carbon atom in a hydrocarbon chain with a higher hierarchical status than the others (28).

Most of Lautemann's publications, alone or coauthored with Kolbe, which originated from the Marburg laboratory, deal directly or indirectly with the "constitution and basicity" of salicylic acid. These include his doctoral dissertation (20) and the already mentioned note of Kolbe on the synthesis of salicylic acid (22). The next one, in chronological order of another five publications related to salicylic acid, is a short note signed by both Kolbe and Lautemann about the acids of gum benzoin (29), followed immediately by their major paper on salicylic acid (30). Kolbe republished the latter five years later, with some notes, in a book, which reviews his work at the Marburg laboratory (31). This republication contains important information concerning Lautemann's working relationship with Kolbe, as will be explained later.

The main article (30, 31) on salicylic acid starts with a study of the composition of metal salts and the ethyl ester of salicylic acid, leading to the conclusion that salicylic acid is a monobasic acid, like benzoic, lactic and propionic acids, and unlike succinic acid, which was then

already known to be a dibasic acid. In Scheme 1 a set of reactions is represented, which they carried out in order to study the constitution of salicylic acid.

The reader should be aware, however, that the structures shown in this scheme were unknown to Kolbe and Lautemann because such structures could only be established years later, after the acceptance of the valence theory of Butlerov, Couper and Kekulé, as well as of Kekulé's proposal of the benzene structure. Kolbe and Lautemann represented the compounds by compositional formulae, in accordance with the results which they had obtained by elemental analysis, assuming the atomic weights for carbon and oxygen to be 6 and 8, respectively. They wrote thus for salicylic acid (1) $C_{14}H_6O_6$, for phenol (2) C₁₂H₆O₂, for the "dichloride" (3) obtained from sodium salicylate C₁₄H₄O₂Cl₂, for the chlorobenzoic acid obtained by its hydrolysis (4) C₁₄H₅O₄Cl and for benzoic acid (5) C₁₄H₆O₆. Their "constitutional" formulae (see Figure 1) were written according to the so-called "carbonic acid theory" developed by Kolbe within his "new radical theory." Kolbe's theories, in spite of soon becoming obsolete due to the structural theories of Butlerov, Couper and Kekulé, were nevertheless able to express some essential features, which allowed, for example, a certain isomer to be distinguished from another one (see Figure 1), and to show how certain groups of atoms do not change their composition, during the transformations of some compounds into others. In the "new radical theory" of Kolbe, the atoms were supposed to be assembled in sub-groups, according to their mutual affinities, and these sub-groups, then called "members," were again parts of a larger assembly of such groups called the "radical." Kolbe used the term "radical," however, in this case (but not always) with a different meaning from today, for what was later called a "molecule" (32). Kolbe was perhaps

the most stubborn of all opponents of Kekulé and never accepted structural formulae. In his own words (33):

In my opinion, the constitution of a chemical compound resembles that of a well-organized state, with a head and various more proximate or more distant subordinate members, which are organized in such a way, that instead of a single *individuum* a group of various *individua* of equal rank can function. As an example one can take the various homologues of ethyl alcohol

Figure 1. "Constitutional formulae" of lactic and salicylic acids, according to the "newer radical theory" (Ref. 31, p 153).

Kolbe and Lautemann interpreted the formation of phenol upon heating salicylic acid, under the loss of carbon dioxide, as evidence for the oxygen in phenol belonging to an "oxyphenyl radical," pre-existing in the constitution of salicylic acid, with oxygen firmly associated with the "phenyl radical." The carbon dioxide ("C₂O₄" for them) in salicylic acid would then have been responsible for its behavior as a monobasic acid. They would not have expected that reaction if salicylic acid had the constitution of a possible isomer, which would be the case for the ester that today we call phenyl hydrogen carbonate (Figure 2).

Phenyloxydkohlensäure: $\begin{array}{c} C_{12} H_5 O \\ HO \end{array}$. $C_2 O_4$

Figure 2. "Constitutional formula" of the isomer of salicylic acid, which today would be called phenyl hydrogen carbonate (reproduced from republication (Ref. 31, p 153).

Regarding the dichloride (3), they understood for similar reasons that it contained two non-equivalent chlorine atoms, one removable by hydrolysis and the other held more strongly. They called compounds (4) and (5) "chlorosalylic" and "salylic" acid, respectively. Because of some slight differences between the physical properties of the samples of their "salylic acid" and samples of benzoic acid obtained from natural products, they failed at first to recognize the identity between "salylic" and benzoic acid. This led them to assume the existence of a new kind of isomerism. They developed this theme in other contributions, focusing on other reactions of salicylic acid as well as on a deeper investigation of the

occurrence of several acids other than benzoic acid in gum benzoin (34). Various chemists, notably Kekulé, disagreed with Kolbe that "salylic acid" was distinct from benzoic acid. The ensuing discussions degenerated into acrimonious polemics, which have been dealt with in detail by Anschütz in his biography of Kekulé (35), as well as by Rocke in his biography of Kolbe (11). The experiment demonstrating that the supposed "salylic acid" was in reality nothing more than benzoic acid was carried out by Reichenbach and Beilstein (36). In a note by Kolbe in the already-mentioned, later updated and annotated republication of these investigations (31), he was sufficiently honest not only to say that "salylic acid" was, after all, nothing more than benzoic acid, but also to admit that Lautemann had for a long time sustained that opinion. Knowing the authoritarian ways of Kolbe, one can venture to guess that Lautemann had been forced to bend to the verdict of the patriarch, against better knowledge.

Although the synthesis of salicylic acid from phenol and carbon dioxide with the help of sodium amalgam (step $2 \rightarrow 1$ in Scheme 1) had been motivated by the investigation of the constitution and basicity of salicylic acid, this reaction became the basis for the later development of its industrial synthesis. This synthesis became known as the Kolbe-Schmitt reaction (37), but it would be fairer to call it the Kolbe-Lautemann-Schmitt reaction, since the starting materials, phenol and carbon dioxide, were still the same. Instead of using carbon dioxide at atmospheric pressure and activating phenol with sodium amalgam, the Kolbe-Schmitt version uses aqueous potassium or sodium hydroxide and carries out the reaction in an autoclave under high pressure and temperature. This was an innovative solution. But does it justify forgetting Lautemann's early contribution to the discovery of the synthesis? Did Kolbe have a motive to play down the importance of his and Lautemann's early contribution? The answer may be found in a patent litigation (38): Kolbe sued the company Schering for infringing the Prussian Patent granted to him in 1874. Schering claimed in defending itself that the invention was already in the public domain before Kolbe's application, because of the paper, which he had published in 1860 together with Lautemann and a book published in the same year. The court decision turned out to be favorable to Kolbe, who had granted an exclusive license to the chemical factory Heyden in Dresden. The importance of salicylic acid as a preserving and antiseptic agent with unique pharmaceutical properties had been recognized long before the synthetic product became available. Its demand increased further dramatically once Aspirin, produced by acetylation of salicylic acid, started to be marketed in 1899 by the company Bayer AG. When Kolbe filed his patent application and sued Schering, Lautemann had already died. Nobody defended his interests. He had thus no share in the huge profits earned from the industrial synthesis of salicylic acid, and his scientific merits in the discovery were diligently forgotten.

Lautemann's most important individual discovery, made while in Kolbe's laboratory, is the alreadymentioned new reduction method of organic substances by hydroiodic acid and "phosphorus diiodide," which allowed him to obtain propionic acid from lactic acid (23). A. Naquet (39), whom Lautemann had met in Paris as his fellow élève in the laboratory of Wurtz, presented in the late fall of 1862 a preliminary communication of Lautemann's to the Societé chimique de Paris (40) on some work still carried out in Marburg before coming to Paris. In that communication, Naquet credits Lautemann in his introduction with the discovery of the reductive effect of hydroiodic acid on organic substances. The work presented in Paris was eventually published in full detail, in 1863, in Germany (41). This report is about the reduction of picric acid to the triiodide of picrammonium (42) and the isolation of other salts of the same base.

There are two further publications by Lautemann resulting from work done in Marburg before coming to Paris: in the first (43), he reports the smooth reduction of quinic acid to benzoic acid by the same method. The reaction is described in Scheme 2 with the structural formulae as we know them today. Obviously the structures of quinic and benzoic acid were unknown to Lautemann. (The structure of the former was only determined in 1932 (44)). He represented the composition of quinic acid as $C_{14}H_{12}O_{12}$ (If he had used the "new" post-Karlsruhe atomic weights, it would be $C_7H_{14}O_7$.) and that of benzoic acid as $C_{14}H_6O_4$ ($C_7H_6O_2$). In the preliminary communication presented by Naquet in Paris about the same work (40), however, the modern atomic weights were already used.



Scheme 2. In vitro by E. Lautemann

Lautemann must have asked himself, since the reduction *in vitro* ("*in der Retorte*") was that easy, what would happen to quinic acid in an animal organism. To investigate this question, he and two friends ingested

calcium quinate at supper and analyzed their urine next morning. He found hippuric acid (benzoylglycine, of which it was already known that it yielded benzoic acid through hydrolysis). This publication has recently been mentioned as a pioneering step in the history of xenobiotic metabolism, because it was the first time that a biochemical reduction had been observed in an animal organism (45).

Scheme 3. In vivo in E. Lautemann and two friends

A last publication based on work done in Marburg reports the action of hydroiodic acid on gaultheria oil, the main component of which is the methyl salicylate, yielding methyl iodide and salicylic acid (46).

Lautemann's first 14 publications, all deriving from his Marburg period, reveal that he did not just carry out projects conceived by Kolbe. There is enough evidence that he had his own ideas and tried to resist the overwhelming authority of Kolbe. He considered the reductions with hydrogen iodide and "phosphorus diiodide" very much an achievement of his own, which he signed as the single author and which was confirmed by the credit given to him by Naquet.

Lautemann's publications from the laboratory of Lisbon Polytechnic School

Although the publications do not mention explicitly the laboratory where the work described in his later publications was carried out, there is no doubt that the bulk of it was done at the Lisbon Polytechnic School. One cannot exclude the possibility, however, that Lautemann might have carried out some preliminary experiments while still in Wurtz's laboratory in Paris.

Lautemann, together with Aguiar, applied the reduction by hydroiodic acid generated by the reaction of "phosphorus diiodide" with water to the case of polynitronaphthalenes. They set out to synthesize several polynitronaphthalenes, including the new compound tetranitronaphthalene, and reduce them to the corresponding polyaminonaphthalenes. This was published first in Paris as a preliminary communication (47) and later, in 1865, as a detailed paper (48). A few years later, the latter was

published again, in several parts, this time in Portuguese, in a scientific journal newly founded under the auspices of the Lisbon Royal Academy of Sciences (49). The structures of the various isomeric polynitronaphthalenes and thus their derived polyaminonaphthalenes were only clarified in 1895, by Will (50), as 1,3,8-trinitro- and 1,3,6,8-tetranitronaphthalene. Aguiar continued alone, after Lautemann's departure from Lisbon in 1864, the work inspired by Lautemann on dinitro- and diaminonaphthalenes, as has been reported earlier (8).

Alexander Bayer: Bielitz – Wiesbaden – Leipzig – Lisbon – Brünn

Neither the publications of Aguiar's co-author, Alexander Bayer (spelled Alexandre, when the language of publication was Portuguese or French), nor the documents accessible in the archives of the Lisbon Polytechnic School give any information of a biographical nature. Since Lautemann had been a student of Kolbe, this was taken as a hint that Bayer too might have been a disciple of Kolbe. The standard biography of Kolbe by Rocke (11) does not, however, mention anybody with that name. The archives of Marburg University are also silent about him. Since Lautemann might have traveled to Lisbon after Kolbe moved to the University of Leipzig, a search in the archives of the latter University was carried out. Surprisingly, a digitized online register of students yielded instantaneously the information that Alexander Georg Bayer had indeed studied Chemistry and Physics there from May to October 1868, and that he was born in 1849, in Bielitz, Austrian Silesia. The keywords Bayer and Bielitz in Google, however, did not yield any information on Alexander Bayer but did instead on the famous inventor of the Bayer process, who produced aluminum oxide from bauxite—Karl Joseph Bayer, born in 1847 (51) apparently coincidentally in the same place. Bielitz today is called Biełsko-Biala and is in southern Poland. In order to find out whether Alexander Georg was a younger brother of Karl Joseph, Dr. Gerhard Pohl of the Austrian Ignaz-Lieben-Gesellschaft for the History of Science was asked whether he knew any more biographical details for Karl Joseph Bayer. Dr. Pohl passed on the request to someone that he knew was preparing a publication on K. J. Bayer and copied him into this e-mail exchange. Soon after, that author in Vienna presented himself as the great grandson of Alexander Bayer (and also great grandnephew of Karl Joseph), and in due course became co-author of the present publication. By pooling the data accessible both from Lisbon and Vienna, it has been possible to reconstruct a biography.

As noted above, Alexander Bayer was born in Bielitz in 1849, to a family of Silesian clothworkers. His father owned brick works and one of his uncles a textile plant. Having finished *Unterrealschule* (four years) in Bielitz and *Oberrealschule* in Troppau (today Opava in the Czech Republic), he worked as *Praktikant* in the laboratory of Fresenius in Wiesbaden in 1867-68, followed, in summer 1868, by another *Praktikum* in the laboratory of Kolbe in Leipzig. Following this he

- •1868 worked as *Preparador* at Lisbon Polytechnic
- •1872 returned to the Austro-Hungarian Empire
- •1872-1882 worked as an independent chemist and occasionally with his elder brother Karl Joseph in Brünn (today Brno in the Czech Republic)
- •1883 was employed by the Brünn gas factory, and later was appointed director of the ammonia factory
- •1928 passed away in Brünn/Brno

Both Bayer brothers had been pupils of the famous analytical chemist Carl Remigius Fresenius in his laboratory in Wiesbaden (52): Karl Joseph as *Praktikant* from 1864 to 1866 and Alexander Georg from 1867 to 1868. The laboratory of Fresenius was highly regarded both for the services offered to its customers and as a teaching laboratory (*Unterrichtslabor*). Many of its pupils were recruited by the emerging German chemical industrial enterprises or entered successful academic careers. For Alexander Bayer this meant that he had received the best available laboratory training both in analytical and in organic chemistry with Fresenius and Kolbe, respectively, before traveling, still aged only 19, to Lisbon.

Publications of Alexander Bayer

A complete list of Alexander Bayer's publications and patents will be published soon in the framework of a biography of Karl Bayer. In the present publication we will concentrate on the work done in Leipzig and Lisbon, i.e., between 1868 and 1871. After Bayer's departure from Lisbon in 1872, there is a long break in his scientific publications until 1882. From then on he published another 14 papers, mostly related to industrial and analytical chemistry as well as chemical engineering. From 1890 on he was awarded at least 22 patents. They reflect very strong activity as an industrial chemist in Brünn and have little relation to his former work done in Leipzig and Lisbon. A captivating aspect of his work in Brünn is the attention paid to the protection of the environment. Several patents and publications deal with

the engineering aspects of treating the highly polluting effluents of the gas factory, which he was heading.

Between 1868 and 1871, Alexander Bayer started his scientific activity by publishing as single author several papers related to his discovery in Kolbe's laboratory of a new compound, obtained from acetonitrile, which he called "Kyanmethin." Some of these were published in Germany and some in Portugal. He had obtained cyanomethine by trimerisation of acetonitrile induced by sodium metal, in analogy to earlier work by Frankland and Kolbe (53), who had carried out a similar reaction with propionitrile, obtaining what they called "Kyanäthin." Only in 1889 were cyanoethine and cyanomethine recognized to have the structures of pyrimidine derivatives 2,6-diethyl-5-methylpyrimidin-4-amine and 2,6-dimethylpyrimidin-4-amine, respectively (54). The first paper (55) was a preliminary communication posted on 20 July 1868 from Kolbe's laboratory, the compositional formula of cyanomethine being represented according to atomic weight 6 for carbon. The next one (56), with the full details, including a thorough crystallographic study by Dr. Pereira da Costa (57), was already submitted from the chemical laboratory of the Lisbon Polytechnic. Kolbe reprinted the first detailed report (56) in his book on the achievements of his laboratory in Leipzig (58), but suppressed the line mentioning that the original report had been submitted from the chemical laboratory of the Lisbon Polytechnic School. A further report (59), dealing with halogenated derivatives of cyanomethine was already based on work carried out entirely in Lisbon. These reports were translated from German into Portuguese and were published in an already mentioned new journal under the auspices of the Lisbon Royal Academy of Sciences (60).

Other publications in co-authorship with Aguiar followed these signed by Alexander Bayer alone. The first reported the discovery that aniline was a good solvent for recrystallizing natural indigo (61). This article was addressed to a readership little acquainted with chemistry and the dyeing of textiles, as can be concluded from the style of a lengthy introduction on this topic. A German translation was published almost simultaneously (62). Since Aguiar was also an enologist (8), he was naturally interested in the chemistry of tannins. He and Alexander Bayer used the reduction method of Lautemann with hydroiodic acid generated by the reaction of "phosphorus diiodide" with water, in order to reduce tannin, which was already known to occur in wines. They obtained just gallic acid and no products that might arise from the reduction of a sugar. They hesitated, though, to draw the conclusion, now known to be correct, that tannin is not a glycoside, because they thought that more experiments would be needed (63). There is, however, no later publication about the intended continuation of this project. Another note, also of a merely preliminary character, is about the nitration of salicylic acid, followed by the reduction of the nitrosalicylic acid obtained (64). They again used Lautemann's reduction method. They almost certainly had their hands on 5-nitrosalicylic acid and the hydrochloride of 5-aminosalicylic acid. These last two notes did not make it, however, onto the international stage. In both cases they intended to complete them by more thorough experimental studies, but there can be no doubt that their work was flawless and that their provisional interpretations were on the right track.

The last joint publications of Aguiar and Bayer had, on the contrary, a quite important international impact. A preliminary note about naphthazarine in French (65) preceded two publications 1871 in German (66). One has to bear in mind in this context that Graebe and Liebermann had recognized, in 1867, the natural dye alizarin (extracted from madder) to be a derivative of anthracene, and had synthesized it for the first time, in 1868, starting with anthracene. In 1869, together with Caro, and in competition with Perkin, two patents were filed for the industrial production of alizarin. Synthetic alizarin was first marketed in 1871. In 1870, Liebermann had reported on the synthesis of a similar compound by oxidation of dinitronaphthalene and called it naphthazarine. Liebermann found it important to identify naphthazarine as a colorant different from alizarin, in order to refute earlier claims that it was alizarin that had been obtained from dinitronaphthalene in the same way (67). Aguiar had noticed, however, that Liebermann had used a mixture of isomeric dinitronaphthalenes. Since Aguiar, in the meantime, between Lautemann's departure and Bayer's arrival, had worked on the separation of these isomers, he had pure samples of each of the two isomers. He and Bayer repeated Liebermann's experiments with "a-dinitronaphthalene" (later recognized to have the structure of 1,5-dinitronaphthalene (50)) with the same result and they studied also some more highly oxidized side products. Carl Liebermann himself presented their work in two sessions of the German Chemical Society in Berlin. Revealing the structural determination of naphthazarine itself, however, was a puzzle of such complexity that only in 1926 were Dimroth and Ruck (68) able to come to the final conclusion that it corresponds to 5,8-dihydroxy-1,4-naphthoquinone, refuting an earlier conclusion of Will (50).

Lautemann: Lisbon – Goa – Biebrich (Wiesbaden)

Since Lourenço had studied medicine in Nova-Goa, the Portuguese historian of medicine Maria Luisa Villarinho Pereira, knowing about our investigations on Lourenco and Aguiar, sent us an annual report of the medical-surgical school of Nova-Goa (69), in which both Lourenço and Lautemann were praised many years later as landmarks in the teaching of chemistry there. Thus it became possible for us to track the next step of Lautemann's whereabouts. From Lisbon Lautemann left on 22 March 1864 for Goa in then Portuguese India, where he had been appointed to lecture on the "Principles of Physics, Chemistry and Natural History." He arrived on 5 May and immediately started his lectures. In October of the same year, however, Lautemann left for "his country" due to the worsening of an illness, "from which it seems that he had been suffering already in Europe" (70). Since no further publications of Lautemann are known, the question remained open as to whether he survived the journey or not, and, if he survived, where he lived and what were his activities after his return to Europe. Since he was born and baptized as a Lutheran in the Electorate of Hessen, an enquiry with the Evangelical Church of Hessen and Nassau seemed the obvious next step in order to gather information on Lautemann. According to parochial records, he passed away on the 5th of May 1868, in Biebrich in the Duchy of Nassau (71). Biebrich is known in the history of the German chemical industry as the place where in 1863 Dr. Wilhelm Kalle (1838-1919) had founded the chemical plant Kalle & Co., one of the first in Germany to produce synthetic dyes. Biebrich was an independent city, which became incorporated in the 20th century into Wiesbaden. Our supposition that Lautemann might have worked at that plant proved right: according to a publication commemorating this company's 75th anniversary (72), personnel had contracted Dr. E. Lautermann [sic] in 1867, who after his death in 1868 was replaced by another chemist, also a disciple of Kolbe, the already mentioned Dr. C. Ulrich.

Lautemann had had health problems at various periods of his short but eventful life: as a youngster, he had to interrupt his studies on medical advice and in Marburg he had to resign as assistant of Kolbe; in Goa, after a short while, he fell so ill that he had to leave for Europe, where he only survived for another four years. Although nothing can be said for sure about the nature of his illness, one should bear in mind that in the 19th century, many youths contracted early pulmonary tuberculosis with periodical relapses followed by death in their early thirties.

The Fresenius Laboratory in Wiesbaden, as a Recruiting Center for Aguiar

Scanning the list of assistants and students who attended the Fresenius Laboratory in Wiesbaden (55) between 1848 and 1873 revealed two very interesting aspects beyond the information on the Bayer brothers.

First, it contains at least two persons related to the foundation of important chemical companies. Wilhelm Kalle was *Praktikant* with Fresenius during the summer semester 1857 and the winter semester 1857-58. After that he went to study chemistry with Kolbe in Marburg, where he got his Ph.D. in 1861. He must have met Lautemann who got his Ph.D. with Kolbe in that same year. In 1863, as noted above, he founded Kalle & Co., producing aniline dyes in Germany, starting with fuchsine red. When hiring Lautemann in 1867, he was addressing somebody he had thus known for many years. The other was Friedrich Bayer Jr. (1851-1920) from Barmen, who was Praktikant during the summer semester 1867 (overlapping with Alexander Bayer) and winter semester 1867-68. His father, Friedrich Bayer (1825-1880) had founded in 1863 another dyestuff factory, together with Johann Friedrich Weskott. From there he developed the still-existing Bayer AG, based in Leverkusen. In spite of having the same surname, Friedrich Bayer, father and son, were not relatives of Alexander Georg and Karl Joseph Bayer.

The second kind of entries of the list that we found interesting were those concerning persons who had some relation with Portugal. The first pupil of Fresenius in chronological order to have a relationship with Portugal was Friedrich Wilhelm Klaas from Hörbach near Herborn. As mentioned before, the name "William Klaas" appears in December 1864 in a proposal of the Lisbon Polytechnic's council to recruit him as successor to Lautemann. Klaas had been *Praktikant* in Fresenius's laboratory in the winter semester 1861-62 and summer semester 1862. He then became Assistent in Fresenius's Privatlaboratorium from winter semester 1862-63 to summer semester 1864. The private laboratory was the place where the analyses ordered by customers were carried out. Klaas was thus prepared to provide that kind of service at the Lisbon Polytechnic School. This explains why there were no publications on research in organic chemistry by him. He probably divided his activity between demonstrating chemical experiments during the lectures of Lourenço and Aguiar and running chemical analyses in the laboratory. Lourenço's activity during that period was indeed, besides lecturing, mainly in providing analyses to Portuguese customers. Klaas served the Lisbon Polytechnic School until August 1868 (73). What had led Lourenço and Aguiar to ask Fresenius to recommend one of his assistants was probably not only the great reputation of the Fresenius laboratory, but also the friendship between Lautemann and Kalle, who had both been contemporaries in Kolbe's Marburg laboratory, after Kalle had left Fresenius's laboratory in 1858.

The next pupil of Fresenius in chronological order, relevant to the network of future *preparadores* in Lisbon was Karl Joseph Bayer, who stayed with Fresenius for two years from the winter semester 1864-65 to summer semester 1866. Although he was not recruited to Lisbon, this Bayer certainly had an influence on the decision of his younger brother to study with Fresenius as well, which he did in the winter semester 1867-68, immediately before moving to Kolbe's laboratory in Leipzig, for the summer semester 1868, from where he traveled to Lisbon in the Fall in order to replace Klaas from December 1868 until August 1872 (74).

Dr. Christian Heinzerling from Biedenkopf, who had been Praktikant in Fresenius's laboratory from summer semester 1869 to summer semester 1870, was the third pupil with a relationship with Portugal. Simultaneously he became an assistant in the private laboratory during the same semester and remained as such until the winter semester 1871. He served the Lisbon Polytechnic School from November 1872 to September 1874 (75). Heinzerling was followed by Carl von Bonhorst from Wiesbaden, who was Fresenius's *Praktikant* from summer semester 1868 to winter semester 1869-70, became an assistant in his teaching laboratory in summer 1870 and continued in that position until the 1872 summer semester, with an interruption in the 1870-71 winter semester when he was wounded in action as a soldier in the Prussian army fighting France. He was recruited in 1872 by Aguiar to the Industrial and Commercial Institute of Lisbon (76) and replaced Heinzerling at the Lisbon Polytechnic School from November 1874 onward (75). After Aguiar's death in 1887, von Bonhorst taught chemistry from 1888 until his own death in 1918 at the Marquis of Pombal School (Escola Marquês de Pombal), a secondary vocational school in the industrial Alcântara borough of Lisbon (77).

Another Fresenius pupil was Vicente Ferreira Ramos (1826-1889) in the summer semester 1869, an artillery officer in the Portuguese army, who had studied at the Lisbon Polytechnic School from 1845 to 1849. (78)

Concluding Remarks

Our research has made it possible, in spite of the absence of any remains of letters in Portuguese public or private archives, to establish a network of Portuguese-German contacts. Figure 2 depicts the travels of the protagonists of our report. The Fresenius laboratory turned thus out to have been the hub of the network of *preparadores* who came to Lisbon. Our research illustrates the knowledge, research traditions and skills which they had brought with them, and which left their marks, despite the fact that most of the *preparadores* only stayed for a short period.

The publications of Aguiar on organic chemistry not co-authored by Lautemann or Bayer show that Lautemann was the one who introduced Aguiar to the world of fundamental research in that area. There was thus a reversal of the usual teacher-student relationship in that the preparador has to be seen

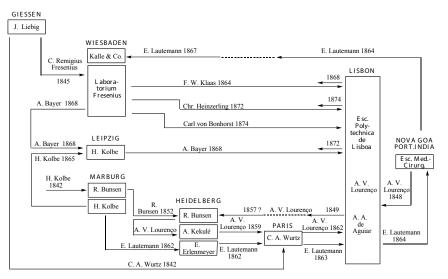


Figure 2. The German-Portuguese network of chemists in the 1860s and 1870s. The similar case is that indicated dates are those of arrivals and departures of their travels. of Bernhard Tol-

as the teacher and the lecturer as the student. Aguiar's relationship with Bayer was more on an equal footing. The whole set of Aguiar's publications bears, however, a strong mark of Lautemann's initial push. Some of the publications co-authored with Bayer go on using, for example, the reduction method, which had been invented by Lautemann ("phosphorus diiodide" and hydroiodic acid) when still in Marburg.

Among the reasons for their early departures, one has to realize that the position of *preparador* was of a low rank (in spite of a better salary than that of a locally recruited one) and did not offer any career prospects. Higher-ranking positions in public institutions were not easily accessible to foreigners. Lautemann as Doctor phil. of the University of Marburg and with Kolbe as supervisor had a much higher academic qualification than the majority of the lecturers of the Lisbon Polytechnic School, including

Aguiar. The only lecturer of the Polytechnic School with a doctoral degree from a foreign university seems to have been Lourenço. Lautemann's early departure from Lisbon and his appointment at the Medical-Surgical School in Goa might be interpreted as a frustrated attempt to start a career as a chemist in the Portuguese public service. At the date of the foundation of the Lisbon Polytechnic School in 1837, the Council had considered the possibility of recruiting foreign professors in the fields of science where no qualified persons could be found in Portugal. This intention was never implemented (4). Instead foreigners were only recruited for the lower ranking

positions of preparadores. Klaas and Bayer did not bring with them academic degrees of the same rank as Lautemann, and therefore were not that overqualified for the job of preparador. In spite of that, the lack of career prospects in Portugal certainly also contributed to the early date of their return to their home countries. A of Bernhard Tol-

lens (1841-1918),

who spent only a short time between 1869 and 1871 in Coimbra as Director of the Chemical Laboratory of the University (79). The career prospects for a young chemist in the German States were so much better than in Portugal that their desire to continue their careers there is easy to understand.

Another question is why, in spite of the knowledge transfer from abroad, it was not possible to establish in Portugal a national research school, according to the often so-called Giessen model. The existing studies on the Giessen school (2) show clearly that transplanting that kind of research school into a different country demanded an environment radically different from that of Portugal. There was no fast-growing chemical industry as in Germany interested in the output of such a research school, both in terms of trained chemists and of services offered by the laboratory. In 19th-century Portugal, chemical analyses were required for quality control of foodstuffs

and water, for drugs sold in pharmacies, for forensic purposes, for minerals, ores and metals, for imported goods by the customs administration and little more. There was no chemical profession. Such analyses were carried out mostly in government or municipal laboratories, by persons whose polytechnic or academic degrees, if any, were in agriculture, commerce, pharmacy, or human or veterinary medicine (in the case of toxicological analyses). There were no private industrial employers to speak of. This environment was in strong contrast to that of the Giessen research school and those places elsewhere in Europe where it was possible to found similar national research schools.

Chemistry at the Lisbon Polytechnic School was seen by the majority of the faculty members as justified only so far as it could be applied to 19th century engineering. Most students, after passing some exams, indeed continued their studies in the army school (Eschola do Exército) to become military or civil engineers employed by the state. These engineers played a very important role in the modernization of the Portuguese state, most prominently in shaping the national territory through planning and managing public works, like the creation of a network of roads and railways, providing water supply, etc. (80). Mathematics, mechanics and strength of materials were the main scientific foundations needed for such activities. Chemistry did thus not play an important role in this context. Making it difficult for foreigners to reach leading positions in teaching and practicing engineering may also have been a consequence of the militaristic and patriotic spirit of both the Polytechnic and the Army Schools. The prospects for an academic career were thus very bleak for a foreign chemist. The chemical industry was also at a too backward stage of development to offer qualified jobs.

In spite of the secondary role to which chemistry was relegated, the Chemical Laboratory (81) of the Polytechnic School, which today has been restored to its original splendor, occupied an important area of the building. Lourenço and Aguiar were unable, however, to overcome the resistance of their colleagues to introducing obligatory laboratory classes. This became possible eventually for the students of the Industrial and Commercial Institute of Lisbon. Aguiar's research collaboration with Lautemann and Bayer had left a positive influence on the quality of experimental training at the Industrial and Commercial Institute, where the latter was also active, though not only as a result of the above-discussed publications. Many years later, a former student of that

institute remembered gratefully the laboratory classes given by Alexander Bayer and Carl von Bonhorst (77).

Was the influx of chemical knowledge from Germany compensated for by any kind of recirculation, once the *preparadores* returned to their homelands? Certainly their sojourn of several years in a country with such a different culture had broadened their horizons and made them more cosmopolitan. As for more specific scientific knowledge, the question is more difficult to answer. An exception may be the attempts made by the Bayer brothers in the production of salicylic acid (82), a subject that certainly had been discussed frequently with Aguiar, who in turn had become interested in that subject under Lautemann's influence.

After Aguiar's death, followed shortly later by Lourenço's, there were for several decades, well into the 20th century, no further publications from Portugal on fundamental organic chemistry. The public debt crisis of the 1890s had a negative impact on public investment in higher education not to speak of the possibilities of financing research, initiating a dark period for the physical sciences. The only domains where Portugal distinguished herself in research achievements were connected to the development of the colonies. During the race of the European powers for domination and exploration of the African colonies in late 19th century, the Portuguese authorities concentrated their resources successfully on subjects like tropical diseases and tropical agriculture. In that economic environment there was no possibility for the development of a chemical profession and thus for a research school in chemistry to survive.

What were the consequences of Lautemann's stay in Goa? The existing reports mention many complaints about lacking support from the central colonial administration throughout the remaining 19th century. The Portuguese governments, at that time, were mainly concerned about the future of the African colonies. Compared to these, the interests of the colonies in India were neglected, and the expectations of an important role for the medical school in the broader context of the Portuguese colonial empire were never fulfilled. It proved impossible to find a permanent lecturer for the chair of Principles of Physics, Chemistry and Natural History of a caliber comparable to Lautemann's (69). No wonder that the research on tropical medicine and agriculture mentioned above was conducted centrally from Lisbon (83). No documents were found, which might give a hint about an influence of Lautemann's activity on the professional achievements of his students in Goa.

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- Museu Nacional de História Natural e da Ciência, Eschola Polytechnica, Actas do Conselho, Livro 5º, fl. 252: Sessão de 30 de Dezembro de 1862 and fl. 253: Sessão de 17 de Janeiro de 1863.
- 14. Ibid., Livro 6°, fl. 14: Sessão de 5 de Abril de 1863.
- 15. Ibid., Livro 6°, fl. 11: Sessão de 14 de Dezembro de 1864.
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- 26. The above five formulae are the ones one would use for the same compounds today. In the original paper they are different from these, because in Kolbe's research group the "old atomic weights" were still used: 6 for carbon, 8 for oxygen. Many names of the compounds were also different from the ones used today. In spite of that, the name phosphorus oxychloride for POCl₃ is still used today as a common name.
- 27. A most detailed description of Kolbe's scientific, societal and political idiosyncrasies, their interconnections and contradictions, can be found in the chapter "Pride and Prejudice" of A. Rocke's masterful biography of Kolbe (Ref. 11).
- 28. H. Kolbe "Ueber einige Abkömmlinge des Cyanamids," *J. prakt. Chem. (Leipzig)*, **1870**, *1*, 288-306 (especially 292-294).
- 29. H. Kolbe and E. Lautemann, "Ueber die Säuren des Benzoëharzes," *Ann. Chem. Pharm.*, **1860**, *115*, 113-114.
- 30. H. Kolbe and E. Lautemann, "Über die Constitution und Basicität der Salicylsäure," *Ann. Chem. Pharm.*, **1860**, *115*, 157-206.
- 31. H. Kolbe, Ed., Das chemische Laboratorium der Universität Marburg und die seit 1859 darin ausgeführten chemischen Untersuchungen nebst Ansichten und Erfahrungen über die Methode des chemischen Unterrichts, Vieweg, Braunschweig, 1865.
- 32. The term "molecule," as understood today, was widely accepted only in 1860 at the famous Karlsruhe Congress, together with the adoption of the new atomic weights, 12 instead of 6 for carbon and 16 instead of 8 for oxygen. Stanislao Cannizzaro (1826-1910) convinced many of the members of the Congress to make this change in order to achieve consistency of the new atomic weights with the

- hypothesis of Avogadro. With the adoption of the new atomic weights, Kolbe's ingenious "carbonic acid theory" became too abstruse compared to structural theory, which he never did accept. According to "carbonic acid theory," the constitutional formulae of organic acids were derived from that of carbonic acid 2HO.[C₂O₂].O₂. The formulae for lactic and salicylic acids shown in Figure 1 were obtained by substituting one of the HO groups (written left of $[C_2O_2]$) together with one of the oxygen atoms O, written on its right side by the formulae of an "oxyethyl" or "oxyphenyl" radical, respectively, enclosed in brackets. In this case Kolbe and Lautemann used the term "radical" with the same meaning as today for what we now call a hydroxyethyl and a hydroxyphenyl radical. The formulae of the kind shown in Figure 1 ceased to make sense after the adoption of the new atomic weights, because the atomic symbols O would not represent oxygen atoms, but half oxygen atoms.
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A CENTURY OF BASE-PROMOTED DECOMPOSITION OF HYDRAZONES: THE EARLY CAREER OF NIKOLAI MATVEEVICH KIZHNER (1867-1935)

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The year 2011 marked the centennial of the first report of the base-promoted decomposition of hydrazones to hydrocarbons (1). The reaction was discovered in 1911 by the 43-yearold inaugural Professor of Organic Chemistry at the Imperial Technological Institute at Tomsk, in Siberia-Nikolai Matveevich Kizhner (Николай Матвеевич Кижнер, 1867-1935) (2, 3). Eighteen months after the appearance of Kizhner's paper, which was in Russian, the reaction was

rediscovered by German chemist, Ludwig Wolff (1857-1919), at Jena, and published in German (4). Since 1912, it has borne the name of both chemists, being known in the west as the Wolff-Kishner reaction, and in Russia as the Kizhner-Wolff reaction.

Kizhner (Figure 1) is an interesting study as both an individual and as a chemist. Over the course of his career, he faced incredible obstacles—physical, politi-



Figure 1. Members of the Chair of Organic Chemistry at Tomsk Technological Institute ca. 1910: (1-r) Laboratory Assistant (later Professor) Georgii Vasil'evich Khonin (1878-1952), Professor Nikolai Matveevich Kizhner, and an unidentified member. Photograph courtesy of Tomsk Technological Institute.

cal, and professional-all of which he overcame. It is a tribute to his resilience and tenacity that he not only built a career as an organic chemistry professor, but that he succeeded as well as he did. Some idea of the course of his career can be gauged from the fact that, while other major figures in organic chemistry were frequently memorialized by plaques placed prominently their universities within a short time of their deaths, it was not until over a quarter century after his death, and over half a century after he

had left Tomsk, that Kizhner was so memorialized at the Technological Institute.

There are no reliable facts available about Kizhner's early life; it has been speculated that his father held the social rank of a court counselor (i.e. not of the nobility, but of a middle social class), or that he came from a family of army medical assistants. Still, his family did have sufficient status to allow him to enter the First

Moscow Gymnasium, from which he graduated in 1886. He then entered Moscow University (now Lomonosov Moscow State University) as a student in the Natural Sciences Division of the Physics-Mathematics Faculty. This faculty by then included chemistry, which had initially been part of the Medical Faculty of the university

(5). By his third year, Kizhner had fixed on organic chemistry as his course of study.

At Moscow, Kizhner came in contact with of two excellent chemistry instructors, who undoubtedly had a strong influence on his eventual choice of a career: organic chemist, Vladimir Vasil'evich Markovnikov (Владимир Васильевич Марковников, 1838-1904), who taught the lectures in organic chemistry, and physical chemist, Vladimir Fyodorovich Luginin (Владимир

Фёдоровч Лугинин, 1834-1911), who supervised the laboratory instruction in chemistry (6). Kizhner's attitude towards Markovnikov, especially, appears to have been what today would be called hero-worship: "'I remember how impatiently I waited for Markovnikov's first lecture, said Nikolai Matveevich. 'His name, in our eyes, was surrounded by a halo of chemical prestige" (7). It is

worthwhile noting that Markovnikov, one of Butlerov's students at Kazan, was one of the few Russian organic chemists to build a lasting international reputation during his own lifetime.

Kizhner rapidly developed as an organic chemist, and his first research publication was published the same year he graduated with the *Diplom*—1890. By that time, Markovnikov's primary focus had shifted to identifying the hydrocarbons of the Caucasus oil, and he was involved in the effort to establish the identity of the hydrocarbon, "hexahydrobenzene," that had been obtained by the reduction of benzene by means of Berthelot's method using hydrogen iodide in a sealed tube at high temperature (8). This hydrocarbon and its constitution

were also the subject of intensive research in Western Europe (9, 10).

Kizhner began investigating this problem while still an undergraduate, and he soon supplemented it with two other projects (Figure 3). This ability to focus simultane-

> ously on more than one problem at a time was one of the hallmarks of his entire career. Thus, while studying hexahydrobenzene, he was also investigating the reactions of hydrogen halides with allyl ethyl ether, reactions that resulted in the cleavage of the ether into the two halides and water (11), and the reaction of epichlorohydrin with sodium metal (12) to give 1,3-diallyloxy-3-propanol. He published these two papers and two on hexahydrobenzene (13) in the first years of his association with Markovnikov.



Figure 2. Kizhner's mentors: Vladimir Vasil'evich Markovnikov (left) and Vladimir Fyodorovich Luginin (Louguinine) (right). Photographs courtesy of the Museum of the Chemistry School of Kazan University (Markovnikov) and Moscow State University Archives (Luginin, provided by Dr. E. A. Zaitseva (Baum)).

Figure 3. Kizhner's early research problems.

Following his graduation with the *Diplom*, Kizhner remained in Markovnikov's laboratory to carry out the research for the degree of Magistr Khimii (M. Chem.). He had been identified by both Markovnikov and Luginin as a student with the potential to enter the professoriate, and at their suggestion, he was funded during this time by means of a supernumerary, "outside statute" position—a position funded internally, rather than by the state—as a laboratory assistant in chemistry at Moscow University. In 1895, he submitted his M. Chem. dissertation (14) to St. Petersburg University. He passed the requisite examinations, and since he now held the M. Chem. degree, he was qualified to hold a junior appointment at a Russian university. He was appointed Docent at Moscow in 1895. During his M. Chem. studies, Kizhner had taught in the laboratories at Moscow, and in his final year (1894) he had been appointed as an instructor at the Alexander Military School; he held this appointment jointly with his position at Moscow until his departure for Tomsk, in 1901.

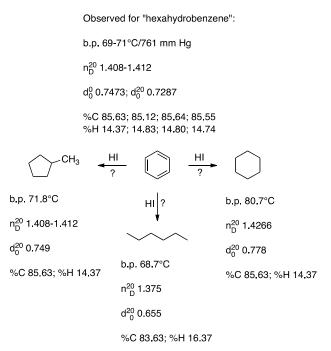


Figure 4. The candidates for the hydrocarbon produced by reduction of benzene under Berthelot's conditions.

Kizhner submitted his dissertation to Moscow University for the degree of *Doktor Khimii* (Dr. Chem.) in 1900 (15). During the independent research on which his Dr. Chem. dissertation would be based, Kizhner continued to work on the hexahydrobenzene problem (Figure 4). The fact that the boiling point of hexahydrobenzene (69-71°C/761 mm Hg) was closer to that of hexane, and not cyclohexane, while its combustion analysis gave values equal to those from cyclohexane, and not hexane, had been problematic for chemists of the period looking to establish the six-membered ring in benzene.

It was Kizhner who first realized what had happened—that there had been a rearrangement during the reduction—and showed that methylcyclopentane (Figure 4) had the required physical and chemical properties (16). The publication of Kizhner's paper was quickly followed by papers by Zelinskii (17) and Markovnikov (18), confirming Kizhner's conclusions. Zelinskii's paper was revealing in another way: it showed he had begun working on Markovnikov's problem without informing him of this fact, a breach of professional etiquette, and Markovnikov made clear his claim to the problem in his "Bemerkung" paper (18b).

The Russian poet, Andrei Belyi (Андрей Белый, nom-de-plume of Boris Nikolaevich Bugaev, Борис Николаевич Бугаев, 1880-1934), who had a dim view of science and its practitioners, painted a vivid caricature of Kizhner as Markovnikov's apprentice in Moscow (19):

For two years I encountered a bald, red, strangely pink, bespectacled man, dressed in devil knows what: something red-soiled and burnt through with holes. You would come across him, awkward, never too far away from bromine, in the basement, in the hallway; you push him here, you stumble across him there, he is not a person, but a dumb animal.

- —Who is that?
- —Kizhner.

... [of the many people in the lab] ... one whistles, another mumbles something to himself, Kizhner is mute. He displays emotion only when you push his elbow in the hallway. In response, you'll get boxed in the ears with the towel usually draped over his shoulders...It would be strange to find that Kizhner has a house or, God forbid, a wife. His home is the organic laboratory.

This description notwithstanding, not only did Kizhner have a wife (Sofia Petrovna), but a son (Boris Nikolaevich, born in 1894).

In the same work, Belyi suggests that in the eyes of the other students, Kizhner, who worked in the laboratory from dawn until dusk, could be represented by the following rather grotesque description (19):

... The crazed look of the small, lidless eyes, like the heads of two rubbed corks, the little red nose, the glasses, the little red beard, and a round bald spot: all parts of his head....

Again, one must recognize in this description the hyperbole used by one with little respect for scientists—in Belyi's eyes a man so dedicated to science could not help but arouse pity and a wry smile.

Graduating with the Dr. Chem. qualified Kizhner to hold a Chair in chemistry as an Ordinary (Full) Professor at a Russian university. The Imperial Tomsk Technological Institute, which had been established by a 1896

decree of Tsar Nicholas II, was officially opened in 1900 under the leadership of Efim Luk'yanovich Zubashev (Ефим Лукьянович Зубашев, 1860-1928), Professor at Khar'kov University, and a sugar chemist and technologist of national standing (Figure 5). Tomsk was somewhat unusual for the time, since its enrollment was open—not subject to the political and religious limitations of most other universities in the empire—and thus was permitted to enroll graduates of technical schools. Its exemption from the enrollment quotas attracted a large number of Jewish students. Zubashev quickly sought candidates to fill the faculty positions there; his efforts to build the chemistry faculty were facilitated by the active assistance of Mendeleev, who helped to attract strong candidates for the positions.



Figure 5. The first Director of the Tomsk Technological Institute, Efim Luk'yanovich Zubashev ca. 1901 (photograph courtesy of Tomsk Polytechnic University)

Tomsk is one of the oldest cities in Siberia, having been founded by the decree of Tsar Boris Godunov in 1604. Two centuries later, Tomsk became the seat of the Tomsk Guberniya, and began a rapid expansion that was accelerated by the discovery of gold in 1830. Because the route chosen for the Trans-Siberian Railway passed through Nizhni Novgorod, the growth of Tomsk was surpassed by that city in the mid-nineteenth century. Nevertheless, at the end of the nineteenth century, Tomsk resurrected itself as a major educational center with the

founding of the Siberian Imperial University in Tomsk (now Tomsk State University) in 1888, and the Imperial Tomsk Technological Institute of Tsar Nicholas II (now Tomsk Polytechnic University) in 1900.

In July, 1901, Kizhner began the most eventful decade of his life, when he joined the faculty at Tomsk Technological Institute (Figure 6). He began teaching, and immediately set about equipping his laboratory (Figure 7), which soon became one of the best in Russia, and building the collection of the chemistry journals into a major resource. During each of his trips to Western Europe, he sought out apparatus and chemical journals to bring back to Tomsk. In addition to the equipment he imported from Germany, Kizhner also made equipment for his laboratory—he possessed not inconsiderable skill as a glassblower and instrument maker.



Figure 6. The Chemistry building at Tomsk Technological Institute, ca. 1903. Photograph courtesy of Tomsk Polytechnic University.

Kizhner's early research work at Tomsk was devoted to a continuation of the chemistry of bromoamines that he had begun during his doctoral research. This was followed some four years later by a major focus on the chemistry of small-ring compounds, especially amines obtained by the Hofmann rearrangement of the corresponding carboxamides (20). He also began studies of Lewis acid-catalyzed reactions of small-ring acid chlorides with benzene under Friedel-Crafts conditions (21). The chemistry of organic nitrogen compounds was to remain a major focus of his research until his death in 1935.





Figure 7. Kizhner in his Tomsk laboratory (above) and lecturing (on osazones) in the auditorium (below). Photographs courtesy of Tomsk Polytechnic University.

Just two years after beginning his tenure at Tomsk, Kizhner was diagnosed with the dangerous and painful "gangrene of the limbs." This disease became so threatening to his life that, in 1904, he traveled to Moscow, where his right leg was amputated above the ankle. On his return to Tomsk, he was still able to attend lectures and lead symposia by using crutches. But he ceased research because he could not endure the long hours of standing at the laboratory bench and the supervision of the laboratory passed to another professor. Although the surgery resulted in a brief respite from the pain, within months, gangrenous lesions began to appear on his left leg. Again, the disease ultimately proved to be resistant to treatment, and his left leg was amputated above the ankle in early 1910.

What should have been career-ending surgery at that time, especially for a synthetic organic chemist, had exactly the opposite effect. Although his teaching career in the auditorium was now in tatters (he could only enter the auditorium on crutches), his research program underwent a remarkable transformation. After his first amputation, Kizhner had effectively stopped doing experimental work. Now he returned to the research laboratory—this time confined to a wheelchair—and began working with a vengeance, as if to make up for lost time. In the words of the pioneering organophosphorus chemist, Aleksandr Yerminingel'dovich Arbuzov (Александр Ерминингельдович Арбузов, 1877-1868), "One must wonder at his powerful spirit and willpower: an invalid in every sense of the word, he continued his experimental work, publishing one paper after another" (22). It undoubtedly also helped that his apartment—like many Russian universities at this time, the Chair carried with it the fringe benefit of an apartment—was close to his laboratory.

In 1911—the year after he had become wheelchairbound—he published the first report of the base-promoted decomposition of hydrazones to give hydrocarbons, and he followed this a year later with the first report of the synthesis of cyclopropanes now known as the Kizhner cyclopropane synthesis; he continued to pursue this research for decades (23). What is even more remarkable is the fact that most of Kizhner's research publications, including those where the work was carried out after his amputations, carry the name of only one author: Kizhner did the work himself, and allowed his students to publish under their own names. In the case of the reaction that is the topic of this paper, after the initial publication with Belov, which described the preparation of cyclohexanone hydrazone hydrate, Kizhner extended the work alone (although paper 1a does carry a section titled, "In collaboration with A. Proskuryakov").

Figure 8. Kizhner's first demonstrations of the basecatalyzed decomposition of hydrazones to give hydrocarbons (the Wolff-Kishner reduction).

Kizhner's study of the base-catalyzed decomposition of hydrazones was carried out initially (1a) using a

variety of saturated ketone hydrazones, including those of some highly hindered ketones, such as camphor and fenchone (Figure 8). In the second publication (1b), Kizhner extended the reaction to a study of aldehyde hydrazones and hydrazones of unsaturated ketones (Figure 8). It is typical of the era that the most common substrates for investigation were terpene-based. In every case but one, the major product

of the reaction, isolated by distillation and steam distillation, was the cor-

1) HN₂NH₂•H₂O, KOH, Δ (95%)(23)2) 180-200°C (-H2O, N2) H₂NNH₂, Na O(CH₂CH₂OH)₂ 210°C, 12 h (69%)(24)KOBu¹ (25)Me₂SO, 25°C KOBu^t (86%) O H₂NCNHN PhMe. A (26)LiAlH₄, THF (27)Δ, 18 h (HNOTBS)₂ cat Sc(OTf) (28)KOBu^f, HOBu^f Me₂SO

Figure 9. Variants of the Wolff-Kishner reduction developed since the original discovery in 1911.

responding hydrocarbon. The reactions with the dihydrocarvones also showed that unsaturation—whether in conjugation with the carbonyl group or not—did not alter the course of the reaction. The decomposition of cyclohexanone hydrazone, however, was unusual, in that it also provided cyclohexanol in an amount approximately equal to the amount of cyclohexane produced.

Some idea of the importance of this reduction can be gathered from its longevity as a method for reducing aldehydes and ketones, and from the observation that nine decades after its discovery, the reaction was still inspir-

into developing variants that would circumvent or overcome deficiencies in the original method (Figure 9). In the nine decades since the discovery of the reaction by Kizhner, no less than six major variants have appeared (23-28), from the Huang-Minlon modification, developed in 1946

ing research

(23), to the variant reported by Myers in 2004 (28).

The year after he had described the deoxygenation of ketones by means of the base-promoted decomposition of their hydrazones, Kizhner described the base-promoted decomposition of pyrazolines in the presence of platinized clay (29). In this case, the product was not an unsaturated hydrocarbon, but an isomeric cyclopropane instead (Figure 10). As shown in Figure 10, the pyrazolines were generally formed by the reaction of hydrazine with an α,β -unsaturated ketone, but in one case, the pyrazoline was formed from the ketazine by the method developed by Curtius and Zinkeisen (30).

Figure 10. The first cyclopropanes prepared by pyrolysis of pyrazolines with base and platinized clay.

It was not only his scientific accomplishments that made his Tomsk years eventful for Kizhner. The beginning of the twentieth century saw the political crises that had been building during the reign of Nicholas II begin to grow out of control, culminating in the first of the Russian revolutions: the Revolution of 1905, which led to a curtailing of the absolute powers of the Tsar. The beginnings of this political unrest were quite evident in Moscow at the end of the nineteenth century. Kizhner may have hoped that by working in far-off, conservative Tomsk, he would be shielded from this unrest and its effects on his research program, and that the Siberian city would become a peaceful haven to pursue his science. Unfortunately for him, it was not to be, as political unrest broke out in Tomsk.

Like all the faculty members at the Institute at the time, Kizhner eventually had to declare for one side or the other. He chose to side with the striking students, and strongly supported the students' demands for the independence of the educational system from what had become oppressive rule by bureaucrats. For this, he was reported (anonymously) to be involved in organizing student and faculty strikes, and in addressing revolutionary groups (31). He was also accused by his enemies of abetting the student strikes by cancelling his lectures. While Kizhner did not punish the students for striking, there is actually little objective evidence to brand him as an agitator, and his writings and speeches were much more concerned with the science he was teaching than the politics of the students (3d).

Regardless, the success of the revolution should have protected Kizhner from serious repercussions of his supposedly revolutionary activities, but the testimony of his personal enemy, Leonid Ivanovich Lavrent'ev (Леонид Иванович Лаврентьев, d. 1914), a curator (trustee) of the Tomsk educational district (this was a powerful position, whose occupant reported directly to the Minister), and the anonymous accusations against him carried substantial weight with the local government, and he was branded a "dangerous free-thinker" (3e). In 1906 he, Zubashev, and other "disloyal" staff members were exiled from Tomsk on 48 hours' notice by the Interim Governor-General of Western Siberia (31). They were saved from a worse fate by sheer luck: the day before his arrest, Zubashev had been summoned to a council on the reform of higher education in Moscow by the Minister of Public Enlightenment, Count Tolstoy. Kizhner and the other exiled professors followed immediately thereafter, and also participated in the council. Even so, Kizhner spent a year and a half in exile, in St. Petersburg, while

Zubashev, who had some connections in higher government circles, remained in Moscow, where he petitioned the Ministry of Education for their reinstatement.

In response to a private letter from the influential minister, Count Sergei Yul'evich Witte (Сергей Юльевич Витте, 1849-1915) to the new Governor-General, Baron Nol'ken, and thanks to the influence of Pyotr Arkad'evich Stolypin (Пётр Аркадьевич Столыпин, 1862-1911), Zubashev and Kizhner were ordered reinstated in the middle of 1907. But, resentment among their colleagues at Tomsk remained. Within a year, Zubashev had been forced to resign. In 1912—the year he was awarded the Greater Butlerov Prize—Kizhner, also, was forced to resign.

It is symptomatic of the times that anonymous denunciations and petty dislikes should overshadow world-class accomplishments, but this is what happened to Kizhner. The overt reasons for his resignation were his health, but his colleagues at Tomsk knew that the real reason was, in fact, that Kizhner had been "advised" that there were local elements in the area, such as the violent gangs known as the "Black Hundreds" (32) who disapproved of his "disloyal" activity; his resignation was simply the result of extortion by threats against his life and his family (31). Another factor that made Kizhner's departure from Tomsk inevitable was the loss of his apartment, which was close to the laboratory. This apartment was one of the perquisites of the kafedra, or chair, and on resigning from his position, Kizhner also forfeited the apartment. For a man confined to a wheelchair, this added hardship eventually became too much to take.

Leaving Tomsk was extremely hard for Kizhner: he was being forced to leave the laboratory he had built from nothing, to leave behind students with whom he had established a close bond, and to abandon research problems that were not yet completed. Although he spent a further two years at Tomsk teaching, his departure was inevitable, and in 1914 he returned to Moscow, where he spent the rest of his career and life.

Kizhner's career in Moscow lacked much of the vibrant creativity that he had shown in Tomsk, although this may be traced, in part, to the dramatic shift from pure to applied research under the Soviet regime. Immediately on his return to Moscow, Kizhner obtained an appointment at the short-lived Shanyavskii People's University, with financial support from "Society to promote the success of the experimental sciences and their practical applications," funded by the philanthopist Khristofor Semënovich Ledentsov (Христофор Семёнович Леденцов,

1842-1907) (33). After the Revolution, he assumed a leadership position at the Aniline Trust Institute ("Aniltrest"), where he became a very conscientious leader of the Russian synthetic dye industry. His research during this period consisted largely of work to improve the synthesis of dyes, but he did continue, somewhat sporadically, with work on the two reactions he had discovered in Tomsk. In 1934, he was elected an Honorary Member of the Academy of Sciences of the U.S.S.R.

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- Russian uses the Cyrillic alphabet, and so names must be transliterated to the Roman alphabet. The exact transliteration used depends on the language into which the transliteration occurs, and even this is not a constant within the same language. In keeping with our previous practice (D. E. Lewis, Early Russian Organic Chemists and Their Legacy, Springer-Verlag, Heidelberg, 2012) throughout this paper, the BGN/PCGN romanization system for Russian is used as the most intuitive for English speakers. In citations of articles in western journals, names are given as transliterated by the journals. The English transliteration most frequently encountered is "Kishner," which was first used by Chemical Abstracts in Kizhner's early papers. It was subsequently replaced in English by the more intuitive, "Kizhner," but since the predominant use of CA has been to refer to Kizhner's original papers, the early transliteration became widespread. German does not have a consonant or combination of consonants corresponding to the Russian, x, but this is now addressed by using the Czech letter, "ž"; the modern German transliteration of Kizhner's name is "Kižner." The German transliteration used by Kizhner himself was "Kijner." Clearly, this spelling does not transliterate the correct pronunciation of Kizhner's name by a German reader, but it does so (or to a closer approximation than in German) in French. This suggests that Kizhner may have used a French transliteration for his name for his three publications in the German journals (although, interestingly, in his sole publication in French, he uses the form, "Kishner").
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THE TWO FACES OF RADIUM IN EARLY AMERICAN NUCLEAR CULTURE

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Introduction

In 1903, the element radium made a spectacular debut in American culture. It had been isolated by Pierre and Marie Curie in 1896 from uranium ore, along with the less radioactive element polonium, but its discovery had attracted little public attention until the Curies and Henri Becquerel won the 1903 Nobel Prize in physics for their work on radioactivity. In the same year, Ernest Rutherford and Frederic Soddy announced their conclusion that radioactivity was, in effect, atom-by-atom transmutation of one element into another. The sudden mania for radium that resulted, presaged in American popular culture only by the craze that had attended the debut of x-rays seven years earlier, was buoyed by the prevailing sentiment that physicists and chemists had at last seized the initiative in their battle with an obstinate universe that jealously concealed its most basic principles. In the crush of newspaper articles that drove the radium fad, few real or imagined powers were not attributed to the substance (1). Readers learned from the daily papers that radium could restore sight to the blind, reveal false gemstones, or power a battleship (or explode one), among many other abilities. Headlines declaring it a "Substitute for Gas, Electricity, And as a Positive Cure for Every Disease" were par for the course, and so were encomiums to the scientists who were exploring its mysteries (2). In newspapers, in lectures, at World's Fairs and in popularizing books, radium was cast as the

apotheosis of modern science and medicine, with a heavy emphasis on modernity.

Almost immediately, though, this presentation of radium came into conflict with another powerful framing. A broad network of commercial actors promulgated a diametrically opposed counter-narrative, in which radium and its decay products were characterized as natural rather than artificial, abundant rather than rare, mineral rather than chemical, healthful rather than medicinal. In this account, radium was the province of those closest to nature—spiritually attuned Native Americans, hardy miners, and wise naturopaths—rather than the scientists who explored it in laboratories or the privileged few physicians who used refined radium in their practice. Even as radium's explorers were hailed as "the mighty men of these days," a coalition including spa owners, municipal boosters, and nostrum makers advanced an alternate understanding of radium that made it both connotatively and commercially accessible to a much broader audience.

They were able to do so because radium had intruded into the American public's awareness at a time when the professional boundaries of scientific and medical expertise had not yet solidified. Accordingly, it served as a *tabula rasa* onto which traditional ideas about the connection between health and the natural environment could be projected, notwithstanding the overtly scientific gloss it was being given by other sorts of popularizers. The apparent "vitality" of the substance, and the evident confu-

sion it had sown in scientific circles, made a naturalistic framing eminently plausible to many Americans. Against the stories of limitless energy and instantaneous cures that newspapers and lecture-demonstrators breathlessly hinted would someday emerge from the laboratory, the purveyors of "natural" radium offered a thing that could be purchased, touched, tasted, and tried in the crucible of everyday experience. Almost no one doubted, in the first few decades of the twentieth century, that radium was the herald of strange and wonderful (or terrible) things to come. The appeal of experiencing those wonders firsthand, and in having them explained in familiar and intuitive terms—rather than exclusively through the mediating authority of the chemist or clinician—was strong enough that this explicitly earthy presentation remained a vibrant part of early American nuclear culture for decades.

There were, therefore, two viable connotative models for radium in the early 1900s. It was simultaneously an "isotope" and a "mineral," at once powerful and gentle, the product of clever modern artifice or ancient natural processes. It was found, depending on the model one subscribed to, in the darkest recesses of the laboratory or the mountain vale, emitting gamma rays or sunshine. It was either the tool of scientists and physicians working at the vanguard of a revolution, or the old familiar tonic of prospectors and Indians. This article will explore the construction of those dual identities, and how each affected the path of early American nuclear culture. The connotations of power and progress bound up in the framing of refined radium element as a story of modern super-science provoked attention from lay audiences, while the availability and practical uses suggested by the mineral construction of radium sustained that attention.

Radium in the Laboratory and Clinic

The impetus behind the initial radium craze derived from the fact that its discoverers had been entirely caught off guard by the bizarre phenomena that it manifested. Science writ large had gradually been gaining currency as a cultural force in turn of the century America, but, counterintuitively, it was the failure of the scientific establishment to really understand what they had seen in radioactive substances that drew the laity's attention. Other scientific or technological novelties of the early twentieth century had fit more easily into the established conceptual frameworks of the educated layperson. Instantaneous transmission of the human voice through radio waves, for example, could be understood by analogy to the near-instantaneous transmission of words through electrical

telegraph wires; hot-air balloons provided a point of reference when the airplane was invented. Radioactive substances, by contrast, were all the more fascinating because there had been no hint of their properties until nearly the moment of their discovery, whereupon they immediately called into question long-dormant assumptions about the nature of matter and energy.

The newspapers of the early 1900s described a scientific revolution unfolding in real time, and the neardaily coverage of every scientific congress or journal article on the subject of radium made celebrities out of the chemists and physicists at the vanguard. Becquerel, the Curies, Soddy, Rutherford, and a host of other actual or purported experts on the element were daily features in a press that had seldom before deigned to seriously report on the work of scientists. Press accounts and popularizing books explicitly framed the phenomenon and the elements that exhibited it as a triumph of modern science, and celebrated the peculiarly scientific virtues that had led the Becquerels and Curies of the world to their discoveries. In such accounts, it was Marie Curie's "determination and patience against detail," that had driven her to investigate why pitchblende was negligibly more radioactive than it should have been from its uranium content, and thus to isolate thimbles-full of radium and polonium through the "toilsome process" of refining tons of scrap ore (3).

Such hagiographical reports, which were often shot through with undigested technical jargon, paid dividends for the scientists who were their subjects. Rhapsodizing on the unprecedented enthusiasm of the laity for news of radium (even as he catered to it), a popularizer wrote in 1905 that "The fact that the general public have been so widely interested in radium, and so deeply impressed by it, is a remarkable testimony to the high position held at present by science, since the public have had to rely, for the most part, on their faith in the teachings of scientific men" (4). But that faith was not taken for granted by its beneficiaries; rather, it was actively reinforced by scientist-popularizers who were determined to reap the benefits of public attention while correcting the more sensational claims made in the newspapers. William Hammer, a respected American chemist and engineer, made radium popularization his full-time occupation when, in 1903, he managed to acquire some refined element directly from his friends the Curies. The professional and personal benefits of doing so were quickly apparent: his lawyer wrote of his confidence in this regard to Hammer, saying, "[y]ou confirm by every address your high standing as a scientist. I believe the reputation you are thus gaining is even more valuable than your lecture fees. ...I am inclined to think that you will get some valuable consulting work as a result of your lectures" (5). This proved to be the case. Others saw the benefits, too: Hammer was soon receiving letters from other colleagues who were hoping to do the same, and looking to borrow some of his radium with which to do it (6).

Hammer's lectures were didactic and cautious in the claims they made, but this did not dampen the enthusiasm with which they were received, so high were the expectations for a radium-based revolution in science. The same was true of books like Frederick Soddy's The Interpretation of Radium (1909), a dense but elementary survey of the state of the field that went through dozens of printings. The effect of these scientist-authored popularizations was to brand radium as a thing born of chemistry and raised in the laboratory. This was a deliberate strategy: it was not a coincidence that the American Chemical Society was among the earliest of the disciplinary organizations to formally institutionalize its outreach and popularization efforts (7). In an era that also saw widespread electrification, aviation, radio, relativity, and many other genuine scientific and technological fads seize the attention of the lay public, chemists had a priority claim on the most popular attraction of them all.

Mindful of the theoretical wreckage that radium was leaving in its wake during those first years, scientists and popularizers often spoke of the element's energies in destructive terms. Henry Adams, in his Autobiography, saw something blasphemous and terrifying in the tiny specks of radium he had observed by 1907: it "denied its God," by which Adams meant the predictable world of the Victorian scientist, and in its maddening inscrutability, "happened to radiate something that seemed to explode the scientific magazine" (8). The language Adams uses to describe the rays was invariably that of violence: it was a "metaphysical bomb" that brought about a "cataclysm" simply by virtue of its existence. It was not only laypersons like Adams who struck this tone. Pierre Curie often obliged interviewers with ominous remarks about the potential dangers of radium's energies: for instance, that a single gram, properly applied, would suffice to kill everyone in Paris (9). Frederic Soddy's otherwise didactic bestseller, The Interpretation of Radium (1909), speculated that a civilization advanced enough to master the energies poured out by radioactive elements would probably destroy itself with those same energies, a speculation that in turn became the inspiration for the first atomic war novel, H. G. Wells' The World Set Free (10).

At the same time that radium's destructive physical effect was being established in this way, it was also being described as an inherently vital thing, with similarities between its energies and that of living things. As Luis Campos has noted, scientists had, from the start, used language to describe radioactivity that reflected its seeming liveliness: radium had a half-life, underwent decay, and was the parent of its daughter elements; in other contexts, radiochemists spoke of radioactive life cycles, extinction, habitats, and families (11). The first round of radium-popularization took its cue from these initial characterizations and presented the substance in starkly vitalistic terms. Harper's Weekly put the question bluntly: "If anything in the world is alive, is not radium alive?" For the medical doctor who wrote those words, radium represented the first hint at a third way between the equally fruitless "old materialism" and "old vitalism" (12). The news in 1905 that John Burke of the Cavendish had apparently produced life in sterile bouillon by seeding it with radium commanded a great deal of commentary in the popular media. Even the eminent chemist William Ramsay's gentle refutation of Burke's initial findings was softened by the comment that "no one would rejoice more" if further study were to reveal that Burke's intuitions about radium's literal vitality were correct (13). In the press, comic articles and cartoons played with the idea of humans being energized by radium directly. A cartoon by Albert Levering titled "The Wonders of Radium, Practically Applied" demonstrated in eight panels what the careful application (with tongs) of a glowing hunk of radium might accomplish: reviving tired messenger boys, cramming more people onto streetcars, stupefying bill collectors, and so forth (14). The wit of such cartoons derived from the popular assumption that radium would act as a sort of all-purpose intensifier of whatever it was applied to, which itself reflected the relentlessly hyperbolic nature of its public profile.

Because radium was perceived as being bound up with vitality and living processes, medical doctors were flattered by association with it just as chemists and physicists were. There was enough refined elemental radium, in quantities rarely exceeding half a gram, to allow a few wealthy and well-connected doctors to offer experimental radium therapy in which tiny glass ampoules of refined radium were taped to tumors near the surface of the body, or implanted surgically. Given how few hospitals had access to such a supply of refined element, and that only one patient could be treated at a time, it was not a viable route to prestige and wealth for individual physicians. Nevertheless, the medical community in the late 1900s and early 1910s, in the midst of its rhetorical and practi-

cal turn towards scientific medicine, collectively basked in the glow of this new icon of scientific modernity. In 1913, when a New Jersey congressman's grave cancer prognosis was temporarily improved by the administration of highly refined radium, the *New York Times* exulted that "[t]he news of scientific effort is overshadowing all other news. More significant than a change of ministry in France or the issue of a Balkan war is the announcement a Soddy or a Ramsay may make tomorrow about the loosening of forces in groups of atoms." Such scientists, and the physicians who developed treatments using radium, the editorial continued, "are the mighty men of these days. They have done much, and they promise more" (15).

The medical profession in the early twentieth century was in the process of reinventing itself under the rubric of "scientific medicine." Physicians embraced the tools and techniques and ethos of the lab bench, but even more enthusiastically its trappings. Radium not only presented physicians with an opportunity for methodological innovation—the history of radiology's first two decades is fairly characterized as a sustained trial-and-error campaign to resolve dosages and tolerances—but also a chance to associate themselves and their profession with the prestige that had attached to such an unimpeachable symbol of modern science. Addressing a group of Yale Medical School alumni in 1904, the radiological pioneer Robert Abbe warned his colleagues not to turn their noses up at the maddeningly audacious claims being made in the press for medical radium: their patients certainly would not, and would be expecting fantastic things of their scientific physicians. It would be better to know what was therapeutically possible, he concluded, so as not to unnecessarily disillusion them about the miracles that modern doctors could perform (16).

Yet because radium's rarity (and hence its cost) were also among the hyperbolic characteristics that newspaper articles dwelt upon, there was no immediate expectation on the part of patients that radium-based medical care would become commonplace. Until the mid-1910s, when new American refineries began to substantially increase the supply of concentrated radium, to be treated with radium required access to the highest reaches of elite medicine. Even Marie Curie was obliged to travel to the United States in 1922, on behalf of her Radium Institute, to accept a donation of a single gram from an American refinery. So much had been made of radium's extraordinary scarcity and cost, in fact, that the few physicians who had access to some worried about being labeled extortionists (17). Cancer was, as one of them put it, a

poor man's disease; refined radium was so scarce that it would necessarily be the rich man's cure (18). Absent a far greater supply of the refined element, it was clear that none of the hoped-for miracle cures or cheap sources of energy could be made widely available.

Radium as a Nature Cure

There was one exception to the general rule of radium's scarcity. In 1903, J. J. Thomson reported that water from very deep wells in England contained a radioactive gas (19). The subsequent discovery of natural radioactivity in springs all over the United States, and in particular in the West, immediately suggested that the cause of the long-suspected benefits of "taking the waters" had been found. The federal government, which administered the waters at Hot Springs, Arkansas, had them tested in 1904, and other spas and resorts followed suit. By the middle of the 1910s, thermal springs were undergoing a renaissance as places not merely to take the waters, but to take the radioactivity (20).

Accordingly, advertisements for the spas quickly began to prominently feature radioactivity as a selling point. The Hot Springs, Arkansas Chamber of Commerce ran a series of ads in eastern and midwestern newspapers trumpeting both the springs' radioactivity and the involvement of the federal government, including the endorsement of several Surgeons General (21). In them, a cartoon Uncle Sam spoke of "recaptur[ing] vitality in my 46 fountains of youth" because "the medical properties of these steaming hot Radio Active waters have a way of ridding your system of rheumatic, high blood pressure, etc., and making you feel ten years younger" (22). It was not only established health resorts that benefited: the cold, sulfurous waters of Claremore, Oklahoma were tested for radium in the early 1900s by an enterprising local doctor, and the radium health industry quickly came to dominate the local economy. Bathhouses and bottling operations sprang up, and operated well into the 1930s. The town adopted the motto "Where the World Comes to Get Well" and enlisted favorite son Will Rogers to endorse the waters in explicitly radioactive terms (23). Following the pattern of soft-pedaling the science and playing up the naturalness of the waters' virtues, the pamphlets pointedly eschewed a "detailed chemical analysis" but explained at length that the radium that reached the Claremore bathhouses had been "assembled centuries ago by Nature's Alchemy" and was "one of Nature's greatest gifts to man" (23). Though most advertisements for Claremore and other springs made

mention of radioactivity, very few discuss or even refer to its physical properties. Instead, radioactivity was represented exclusively in terms of its restorative ability, the mechanism for which was never referred to except in broadly naturopathic terms.

This hazy vitalism was an effective marketing technique, and its lack of specificity was probably inevitable, as there was no real consensus among doctors of any stripe as to the cause of the springs' salubrious effects—although many entirely orthodox physicians believed that the waters' radioactivity was a cause of those benefits. Nevertheless, the presentation of radium in these terms contrasted sharply with the language used in other channels of the public discourse about radioactivity. The trace "radium emanations" were not spoken of as powerful, or as panaceas; they did not even have the energy to make a watch-dial glow. Instead, they were presented as the last piece of a puzzle; as a sort of nutrient that worked subtly in concert with other natural processes to restore the body to its natural state.

Notwithstanding the apparent appeal of this framing, most health-conscious Americans simply did not have the time or money to go to the spas. The waters could be bottled and shipped, a solution some spa owners adopted, but there was an unforeseen problem with these bottled waters: by the time they reached their destinations, they were no longer radioactive. In transit, within a few days, the dissolved radon gas that was responsible for most of the measurable radioactivity would either escape or decay. A solution arose in the form of radium emanators: devices that introduced some amount of low-grade radium-bearing ore into contact with water, usually by simply adding ore to an earthenware water jug. The infinitesimal (but detectable) amounts of radon gas that escaped from the decay of the radium then went into solution in the water.

Emanators took a wide variety of physical forms, and were sold under dozens of brand names (24). The Radium Ore Revigator Company, the largest maker of emanators, claimed at one point that they had sold 500,000 of them, a figure that might at least be taken as a safe estimate for the total number of emanators produced by all manufacturers (25). Some doctors sold them on commission: physicians were often as susceptible as the layperson to the health claims that were made on behalf of radioactivity, and were certainly, as a class, interested in the profit that came with referring or reselling the devices (26). They were also sold door-to-door and through catalogs.

The fact that low-grade ore was available for such a purpose in the United States was a result of the domestic radium industry coming online. Until about 1915, some of the scarcity of pure radium compound in the United States had to do with the fact that the country was largely dependent on imports from European mines and refineries. Press reports of an overseas "radium trust," if somewhat inaccurately conspiratorial, were effective in spurring commercial interest in a domestic radium industry. So too were emotional appeals by prominent doctors, pleading in Congressional hearings for the government to act to bring more ore to market (27). The resulting increase in the flow of pure radium from the new refineries built in Pittsburgh and Denver also created a much larger glut of mildly radioactive tailings, from which the emanators and a host of other "radium" products were made.

In spite of the fact that some orthodox physicians sold emanators, the overall language of the brochures, the advertisements, and their discussion in the popular press were carefully designed to rhetorically divorce them from any connection with the medical establishment. "IMPORTANT," a typical disclaimer read: "RADIOAK is not a medicine in the general acceptance of that word. It is absolutely not a drug" (28). Rather, the emanators were presented as a mineral-for-mineral recreation of the waters at the world's famous health spas. That sort of characterization made this sort of radium therapy palatable to potential customers who mistrusted orthodox medicines, of which refined radium was certainly one. (Not insignificantly, it also ensured that the product escaped regulation under the Pure Food and Drug Act.) The marketing of these devices did not simply rely on consumers to know that those healing waters were out there; they actively made the connection and, in fact, educated the public about them—simultaneously creating a demand for their product and reinforcing the understanding of radium as a natural medicine.

Revigators were promoted as "a perpetual health spring in your home," and references to the famous health resorts of the western United States and Europe were made profligately in the advertisements for all emanators. "Don't drink [Revigator water] with the attitude that you are trying something new," one manual cautioned, but "accept it as the blessing it is, for the famous springs of the world such as Gastein, Hot Springs Ark., Vichy, France, have performed health miracles for centuries. And it is now agreed that this is due to the high radioactivity of the water. The Revigator truly duplicates the radio-activity of these springs" (29). Another Reviga-

tor ad told of Estreyes, "a lucky town in France: ... No one in the town ever has cancer or dies of that fearful disease. There is a highly radioactive spring in the town and everyone drinks the water from it—apparently the water PREVENTS the cancers" (30).

By framing radium as a beneficial part of the landscape, the spa owners and emanator vendors paved the way for other kinds of purportedly radioactive health products ranging from impotence cures to veterinary medicines, and the marketing for these products hewed closely to the naturalistic depiction of radium's virtues. "Radium makes things grow," asserted advertisements for the Radium Fertilizer Company's products, and plants needed radium "because they need food, just as people need food" (31). Radior brand beauty products continued the association between radium and natural growth with its claim that "Radium Rays are, in fact, 'accepted by the human system as harmoniously as sunlight by the plant" (32). Another advertiser explained the sun-like means by which radium—which was not a "chemical" or a "metal" but "life itself" in mineral form-worked on the body (33):

If your blood could be frequently taken from your body, exposed to the sunlight and then put back, your physical troubles would disappear and you would remain strong and healthy to a very old age. Radium emanation has the same effect upon the blood as exposing it to sunlight. But, while sunlight is unable to penetrate beyond the skin, radium emanation penetrates entirely through the body, reaches the farthest blood cells and tissues and restores them to life.

Promoting radium's "rays" as akin to sunlight served several purposes for entrepreneurs. Not only did it call to mind other nature-cures popular at the turn of the century (alpine heliotherapy, in particular), but it also invited consumers to compare the light of the mineral radium with other contemporary healing lights: heat lamps, Finsen lamps, and especially x-rays. The devices that generated such rays were expensive, ostentatiously technological, closely associated with orthodox medicine, and inherently intimidating to many patients (34). Radium, by contrast, could be characterized as a simple mineral supplement as easily as it could be discussed in the context of its chemical and physical properties, and those who sold it almost always chose the former. Radithor, a genuinely radioactive patent medicine sold by commercial impresario William Bailey, traded heavily on the fact that radium could be construed as a sort of sunlight-infused mineral, rather than a manufactured drug. Its advertisements blared that Radithor "puts the sunbeams in your bloodstreams." "Perpetual sunshine"

(or "internal sunshine") was the slogan of the innumerable pamphlets and brochures Bailey produced to sell Radithor. More sunlight, the Radithor literature reminded the reader, made plants grow faster, let chickens lay more eggs, and accounted for the "splendid physical condition and virility" of "South Sea Islanders," at least until they adopted sun-shielding Western dress. Radium was, in Bailey's reckoning, "an entirely unique and revolutionary means of using rays to replace the lack of sun rays," even more conveniently and thoroughly than could be done by x-ray or quartz light treatment, or other methods reminiscent of the modern clinic that "permit only the application of the rays externally." Bailey carefully clad Radithor in the garb of the nonmedical restorative tonic — "not a drug, not a patent medicine," as the advertisements disclaimed, but "the water of life direct from Nature's laboratories" (35).

Other manufacturers of radium products went even further in their emphasis on radioactivity as a natural phenomenon, explicitly promoting their products as means by which consumers could in some way restore a connection with the natural world that had been severed by technological modernity. The Curie Radium Company of America, whose emanator was variously known as the "Stone-Filtered Radio-Active Regenerator" or the "Liquid Sunlight Re-Generator," warned customers that "something is missing in water" that city dwellers drank: specifically, the "radium gas" that was the difference between the "pure, live, healthful freshness" of spring water, and "stale" municipal water (36). Yet radium did more than provide a connection to nature absent in the modern world, according to many of its suppliers: it also relieved the excesses of artificiality. Colorado's Radium Hot Springs resort blamed the accumulated "toxins" and "poisons" of "drug residues" for ill health. Radium waters, superior to the "artificial rays" deployed in clinics, reversed the accumulated ills of modern living by "radiat[ing] outward, as if the sun were shining out from inside" (37).

Where the inherent vitality and naturalness was sufficiently stressed, no further explanation was needed for consumers. For example, Degnen's Radio-Active Lenses, wire-rimmed glass spectacles coated with an opaque greenish film, capitalized on the perception that mere proximity to radium would have a potent (and holistic) revivifying effect on the flesh to which it was exposed. A similar logic applied to the many brands of pads and compresses purportedly filled with radium ore (38). No elaboration as to how the ore would work was offered; their sellers trusted that the general belief in radium's

uncanny connection with the processes of life, so often reiterated in popular treatments of the subject, would suffice to recommend a product that (allegedly) contained it.

In the advertisements for radium-based products, the substance's earthy pedigree was stressed at the expense of any reference to its alter ego, the chemical element that was the emblem of scientific modernity. Radium's effects might be magical, but it was the magic mineral in the advertising literature of Claremore Radium Water (among others) (39). This framing departed sharply from the clinical gloss that radioactivity was receiving in the science journalism and popularizing books of the early twentieth century, which tended to rhetorically situate the element in the laboratory or the university hospital. Radioactive springs, too, clothed themselves in pastoral mythologies, the better to profit from the contrast with the enervating modern lifestyle. A Colorado spa, pointedly noting the many nearby radium mines and "strongly radio-active rocks," invoked the folk wisdom of the miners who had settled the area: "The old prospector used to cure all his ills in these waters. He didn't know how or why, but he knew there was something wonderful about them. Today we know that the marvel of these waters is that powerful and elusive quality known as Radio-Activity" (40). This was commercial myth-making, but it may have had some basis in fact. The Chicago Chronicle introduced radium to its readers by claiming that Montana miners had carried what they called "medicine ore" and "rheumatism rock" in their pockets for years, as a means of curing that and other illnesses (41). Indeed, when, in 1904, a prospector hoped to interest an investor in radium ores, but could not immediately send samples, he cited the fact that the waters flowing through the claim had cured several illnesses as proof of their radioactivity (42). Three decades later, radium ore miners with perfect complexions populated the advertisements for Adium skin cream, whose (purported) radium content "proves as beneficial as when fresh from the mines" (43).

Another common form of the trope replaced miners with Native Americans, by then stereotypically regarded as nature-conscious and innocent of modern technology's depredations. Hot springs from Arkansas to Montana repeated the same apocryphal legend of warring tribes who observed a truce at the sacred healing waters. Idaho Springs of Colorado, named after the (probably apocryphal) Chief Idaho, published brochures in which he offered these words of native wisdom across the centuries to potential health tourists: "Happy the rheumatic that takes Radium baths and is benefited, but more happy is the one that takes a Radium bath every month and never

has rheumatism" (44). Lest anyone think their spa was not equally desirable, the letterhead of the nearby rival Radium Hot Springs resort also prominently featured a stylized drawing of a Native American complete with feathered headdress, along with guarantees that their waters were "highly radio-active" (45). Emanator manufacturers elaborated on this theme, claiming that Indians had never presumed to fight over Arkansas' Hot Springs, "even in their most deadly wars. The Indian Medicine MAN KNEW WHAT HOT SPRINGS WOULD DO" (46). When Claremore, Oklahoma's booming radium-water-bottling industry took a potshot at the ubiquity of such claims by cheekily confiding that "there is no historic legend back of Claremore's famous Radium Water-no mystic past linked with early Indian life," it was a backhanded acknowledgement of the potency of such prelapsarian endorsements (47).

The sum effect of the naturalistic framing of radium as *ore* or *mineral* or *earth*, rather than a *chemical* or an *element*, was to democratize its appeal. By taking radium connotatively out of the realm of elite science and medicine, even if only through the sale of fraudulent or non-radioactive products, its commercial promoters provided a means by which the broader American public's engagement with nuclear culture could be sustained. In the absence of progress towards the marvels that science popularizers had touted—radium-powered cities and glowing panaceas in every doctor's cabinet—the perception that radium was abundant in the unspoiled places of the earth and capable of working quiet miracles, in ways still hidden even from the great names of the age, was sufficient to capture the attention of the consumer public.

The Long Half-Life of the Radium Craze

In a 1934 medical treatise on radiation injuries, the authors, physicians S. Russ and H. A. Colwell, admitted that they were puzzled by the "widespread tendency in the public mind to regard everything connected with 'rays' as on that account conducive to health and vitality," notwithstanding the abundant evidence that radiation could far more easily harm than heal. This irrational but persistent belief, they concluded, was "undoubtedly" the result of the much-publicized successes of radium therapy, orthodox and otherwise. "The argument in this appears to be that because radium is employed successfully in cancer, and because cancer is notoriously intractable—and when intractable fatal—therefore radium must be a panacea for all the ills that flesh is heir to" (48).

Notwithstanding Russ and Colwell's consternation that medical frauds were exploiting ray-crazed patients, the perception of radium as a cure-all was quickly fading by the mid-1930s. By then, the laity knew of the dangers that radiation presented to patients: indeed, medical irradiation in the form of enormous x-ray machines and carefully monitored radium-filled ampoules had become something most patients regarded as simultaneously a triumph of modern medical science and as something chaotic and dangerous. In short, they had become, at best, "heroic" medicines - inherently harmful, but, under certain dire circumstances, preferable to inaction. This perspective was actively encouraged by the American Medical Association, which hoped to establish a professional monopoly on the use of those energies. "Gamma rays cure because they kill," a 1932 magazine article promoted by the AMA proclaimed, and alpha particles were "not only murderous... but treacherous." The photographs accompanying the article showed white-coated physicians and nurses carefully manipulating intricate mechanisms that stored and applied medical radium; they also showed the complicated mix of laboratory equipment used to refine radium ore and to siphon off the radon its decay produced (49). The unmistakable message of this and many similar entries in the AMA's own popular magazine, Hygeia, was that radium could be brought to heel only with the utmost efforts of expert clinicians.

That was a message its audience, health-conscious consumers in the early 1930s, was largely willing to hear. A series of tragic events of the late 1920s and early 1930s had soured the public sentiment towards radium. They began in 1925, when news broke that dozens or hundreds of women employed as luminous watch-dial painters had been poisoned by accidental ingestion of radium. Their obituaries were treated as news items for years, and laid out in gruesome detail the pain, disfigurement and hopelessness that the painters had to suffer through because they had accumulated infinitesimal amounts of radium in their bones (50). Worse, for those who sold radioactive medicines, some radium tonic consumers had suffered a similarly ghastly fate. In November 1935, the United States Department of Agriculture's weekly radio program opened with a bulletin announcing the seizure of fraudulently labeled "radioactive" cosmetics, but lamenting the FDA's inability to seize injurious yet properly-labeled radioactive products. The announcer proceeded to retell the story of Eben Byers, a steel baron who had famously fallen victim in 1932 to Radithor's "internal sunshine." "Like many ill people, he was willing to try anything that offered a cure," the announcer declared. "Perhaps he reasoned that if Radithor didn't

cure him, at least it wouldn't do him any harm. But the medicine killed him. It literally disintegrated the bones of his head" (51). By the time Marie Curie died in 1934, universally characterized as a "martyr" to radium, the reference to death by radium exposure was a familiar one.

In the climate of opinion that was generated by that kind of rhetoric, radioactive merchandise was difficult to sell, and had mostly disappeared from the market by 1940. Yet radium's long connotative tenure as a thing of the mountains and springs, rather than the refineries and laboratories, has had a persistent effect on American nuclear culture going forward. Whereas x-rays and other forms of electromagnetic radiation that had caused alarm in patients during their early clinical use were generally understood by the 1940s to have been "domesticated" transformed by the gradual refinement of the technology that generated them into reliable and safe servants of medical science-radium remained rhetorically the wild child of nature, only barely controllable and fundamentally untamed. When radium "escaped" into the floorboards and pipes of hospitals, it was stalked by "radium hunters," whom the press treated as lion tamers in lab coats (52).

To the extent that radium had retained its aura of health and vitality up to that point, it was because it had been successfully portrayed as a natural phenomenon, free of the connotations of materialism and moral ambiguity that sometimes attended scientific medicine. Those who traded in "radium" products also appealed whenever possible to the sun whose energy they mimicked, the water they could infuse with energy, the mountains from which they were mined, or even the plants they could revitalize. The ubiquitous language on ersatz radium nostrums asserting that they were a "natural cure" and "not a drug" was not simply there to escape regulation or signal allegiance to a particular healing sect, but also to encourage the belief in the fundamental wholesomeness of energies whose magnitude might otherwise be cause for alarm. The more that orthodox medicine became "scientific," both in philosophy and in the patient's impression, the less that the pamphlets for emanators and ointments and spas traded in the argot of the scientist. And even when they did, it was almost always the language of the natural historian that they used: radium tonics spoke of essential minerals and of stimulating cells and tissues, but rarely of alpha particles or ionization. Consumer radium products, relentlessly associated by their advertisers with healing nature and often pointedly contrasted with the artificial, more vividly technological manifestations of medical irradiation, thus served as a

bulwark of positive associations for radioactivity. Thus, even in the midst of newspaper stories about chemists killed by long exposure to the radioactive substances they researched, the manufacturers of the Ra-Tor Radium Mineral Water jar could characterize the traces of radium it contained as "a natural product brought to you straight from the treasure vault of Nature—a God-given, healing substance for suffering mankind" (53).

The association between radioactivity and vitality has lasted even into the post-Hiroshima era: one can still pay to descend to the bottom of a mine shaft in Montana to breathe in radon gas, and homeopathic doses of natural radioactivity are once again regarded favorably by some alternative health practitioners. Furthermore, radioactivity was indelibly established as a part of the physical landscape by two decades of advertisements, a fact that was omitted by the tourist brochures of later decades, but not easily forgotten—especially as nuclear testing in the postwar era brought new kinds of radioisotopes to the western United States, and points downwind.

References and Notes

Archival materials referenced more than once below are abbreviated as follows:

- AMA: Historical Health Fraud Collection of the American Medical Association.
- CRI: Consumers' Research, Inc. Collection, Box 448,
 Folder "Radium Nostrums and Radium Water Machines
 Misc., 1930-1939," Rutgers University Special Collections.
- Hammer papers: William Hammer papers, American History Museum, Smithsonian Institution
- To take one measure of the sudden public interest, between 1896 and 1902, the *New York Times*, the *Chicago Daily Tribune* and the *Los Angeles Times* printed 15 articles dealing with radioactivity, compared with 170 in 1903 and 254 in 1904.
- 2. "Radium as a Substitute for Gas, Electricity, And as a Positive Cure for Every Disease," undated news clipping. Hammer papers. For the other claims mentioned here see for example "She That Was in Darkness Tells How by Radium She Saw the Light," *New York American*, Aug. 24, 1903; "The Discoverers of Radium Can Detect False Diamonds by Its Use," *Syracuse Telegram*, Feb. 25, 1904; "Handful Would Destroy London," *Springfield* [Massachusetts] *Union*, Nov. 29, 1903.
- C. Moffett, "The Wonders of Radium," McClure's Magazine, Nov. 1903, 5.
- 4. W. Hampson, Radium Explained: A Popular Account of the Relations of Radium to the Natural World, to Scientific Thought, and to Human Life, Dodd, Mead and Company, London, 1905, 1.

- James Beck to William Hammer, Oct. 29, 1903. Hammer papers, Box 2, Folder 9.
- 6. Dayton C. Miller to William Hammer, Nov. 5, 1903. Hammer papers, Box 2, Folder 9.
- 7. D. Rhees, The Chemists' Crusade: The Rise of an Industrial Science in Modern America, 1907-1922, Ph.D. thesis, University of Pennsylvania, 1987, 210.
- 8. H. Adams, *The Education of Henry Adams: An Autobiography*, Houghton and Mifflin, Boston, 1918, 381.
- 9. This language is taken from a 1926 draft *Encyclopedia Americana* article by radium lecturer William Hammer. Hammer papers, Box 17:8. It is rendered in his surviving lecture notes from circa 1903 as "Curie in room containing kilo of radium," suggesting that Hammer found the story compelling enough to tell for more than twenty years.
- F. Soddy, The Interpretation of Radium, Being the Substance of Six Free Popular Experimental Lectures Delivered at the University of Glasgow, 1908, John Murray, London, 1909, 244-245. H. G. Wells, The World Set Free, Collins' Clear-Type Press, London, 1921.
- 11. L. Campos, "The Birth of Living Radium," *Representations* **2007**, *97*, 1-27. See also his dissertation, Radium and the Secret of Life, Ph.D. thesis, Harvard University, 2006.
- 12. C. W. Saleeby, "Radium and Life," *Harper's Weekly*, July 1906, 226.
- 13. "Can Life Be Produced by Radium?" *The Independent*, Sept. 7, 1905, 556.
- 14. This appears in a magazine clipping, untitled and undated (circa 1904), Hammer papers.
- 15. "Shifted Emphasis in News," *New York Times*, Dec. 28, 1913, 14.
- 16. R. Abbe, "Radium and Radioactivity," reprint from the *Yale Medical Journal*, **June 1904**, 2.
- 17. E. Daland, "Radium Therapy—Use and Abuse," *New England Journal of Medicine* **1928**, *198*(19), 1005.
- 18. "Dr. Kelly to Confer with Congressmen," *Baltimore Sun*, Jan. 14, 1914.
- 19. J. J. Thomson, "Radio-active Gas from Well Water," *Nature*, **1903**, *67*, 609.
- Carolyn Thomas de la Peña has observed that, at the turn of the twentieth century, the prominent Fordyce Bath House at Hot Springs, Arkansas, successfully melded a sleek, ostentatiously modern aesthetic with the traditional understanding of a spa cure, appealing to patients' desire for the potential revivification that impressive hydrotherapeutic and electrotherapeutic equipment promised while allowing a veneer of the traditional bucolic setting to blunt the anxiety that attached to new technology in general at the time. Where radioactivity was concerned, however, the rhetoric of modernity is seldom found. Advertisements dwelling on the radioactive virtues did not use words like "balneology" and "hydrotherapy," but typically invoked science only in the person of the geologist or chemist that had certified a place's waters to be radioactive. C. Thomas de la Peña, "Recharging at the Fordyce: Confronting the

- Machine and Nature at the Modern Bath," *Technol. Cult.* **1999**, 40:4, 746-769.
- 21. For example, Rupert Blue's characterization of the "amazing curative properties" of radium springs ["Discusses Closed Spas," *New York Times*, Sept. 17, 1914, 8], or George Henry Torney's commendation of the Arkansas hot springs in "Fordyce Bath House," [advertising pamphlet, undated (c. 1910), Oak Ridge Associated Universities Health Physics Historical Instrument Collection, Oak Ridge, Tennessee].
- Hot Springs National Park [advertisement], Minneapolis Journal, Jan. 12, 1931. The second excerpt is from an ad reproduced in Hot Springs Chamber of Commerce, Garland County (Ark.) Historical Society, Box 30, binder labeled "Chamber of Commerce, Paid Advertising, 1929-1934."
- Claremore Chamber of Commerce, advertising pamphlet, undated, CRI.
- 24. A 2008 report to the Nuclear Regulatory Commission, drawing largely on the collection assembled by Paul Frame of the Oak Ridge Associated Universities, identified almost fifty brands of emanators sold in the United States before 1945. M. A. Buchholz and M. Cervera, "Radium Historical Items Catalog," August 2008. http:// pbadupws.nrc.gov/docs/ML1008/ML100840118.pdf. Last accessed July 22, 2014.
- 25. Radium Ore Revigator Agency, New Orleans, advertising pamphlet, undated (circa 1930), ORAU. The relevant text reads, "There Are Now Over 500,000 Satisfied Revigator Users," followed by a list of consumers local to the New Orleans area.
- 26. The AMA received many letters of inquiry from patients whose doctors had recommended (or sold) emanators to them. They are collected in AMA, Box 723.
- "Bust Radium Trust—Lane to Congress," photocopy, *Denver Times*, Jan. 26, 1914. Forbes Rickard Papers, WH333, Box 1. Denver Public Library Special Collections.
- 28. Radioak, advertisement, c. 1925. AMA, Box 720, Folder 19.
- 29. Radium Ore Revigator, owner's manual, c. 1926. AMA, Box 723, Folder 2.
- Radium Ore Revigator Company, advertisement, c. 1925.
 AMA, Box 723, Folder 1.
- 31. Radium Fertilizer Co. of Pittsburgh, "Radium Makes Things Grow," advertisement, *Washington Post*, April 25, 1915. ORAU.
- 32. Radior Toilet Requisites, "Radium and Beauty," copy of newspaper advertisement, n.d. (circa 1925), ORAU.
- 33. American Radium Company, "Radium, the Master Key to Health, Youth and Beauty," advertising folio, circa 1925. AMA, Box 719, Folder 8.
- 34. On the impression made by medical x-ray machines, see M. Lavine, "The Early Clinical X Ray in the United States: Patient Experiences and Public Perceptions," *J. Hist. Med. Allied Sci.*, **2012**, *67*(*4*), 587-625.
- 35. Radithor advertising materials survive in several archives,

- including those curated by Paul Frame of the Oak Ridge Associated Universities, and the Historical Health Fraud Collection of the American Medical Association.
- 36. Like all of the many commercial products that used the word "Curie" in their brands, it had no connection with the discoverers of radium. See W. Kolb and P. Frame, *Living With Radiation: The First Hundred Years*, 2nd ed., self-published, 2000, 32.
- 37. Radium Hot Springs, advertising flier, July 3, 1930. Denver Public Library Special Collections.
- 38. Radium Appliance Co. of Los Angeles, advertisement, circa 1930, AMA, Box 719, Folder 1. The Degnen line also included radioactive appliances specifically designed to be applied to the nose, ears, prostate, uterus, and throat; other manufacturers made appliances worn on the gums, insoles, or in trusses.
- 39. Cf. S. Hopkins, *The Great American Fraud*, P. F. Collier & Son, 1905, 93.
- 40. Radium Hot Springs, "Rheumatism Cured," advertising flier, 1929. Denver Public Library Special Collections.
- 41. "Medicine Ore of Montana: Radiumite, Which Occurs in the Mines, Effects Cures," *Chicago Chronicle*, Sept. 25, 1904.
- 42. Leopold Biddle to George F. Kunz, July 5, 1904. George Kunz papers, Center for Southwest Research, Albuquerque, New Mexico.
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THE PATH TO CONDUCTIVE POLYACETYLENE

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Introduction

In 2000, the Nobel Prize in Chemistry was awarded to Professors Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa "for the discovery and development of electrically conductive polymers" (1). This award was in acknowledgement of their early contributions to the field of conjugated organic polymers (Figure 1), particularly their collaborative work on conducting polyacetylene beginning in the mid-to-late 1970s (2). Conjugated organic polymers are a class of organic semiconducting materials that exhibit enhanced electronic conductivity (quasi-metallic in some cases) in their oxidized (p-doped) or reduced (n-doped) state (3). As such, these materials have been referred to as synthetic metals (4) and combine the conductivity of classical inorganic systems with many of the desirable properties of organic plastics, including

mechanical flexibility and low production costs. This combination of properties has led to the current field of organic electronics and the development of modern technological applications such as sensors, electrochromic devices, organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and field effect transistors (FETs) (3).

polyacetylene polythiophene polythiophene polythiophene

polypyrrole polyphenylene polyaniline

Figure 1. Common conjugated organic polymers.

Needless to say, this class of materials has changed the way that the scientific community views plastics, as was outlined by the initial press release for the 2000 Nobel Prize in Chemistry (1):

We have been taught that plastics, unlike metals, do not conduct electricity. In fact plastic is used as insulation round the copper wires in ordinary electric cables. Yet this year's Nobel Laureates in Chemistry are being rewarded for their revolutionary discovery that plastic can, after certain modifications, be made electrically conductive.

In both quotes from the Nobel press release, however, credit for the discovery of conducting polymers via doping (i.e. oxidation or reduction) is specifically attributed to Heeger, MacDiarmid and Shirakawa, although investigations of electrically conductive conjugated polymers date back to the early 1960s, nearly 15 years before their

collaborative work on polyacetylene. That these previous studies are overlooked in most discussions of the history of conjugated polymers is unfortunate and I have attempted to rectify this in a recent publication that presents the prior contributions of Donald Weiss on conducting polypyrrole, as well as that of René Buvet and Marcel Jozefowicz on conducting polyaniline (5). In

addition, two other short historical accounts have also been recently published that have tried to shed light on some of these previous contributions (6). In continuing these collective efforts, the current manuscript aims to focus more deeply on the history of polyacetylene and will present a more complete picture of all those that contributed to the ultimate discovery of its highly conductive nature upon doping.

From Carbon Blacks to Conjugated Polymers

As early as the 1930s, scientists began to speculate about the possibility that electronic conduction might be observed in organic materials (7). However, it wasn't until the 1950s that significant experimental work began to appear on the subject. Of the various materials investigated, it was graphite and the carbon blacks (material from the partial burning or carbonizing of organic matter), that gave the most significant electrical conductivity (up to $50 \ \Omega^{-1} \ cm^{-1}$) (7, 8).

Although the modern description of carbon blacks is a particulate, quasigraphitic material (8a), these materials were initially thought to be three-dimensional, cross-linked organic polymers with various structures and elemental constitutions depending on their origin (8b). As these "carbonaceous polymers" were considered to have chemical structures that were too complex and ill-defined, efforts turned to the production of related organic polymers as potential model systems with more defined and controllable compositions (8b).

The simplest of these model systems were *polyenes*, $(-CH=CH-)_n$ (9,10), sometimes referred to as *polyvinylenes*. Formal polyenes were often limited to shorter oligomers (n=2-10) and were used to correlate physical and optical properties with conjugation length (9). The related polyvinylenes were polymeric analogues of the polyenes, with identical empirical formulas under ideal conditions. However, as these polymeric analogues were produced via the chemical elimination of poly(vinyl halide)s (11) or poly(vinyl alcohol) (12), they typically contained various defects from incomplete elimination. The first successful direct polymerization of acetylene was then accomplished by Giulio Natta and coworkers beginning in 1955 (13).

Natta and the Polymerization of Acetylene

Giulio Natta was born February 26, 1903, in the small Italian city of Imperia, near the French border

(14). His father was a judge in Genoa (14be), where he attended school (14bd) before continuing on to the University of Genoa to study mathematics (14be). After two years, however, he moved to the Polytechnic of Milan in 1921 (14be) to study chemical engineering (14). In 1922, he began research at the Polytechnic's Institute of General Chemistry under Giuseppe Bruni and Giorgio Renato Levi (14e). Natta then received his Dottore degree in 1924 (14) and continued on as Bruni's assistant (14e). In 1927, he obtained the position of Libero Docente (14abc) which allowed him to teach (14a). After a period as assistant lecturer in chemistry at Milan (14b), he was made full professor and director of the Institute of General Chemistry at the University of Pavia in 1933 (14abcd). He then moved to occupy the chair of physical chemistry at the University of Rome in 1935 (14abcd), but left shortly thereafter to take the chair of industrial chemistry at the Polytechnic of Turin in either 1936 (14a) or 1937 (14bd). Finally, he was called back to his alma mater to take the chair of industrial chemistry of the Polytechnic of Milan in either 1938 (14abcd) or 1939 (14e), where he would remain until his retirement in 1973 (14).

Natta is best known for his work in high polymers, beginning with work on butadiene and synthetic rubber in 1938 (14abc). The same year he began work on olefin polymerization (14ab), which ultimately led to the extension of Karl Ziegler's work on metal-based polymerization catalysts and resulted in the discovery of new classes of polymers with a sterically-ordered structure (i.e. isotactic, syndiotactic and diisotactic polymers), as well as linear non-branched olefinic polymers and copolymers with an atactic structure (14). For these accomplishments, Natta shared the Nobel Prize in Chemistry with Ziegler in 1963 (14).

Following his successful catalytic polymerization of α-olefins and diolefins in the early 1950's, Natta then began investigating the application of the previously successful catalysts to the polymerization of the acetylenes (13). These efforts resulted in an initial Italian patent in 1955 (13a), followed by the publication in 1958 of the successful catalytic polymerization of acetylene via triethylaluminum (Et₃Al)/titanium alkoxide combinations (13b). As outlined in Figure 2, the best results were obtained using Et₃Al and titanium(IV) propoxide at 75°C, with a catalyst molar ratio (Al/Ti) of 2.5. These conditions resulted in 98.5% monomer conversion to give a dark, crystalline polymer that was completely insoluble in organic solvents (13b).

$$H = H \xrightarrow{\text{Et}_3\text{Al/Ti}(\text{OC}_3\text{H}_7)_4} \begin{cases} 75 \text{ °C} \\ \text{heptane} \end{cases}$$

Figure 2. Catalytic polymerization of acetylene.

The polymers were characterized by X-ray diffraction of powder samples, which were found to be ~90-95% crystalline, with low amorphous content. The collected X-ray data were consistent with linear chains of polyacetylene in which the double bond configuration was thought to be predominantly *trans* (13b). The combination of the black color, the metallic luster, and the relatively low electrical resistivity ($\sim 10^{10} \Omega$ cm, compared to 10^{15} - $10^{18} \Omega$ cm for typical polyhydrocarbons) led them to conclude that their polyacetylene was structurally identical to a very long conjugated polyene, although Shirakawa later stated that this conclusion was not accepted widely at the time (10).

It was also noted that the polyacetylene samples exhibited high reactivity, particularly with oxidants such as O_2 and Cl_2 (13b). Reaction with chlorine resulted in a while solid that was amorphous by X-ray characterization. Heating this product at 70-80 °C resulted in a rapid loss of HCl and darkening of the polymer. Alternately, nearly all of the chlorine could be removed by treatment of the polymer with potassium in hot ethanol, giving a black amorphous solid (13b).

Although Natta states in his 1958 paper that these results only represented an initial communication with additional reports planned (13b), no further work on polyacetylenes was ever published by Natta and his coworkers. Others, however, did not hesitate to continue this work (15) and as a result, *polyacetylene* gradually replaced the term *polyene* as more studies began to utilize Natta's polymerization methods (10). One of these research groups was that of Prof. Sakuji Ikeda at the Tokyo Institute of Technology, and it is with their work that we will continue our discussion.

Hideki Shirakawa and Polyacetylene Films

In the mid-1960s, Ikeda began studying the mechanism of acetylene polymerization by Ziegler-Natta catalysts (15cd), as well as developing new transition metal polymerization catalysts (16). In the process, it was found that in addition to polyacetylene, these methods also produced benzene and that the ratio of products varied with

the catalyst used (10,15cd). These ongoing mechanistic investigations were then continued by a new research associate, Hideki Shirakawa, who joined Ikeda's group in April of 1966 (10,17).

Shirakawa (Figure 3) was born August 20, 1936, in Tokyo (10a,17). Spending his childhood in in the small city of Takayama, he entered Tokyo Institute of Technology in April of 1957 (17). For his undergraduate studies, he focused primarily on applied chemistry, although he did some work in polymer physics during his final year (17). He then changed his focus to polymer synthesis for his graduate studies (17), receiving a Doctor of Engineering degree in March of 1966 (17,18). In 1979, he moved to the University of Tsukuba, where he was appointed associate professor. He was later promoted to full professor in 1982 and formally retired from the University of Tsukuba as professor emeritus at the end of March 2000, shortly after being awarded the Nobel Prize in Chemistry with Heeger and MacDiarmid (17).



Figure 3. Hideki Shirakawa (1936-). Reproduced from Ref. 19a with permission of the Royal Society of Chemistry.

While working with Shirakawa in the fall of 1967 (10,17,19), a visiting Korean coworker (20) named Hyung Chick Pyun had attempted to make polyacetylene using conditions nearly identical to those reported by Natta (21), as shown in Figure 2 (13b). However, rather than generating polymer powder as expected, ragged pieces of a polymer film were produced instead (17,19ab). Upon reviewing the reaction conditions, Shirakawa found that the film formation was a result of the fact that the catalyst concentration used had been 1000 times higher than intended (10,17,19ab). Shirakawa explained the mistake as follows (17):

I might have missed the "m" for "mmol" in my experimental instructions, or the visitor might have misread it.

Curiously, MacDiarmid gives a quite different account, stating (19c):

...and he [Shirakawa] replied that this occurred because of a misunderstanding between the Japanese language and that of a foreign student who had just joined his group.

It has been pointed out, however, that Pyun spoke fluent Japanese (19d), which casts doubt on MacDiarmid's account. Regardless of what caused the error, the resulting highly concentrated catalyst solution accelerated the rate of polymerization to the point that the acetylene polymerized at the air-solvent interface, rather than in solution as was typical (17,21). As a result, Shirakawa was now able to reproducibly generate silvery plastic polyacetylene films via polymerization of acetylene on the surface of unstirred, concentrated catalyst solutions (21,22).

It was found that the backbone configurations of the resulting polyacetylene films were strongly temperature dependent (Figure 4) due to an irreversible isomerization of the cis to trans forms at temperatures above 145 °C (10a,21,22). The resulting copper-colored all-cis samples gave conductivities of 10⁻⁹-10⁻⁸ S cm⁻¹, while the silver-colored, all-trans samples gave higher values of 10⁻⁵-10⁻⁴ S cm⁻¹ (22d). Surprisingly, the values of the all-trans samples are essentially the same as those previously reported for highly crystalline polyacetylene powders (15ab). As it had been previously shown the conductivity increased with polymer crystallinity (15a), one could expect the film to provide increased order and a corresponding rise in conductivity, but this did not seem to be the case (10a). Characterization of the films by X-ray diffraction (22b) gave data nearly identical to the previous studies of Natta (13b).

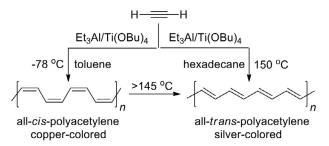


Figure 4. Temperature dependence of polymerization.

Attempts were then made to convert the polyacetylene to graphitic films. Initial attempts via pyrolysis failed and thus a chlorination/HCl elimination approach was then investigated (10). Treatment of polyacetylene with chlorine resulted in the formation of a white product (2a), similar to that previously reported by Natta (13b). This product was then treated with base and heated at high temperature, but resulted in little graphitization of the material (10).

Smith and Doped Polyacetylene

About the same time that Shirakawa and Pyun accidently produced the first polyacetylene films, Dorian S. Smith and Donald J. Berets at the American Cyanamid Company were investigating the effects of additives on the conductivity of polyacetylene powders (23). Dorian Sevcik Smith grew up in Winthrop Harbor, Michigan (24), before attending Illinois State Normal University (24,25). In addition to his coursework, he played football and was part of the University's sole undefeated football team in 1950 (24). For this distinction, the 1950 Redbirds team was inducted into the Illinois State Athletics Percy Hall of Fame in 1990 (26). After earning a B.S. in Education in 1953 (25), he was appointed by the Teachers College Board of the State of Illinois as a faculty assistant for the 1953-54 academic year (27). He then moved to the University of Illinois at Urbana-Champaign to continue his education with graduate studies in chemistry (24,25). There he studied the chemistry and electrochemistry of rare earth salts under the guidance of Prof. Therald Moeller (1913-1997). He received a M.S. in 1956, followed by a Ph.D. in 1958 (25).

Smith enjoyed a 10-year career as a chemist (24) at the American Cyanamid Company in Stamford, Connecticut, and the Enjay Chemical Company in New York (23), before becoming a financial analyst for various firms, including Donaldson, Lufkin and Jenrette, Chemical Bank and Yamaichi International, where he was Director of Research (24). After spending the majority of his working life in New York City, he retired to Wilmington, North Carolina, in 1996. He passed away peacefully at his home on December 4, 2010, at the age of 77 (24).

Initially, Smith and Berets were investigating the effect of oxygen impurities on the conductivity of pressed pellets of polyacetylene powder, finding that samples with lower oxygen content gave lower resistivity. In the process, however, they observed an interesting phenomenon (23):

On admission of 150 mm pressure of oxygen to the measuring apparatus (normally evacuated or under a few cm pressure of He gas), the resistivity of polyacetylene decreased by a factor of 10. If the oxygen was pumped off within a few minutes and evacuation continued at 10^{-4} mm pressure for several hours, the

original electrical properties of the specimen were restored.

They went on to conclude that oxygen is first adsorbed in a reversible manner, reducing the resistivity, but ultimately reacts with the polymer irreversibly resulting in the typically observed increase in resistivity.

The effects of various gases on the conductivity were then investigated to find that electron acceptors (BF₃, BCl₃, Cl₂, SO₂, NO₂, O₂, etc.) all resulted in a decrease in resistivity (i.e. an increase in conductivity), although oxidizing gases (O₂, Cl₂, and NO₂) ultimately resulted in chemical reaction with the polymer. In contrast, electron donors (NH₃, CH₃NH₂, H₂S, etc.) had the opposite effect on resistivity. The best results were obtained using BF₃, which resulted in an increase in conductivity of three orders of magnitude (to ~0.0013 S cm⁻¹). These results were explained as follows (23):

The effect on conductivity of the adsorbed electron-donating and electron-accepting gases is consistent with the p-type nature... If holes are the dominant carriers, electron donation would be expected to compensate them and reduce conductivity; electron acceptors would be expected to increase the concentration of holes and increase conductivity; this is observed.

Although they didn't completely understand the effect of the gaseous additions, they quite clearly state (23) that the *electrical conductivity depended on the extent of oxidation of the samples!* These results, however, did not seem to generate much interest and Berets and Smith never followed up this work with any additional studies. In fact, this work seems to be the only paper Smith ever published after completing his Ph.D. A few years later, however, two professors at the University of Pennsylvania began a related study with the addition of gaseous bromine to the inorganic polymer poly(sulfurnitride) (28).

MacDiarmid, Heeger, and Poly(sulfurnitride)

Alan Graham MacDiarmid (Figure 5) was born April 14, 1927, in Masterton, New Zealand (19c,29). Coming from a self-described "poor family," he was forced to leave high school at age 16 in order take a part-time job after his father retired (19c,29). His job working as janitor and lab boy in the chemistry department at Victoria University College (19c), however, allowed him to apply himself as a part-time student and he was able to complete his B.Sc. in 1948 (29). After completing his B.Sc. at age 21, he was promoted to the position of demonstrator (19c) and he began studying the chemistry of S_4N_4 for

his M.Sc. thesis under Mr. A. D. Monro (19c,29). He published his first paper in 1949 (30) and completed his M.Sc. the following year (4,29).

MacDiarmid then received a Fulbright fellowship to attend the University of Wisconsin, where he studied inorganic chemistry under Prof. Norris F. Hall (19c,29). There he earned a M.S. in 1952 and a Ph.D. in 1953 (4,29,31). While still at Wisconsin, he obtained a New Zealand Shell graduate scholarship to study silicon hydrides under Prof. Harry J. Emeléus at Cambridge University (19c,29). He completed his second Ph.D. in 1955 (4,29) and held a brief appointment as assistant lecturer at the University of St. Andrews in Scotland before joining the Department of Chemistry at the University of Pennsylvania (29). MacDiarmid maintained his position at Penn until the end of his career, but also held positions at the University of Texas at Dallas, becoming the James Von Ehr Chair of Science and Technology and professor of chemistry and physics there in 2002, and at Jilin University in China, becoming professor of chemistry there in 2004 (29). MacDiarmid continued to work until his death on February 7, 2007 (29,32).





Figure 5. Alan G. MacDiarmid (1927-2007) and Alan J. Heeger (1936-). Reproduced from Ref. 19a with permission of the Royal Society of Chemistry.

Alan Jay Heeger (Figure 5) was born January 22, 1936, in Sioux City, Iowa (33). His family moved to Omaha when he was nine and later attended the University of Nebraska with the initial goal of becoming an engineer (33). However, that changed after his first semester and he pursued dual studies in physics and mathematics (33). After completing his B.S. in 1957, he began graduate studies in physics at Berkeley, ultimately joining the research group of Alan Portis (33). After completing his Ph.D. in 1961 (34), he went directly to join the Physics Department at the University of Pennsylvania in 1962 (33a), working initially on the metal physics of tetrathiafulvalene-tetracyanoquinodimethane

(TTF-TCNQ) (33). In 1982, Heeger moved to the University of California, Santa Barbara (UCSB), where he still actively pursues research in conjugated materials. In addition to his faculty position as professor of physics, he also served as the director and co-founder of UCSB's Center for Polymers and Organic Solids.

The collaboration between the two Penn colleagues began in 1975, after Heeger became intrigued by re-ports of the metallic polymer poly(sulfurnitride), (SN)_r (19ac,33). Learning that MacDiarmid had some experience with sulfurnitride chemistry, he approached him about working together on a study of this new polymer (19a,33). Their collaboration then began with development of the first reproducible preparation of analytically pure (SN)_x via the solid-state polymerization of S_2N_2 to give a lustrous golden material (28ab). The following year they reported the characterization of its electronic properties, giving conductivities of 1.2-3.7 × $10^3 \Omega^{-1} \text{ cm}^{-1}$ (28c). Finally, following up on previous reports that (SN)_r reacted with halides, they treated the polymer with bromine vapor to produce the derivative (SNBr_y)_x that resulted in a 10-fold increase in conductivity in comparison to (SN)_r (19ac,28c).

Doped Polyacetylene Films

Shortly after the beginning of the collaboration with Heeger (33), MacDiarmid spent three quarters of a year as a visiting professor at Kyoto University (19c,29). During his visit, he was asked to give a lecture at the Tokyo Institute of Technology and met Shirakawa over tea after his lecture (19ac,29). After seeing MacDiarmid's golden (SN), film, Shirakawa said that he had a similar material and returned to his lab to retrieve a sample of his silver-colored polyacetylene film to show MacDiarmid (29). The film captured MacDiarmid's interest and after returning to the states, he inquired into the possibility of supplemental funding in order to bring Shirakawa to Penn to work on polyacetylene (19c,29). ONR Program Officer Kenneth Wynne agreed to support Shirakawa's visit (19a) and thus he began working with MacDiarmid and Heeger as a visiting scientist in September of 1976 (10a,17).

Upon arriving at Penn, Shirakawa and MacDiarmid first worked to improve the purity of the polyacetylene films in order to increase its conductivity (19c). As discussed above, previous studies by Smith and Berets (23) had shown that conductivity did increase with decreased oxygen content and thus limiting other impurities could possibly further increase the film's conductivity.

Eventually, they were able to make films with purities as high as ca. 98.6% (29), but found that conductivity actually decreased as the film purity was enhanced (38,55). Temperature-dependent conductivity measurements were also made to determine whether polyacetylene had the temperature profile of a metal or semiconductor (55). As Hatano had previously reported such measurements for polyacetylene powders in 1961 (28), resulting in a temperature profile consistent with that of a semiconductor, it is unclear if it was thought that the film might have a different response in comparison to the pressed pellets, or if they were just unaware of Hatano's work at the time.

Based on the observed relationship between purity and the resulting conductivity, it was proposed that perhaps the impurities in the film were acting as dopants which thus increased the conductivity of the polyacetylene (19c,29), as Heeger and MacDiarmid had previously seen in the addition of Br_2 to $(\text{SN})_x$ (19c,28d). This reasoning was also supported by previous in situ IR measurements by Shirakawa and Ikeda during the treatment of polyacetylene films with halide vapors, which revealed a dramatic decrease in IR transmission (10). This change in transmission suggested that the initial halogentreated material might have unusual electronic properties (19a) and thus it was decided to study the conductivity of the films upon bromine addition.

The critical measurements were then carried out on November 23, 1976 (10,17), by Shirakawa and Dr. Chwan K. Chiang, a postdoctoral fellow of Heeger (17). The conductivity of a *trans*-polyacetylene film was measured by four-point probe while being exposed to bromine vapor (2a,17,19a). The conductivity rapidly increased with the addition of 1 Torr of bromine, resulting in a change of approximately four orders of magnitude (from 10⁻⁵ to 0.5 S cm⁻¹) within only 10 minutes (2a). These measurements were then repeated using iodine in place of bromine to give an even greater increase in conductivity (up to 38 S cm⁻¹) (2a).

Later that same year it was demonstrated that higher conductivities of 160 S cm⁻¹ could be obtained with further optimization of the iodine treatment, although the substitution of AsF₅ for iodine could pro-duce even higher conductivities (2bc). Thus the treatment of polyacetylene films with AsF₅ gave conductivities of 220 S cm⁻¹ for the *trans* isomer, with even higher values (560 S cm⁻¹) for the *cis* isomer (2b). The very high values for the AsF₅-doped *cis*-polyacetylene films then led them to repeat the iodine treatments using *cis*-polyacetylene in 1978, resulting in conductivity values above 500 S cm⁻¹ (2d). That same year, it was also demonstrated that

polyacetylene could be doped with electron-donating species such as sodium to give conductivities of 8 S cm⁻¹ (2c). Heeger and MacDiarmid then reported maximum values of 200 S cm⁻¹ for electron-donor treated films in a final 1978 paper (35).

Conclusions

Beginning with the work of Hatano in 1961 (15a), these collective studies demonstrated that the conductivity of polyacetylene was electronic in nature and not consistent with an ionic mechanism. Also demonstrated was the fact that these organic could be chemically doped with electron-acceptors (*p*-doping) or electron-donors (*n*-doping) in a manner analogous to classical inorganic semiconductors such as silicon. Lastly, it was shown that polyacetylene could be transformed from an insulator to a semiconductor or even quasi-metal, depending on the extent of chemical doping. As such, it represented the first example of an organic material capable of undergoing a metal-insulator transition.

While all of these discoveries are typically credited to Heeger, MacDiarmid, and Shirakawa, the above discussion has hopefully illustrated that their seminal work was built upon previous studies, some of which had already shown aspects of these properties. In particular, while the work of Smith and Berets (23) was less developed and they never described their studies as "doping," it is quite clear that they were showing the same effects that later resulted in the more dramatic conductivity increases reported nearly a decade later. As such, it is curious to imagine how much their previous work influenced the doping studies in the late 1970s. At least Shirakawa was familiar with the work, as he repeatedly referenced Smith and Berets as early as 1973 (22ab). In terms of the collaborative papers with Heeger and MacDiarmid, however, Smith and Berets are not mentioned until the third paper, where it is acknowledged that polyacetylene powder had been previously treated with electron-withdrawing species, but state that the conductivities were still very small (2c). In the following paper, they also refer to the oxygen content study of Smith and Berets (2d). Curiously, however, they do not mention this previous work when reporting in 1977 that treatment of trans-polyacetylene films with NH3 vapor results in a decrease in conductivity by four orders of magnitude (2bc), the same result previously reported by Smith and Berets in 1968 on pressed pellets (23).

Acknowledgements

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About the Author

Seth C. Rasmussen is a Professor of Chemistry at North Dakota State University (NDSU) in Fargo. He received his B.S in Chemistry from Washington State University in 1990 and his Ph.D. in Inorganic Chemistry from Clemson University in 1994, under the guidance of Prof. John D. Peterson. As a postdoctoral associate at the University of Oregon, he then studied conjugated organic polymers under Prof. James E. Hutchison. In 1997, he accepted a teaching position at the University of Oregon, before moving to join the faculty at NDSU in 1999. In addition to ongoing research efforts in the area of conjugated materials chemistry, Prof. Rasmussen maintains an active interest in the teaching and research of the history of chemistry, currently serving as the Program Chair for the History of Chemistry division of the American Chemical Society and as Series Editor for Springer Briefs in Molecular Science: History of Chemistry.

IN DEFENSE OF THE USE OF THE FRENCH LANGUAGE IN SCIENTIFIC COMMUNICATION, 1965-1985: NATIONAL AND INTERNATIONAL DELIBERATIONS AND AN INGENIOUSLY CLEVER TAKEOFF ON THE THEME BY R. B. WOODWARD

Joseph Gal, Departments of Medicine and Pathology, School of Medicine, University of Colorado Denver, Anschutz Medical Campus, Aurora, CO 80045, Joe.Gal@ucdenver.edu and Jeffrey I. Seeman, Department of Chemistry, University of Richmond, Richmond, VA 23173, jseeman@richmond.edu

Supplemental Material

Abstract

For many decades, French scientists, the French Académie des Sciences, and the government of France have been concerned about the declining use of French within the scientific milieu and the trend toward English as the universally-accepted language to communicate science. This trend is discussed with a focus on the issues most vigorously debated in the time period 1965-1985, including the reduced use of French in international scientific communication resulting from the dominance of English. A summary of the merging of national-chemicalsociety journals into international journals is also presented. A set of previously unpublished documents from 1965 written by the late Robert Burns Woodward—actually a linguistic twist on La Marseillaise, the French national anthem, that addresses the French-English debate—and his letter and enclosures to Jean-Marie Lehn are included and discussed.

It shall and may be lawful by the said society by their proper officers, at all times, whether at peace or war, to correspond with learned Societies, as well as individual learned men, of any nation or country ...

-American Philosophical Society charter 1780

Introduction

The international nature of chemistry—indeed, of science—is a truism. Operationally, however, the practice of doing and communicating chemistry is not equally and symmetrically shared throughout the world. That is also a truism. The evidence that English has become the unofficial language throughout the world in chemistry is multifold. For example, English is the only accepted language of *Pure and Applied Chemistry*, the official journal of the International Union of Pure and Applied Chemistry (IUPAC). Indeed, there has been a gradual disappearance of non-English chemistry journals over the past several decades.

In the late 1990s, the 14 European chemical societies listed in Table 1 founded the organization ChemPubSoc Europe "as a consequence of the amalgamation of many chemical journals owned by national chemical societies into a number of high-quality European journals" (2). The journals listed in the top portion of Table 2, all published by ChemPubSoc Europe, are solely in English, "replac[ing] 14 traditional national journals" (2). In 2005, surely influenced by the model and success of ChemPubSoc Europe, the Asian Chemical Editorial Society (ACES) was founded as a "conglomeration of [13] chemical societies [Table 1] with the mutual aim of

creating a modern publishing forum for research in Asia and coordinating future publishing activities" (3). ACES publishes two journals, both in English: *Chemistry—An Asian Journal* and *Asian Journal of Organic Chemistry*. (See the bottom portion of Table 2.)

Table 1. Participating societies in ChemPubSoc Europe (2) and the Asian Chemical Editorial Society (ACES) (3)

ChemPubSoc Europe Gesellschaft Österreichischer Chemiker (GÖCH) Austria Société Royale de Chimie (SRC) Belgium Koninklijke Vlaamse Chemische Vereniging (KVCV) Belgium Česká Společnost Chemická (ČSCH) Czech Republic Société Chimique de France (SCF) France Gesellschaft Deutscher Chemiker (GDCh) Germany Association of Greek Chemists (EEX) Greece Magyar Kémikusok Egyesülete (MKE) Hungary Società Chimica Italiana (SCI) Italy Koninklijke Nederlandse Chemische Vereniging (KNCV) The Netherlands Polskie Towarzystwo Chemiczne (PTChem) Poland Sociedade Portuguesa de Química (SPQ) Portugal Real Sociedad Española de Química (RSEQ) Spain Svenska Kemistsamfundet (SK) Sweden Asian Chemical Editorial Society (ACES) Royal Australian Chemical Institute Inc. (RACI) Australia Chinese Chemical Society (CCS) China Hong Kong Chemical Society of India (CRSI) India Himpunan Kimia Indonesia (HKI) Indonesia Korean Chemical Society (KCS) Korea	Participating societies (abbreviation)	Country		
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Himpunan Kimia Indonesia (HKI) Korean Chemical Society (KCS) Chemical Society of Japan (CSJ) Institut Kimia Malaysia (IKM) New Zealand Institute of Chemistry (NZIC) Singapore National Institute of Chemistry (SNIC) Chemical Society Located in Taipei, China (CSLT) Chemical Society of Thailand (CST) Indonesia Iapan Iapan Taipan Taipan Thailand	Hong Kong Chemical Society (HKCS)	China		
Korean Chemical Society (KCS) Chemical Society of Japan (CSJ) Institut Kimia Malaysia (IKM) New Zealand Institute of Chemistry (NZIC) Singapore National Institute of Chemistry (SNIC) Chemical Society Located in Taipei, China (CSLT) Chemical Society of Thailand (CST) Korea Korea Korea Korea Korea Karea Malaysia New Zealand Singapore Singapore Taipei, China (CSLT) Thailand	Chemical Research Society of India (CRSI)	India		
Chemical Society of Japan (CSJ) Institut Kimia Malaysia (IKM) New Zealand Institute of Chemistry (NZIC) Singapore National Institute of Chemistry (SNIC) Chemical Society Located in Taipei, China (CSLT) Chemical Society of Thailand (CST) Taipei, China	Himpunan Kimia Indonesia (HKI)	Indonesia		
Institut Kimia Malaysia (IKM) Malaysia New Zealand Institute of Chemistry (NZIC) New Zealand Singapore National Institute of Chemistry (SNIC) Singapore Chemical Society Located in Taipei, China (CSLT) Taipei, China Chemical Society of Thailand (CST) Thailand	Korean Chemical Society (KCS)	Korea		
New Zealand Institute of Chemistry (NZIC) New Zealand Singapore National Institute of Chemistry (SNIC) Singapore Chemical Society Located in Taipei, China (CSLT) Taipei, China Chemical Society of Thailand (CST) Thailand	Chemical Society of Japan (CSJ)	Japan		
Singapore National Institute of Chemistry (SNIC) Chemical Society Located in Taipei, China (CSLT) Chemical Society of Thailand (CST) Taipei, China Thailand	Institut Kimia Malaysia (IKM)	Malaysia		
(SNIC) Singapore Chemical Society Located in Taipei, China (CSLT) Taipei, China Chemical Society of Thailand (CST) Thailand	New Zealand Institute of Chemistry (NZIC)	New Zealand		
(CSLT) Taiper, China Chemical Society of Thailand (CST) Thailand		Singapore		
		Taipei, China		
Chemical Society of Vietnam (CSV) Vietnam	Chemical Society of Thailand (CST)	Thailand		
	Chemical Society of Vietnam (CSV)	Vietnam		

Table 2. ChemPubSoc Europe's and Asian Chemical Editorial Society's journals (2, 3).

ChemPubSoc Europe's Journals		
Chemistry—A European Journal		
European Journal of Organic Chemistry		
European Journal of Inorganic Chemistry		
ChemBioChem		
ChemPhysChem		
ChemMedChem		
ChemSusChem		
ChemCatChem		
ChemPlusChem		
ChemElectroChem		
ChemistryOpen		
ChemViews		
Asian Chemical Editorial Society's journals		
Chemistry—An Asian Journal		
Asian Journal of Organic Chemistry		

The transition to English as the single most-dominant language of communication in chemistry from 1985 to the present is surely based on the preparative 20-year period 1965-1985. A variety of practical considerations—economics of publication being just one—have funneled many chemical forums around the world into English and away from French and German, the dominant languages of chemical communication in the 19th and first half of the 20th centuries. Other factors can be cited for the choice of English as today's preferred language of the chemical community, a critical one being the dramatic rise of American chemistry after World War I and further powered by World War II and post-World War II chemical advances in the USA (4).

Ironically, French and German substituted for another native language in 19th-century chemical communications. For example, instead of Russian in the *Bulletin scientifique publié par l'Académie Impériale des Sciences de Saint-Pétersbourg*, Russian chemists published their research in French and German. Apparently, Russian chemists during that time felt that their work would be better disseminated by using what were then the international languages of science. There are other similar cases, a full discussion of which is outside the scope of this article.

Almost certainly, nowhere has the discussion of the choice of English as the universal scientific language

been more pronounced and publicly more vigorous than in France. However, recent discussions on the decreasing use of languages in science communication have taken place in countries other than France, especially in Germany, Italy, and Japan (5). There is substantial national pride by the French, and indeed in other countries, for their own language. Given the emphasis in this article on the French-to-English conversions in science communications, we note that in 1998, the venerable Bulletin de la Société Chimique de France and Chemische Berichte/ Recueil and Liebigs Annalen/Recueil merged with other journals to form the European Journal of Organic Chemistry and the European Journal of Inorganic Chemistry. One year earlier, in 1997, Chemische Berichte and Liebigs Annalen were merged with the Dutch journal Recueil des Travaux Chimiques des Pays-Bas to form Chemische Berichte/Recueil and Liebigs Annalen/Recueil. For a personal account of some of these transitions, see the autobiographical essay by Wiley-VCH publishing executive and Ph.D. chemist Eva Wille in the journal The Chemical Record (6).

In this essay, we shall review some of the *highlights* of the concerns and trends expressed between 1965 and 1985 dealing with the choice of English as the universal language in chemistry and the French resistance to this trend. We emphasize the word "highlight" as this is neither a comprehensive research study of this communication trend nor of the various national responses

to English, today, or German and French in the 19th and early 20th centuries, becoming the international language of chemistry. We also emphasize that we focus on the French response because it has been the most evident and perhaps the most persistent and vocal opposition. We shall also showcase a set of several previously unpublished yet remarkable

documents written in 1965 by the then pope of organic chemistry (7), Nobelist Robert Burns Woodward. These documents call for French resistance to this takeover by the English language. Also included is a letter from Woodward to his then-recent postdoctoral student and future Nobelist French chemist Jean-Marie Lehn. These documents reveal Woodward's French literary capabili-

ties coupled with his wittiness, subtle sense of humor, and adroit political savvy. We first discuss the context in which these Woodward documents are best viewed.

On English Becoming the Universal Language of Science and the Resistance to this Trend by the French

At the March 1, 1965 meeting of the French Académie des Sciences ("Académie" henceforth) in Paris, the following was adopted on the basis of a decision by a Comité Secret (i.e., secret committee, that is, one that meets behind closed doors) of the Académie, as reported in the official journal of the Académie (8). (See Figure 1 for the original.)

COMITÉ SECRET.

The following wish, to be addressed to the President of the Republic, concerning the maintaining of the use of the French language in international scientific meetings is adopted unanimously:

L'ACADÉMIE DES SCIENCES,

committed to the active defense of the French language in international scientific events and troubled by pressures in favor of the exclusive use of the English language exerted by certain international organizations of intergovernmental nature, expresses its wish for a firm intervention by the [French] state to assure from now on the respect of the French language in the scientific domain within the framework

> of meetings sponsored by the above organizations.

The statement by the Académie was also communicated to Georges Pompidou, Prime Minister of France (9).

At the March 29, 1965, meeting of the Académie, the reply (dated March 23, 1965) from Charles de Gaulle, President of the Repub-

lic, was placed into the record. (See also Figure 2.) The President's letter stated (9):

The unanimous wish recently expressed by your

society concerning the use of the French language in international meetings has my highest approbation. It is in fact deplorable that the French language, so

remarkably suited by its clarity and precision to the

COMITÉ SECRET.

Est adopté à l'unanimité pour être adressé à M. le Président de lA République le vœu suivant concernant le maintien de l'usage de la langue française dans les Assemblées scientifiques internationales.

L'Académie des Sciences,

— attachée à une défense active de la langue française dans les manifestations scientifiques internationales,

inquiète des pressions exercées par certains organismes internationaux à caractère intergouvernemental en faveur de la seule langue anglaise,

ÉMET LE VŒU

-- d'une intervention ferme de l'État pour que soit désormais assuré, dans le cadre des réunions suscitées par ces organismes, le respect de la langue française en matière scientifique.

Figure 1. Letter to the President of the French Republic, Charles de Gaulle, on March 1, 1965, from the French Academy of Sciences (8).

expression of scientific thought, should be too often betrayed by the very people whose responsibility it is to maintain or compel its use.

While assuring that the necessary instructions are renewed and specified by the government, I want to express to you how much I appreciate the confidence that you provide me concerning the engagement of the members of the Academy of Sciences in this essential domain. It is, in fact, of national interest that scientists and technologists draw inspiration for the use our language from the respect that French science owes itself.

On March 26, 1965, the Académie (8) reproduced in the Prime Minister, Georges Pompidou, also responded to the Académie (10). (See also Figure 2.)

For my part, taking into consideration the reply that will be communicated to you by the President of the Republic, I am ready to support any concrete measures that will be deemed appropriate, according to your suggestions.

These events were reported in a number of newspapers in the United States (11) and in France (12) and car-

Parlez Francais, De Gaulle Demands

CORRESPONDANCE.

En réponse au vœu que lui avait adressé l'Académie, M. le Président de la République par lettre en date du 23 mars 1965, écrit :

MESSIEURS LES SECRÉTAIRES PERPÉTUELS,

Le vœu unanime récemment exprimé par votre Compagnie en ce qui concerne l'usage de la langue française dans les réunions internationales a mon assentiment le plus entier.

Il est, en effet, déplorable que la langue française, si remarquablement adaptée par sa clarté et sa précision à l'expression de la pensée scientifique, soit trop souvent trahie par ceux-là mêmes auxquels il incombe d'en maintenir ou d'en imposer l'usage.

Tout en faisant en sorte que les instructions nécessaires soient renouvelées et précisées par le Gouvernement, je tiens à vous dire combien j'apprécie la certitude que vous voulez bien me donner quant à l'action des membres de l'Académie des Sciences dans ce domaine essentiel. Il est, en effet, d'intérêt national que savants et techniciens s'inspirent dans l'emploi de notre langue du respect que la science française se doit à elle-mème.

Veuillez agréer, Messieurs les Secrétaires perpétuels, les assurances de ma haute considération.

Par lettre en date du 26 mars, M. Georges Pompinou, Premier Ministre, à qui le vœu avait été communiqué, écrit notamment :

« Je suis prêt, pour ma part, compte tenu de la réponse qui vous sera faite par Monsieur le Président de la République, à appuyer telle ou telle mesure concrète qui pourra paraître opportune, en fonction de vos suggestions. »

Figure 2. Responses by Charles de Gaulle (9), President of the French Republic, and Georges Pompidou (10), Prime Minister, to the request of the Académie (8) reproduced in Figure 1.

ried by the Associated Press (AP). (See, for example, Figure 3.)

Likely as a result of the above initiative by the Académie and its highly positive reception by the President of the Republic and the Prime Minister, on March 31, 1966, the President decreed the creation of a High Commission for the Defense and Expansion of the French Language. (See Figure 4 for an excerpt of that decree.) The decree begins as follows, citing the tasks of the Commission (13):

DECREES, ORDERS, CIRCU-LARS

PRIME MINISTER

Decree no. 66-203, March 31, 1966, implementing the creation of a High Commission for the defense and expansion of the French language.

The President of the Republic

Acting on the report of the Prime Minister,

The council of ministers having been heard,

Decrees:

French Told To Keep Saying It in French

Figure 3. Headlines of two newspaper articles (New York Times and Associated Press from an unknown newspaper) reporting the letter by President Charles de Gaulle to the Académie (Figure 2). De Gaulle was responding to the Académie's request (Figure 1) for the French government's intercession regarding the maintenance of French as a language in scientific communications. These two newspaper clippings were sent by R. B. Woodward to Jean-Marie Lehn on April 21, 1965; see the text and Figure 9 for more details. The date, March 30, 1965, is handwritten on the top right edge of each clipping, likely by Dolores Dyer, Woodward's assistant. A copy of the newspaper clippings provided courtesy of Lehn.

Article 1.—A high commission for the defense and expansion of the French language is created under the Prime Minister's authority.

The high commission is charged with the following tasks:

To study the appropriate measures for assuring the defense and expansion of the French language;

To establish the necessary connections with the competent private organizations, specifically in matters of cultural and technological cooperation;

To prompt or encourage all initiatives relevant to the defense and expansion of the French language ...

DÉCRETS, ARRÊTÉS ET CIRCULAIRES

PREMIER MINISTRE

Décret n° 66-203 du 31 mars 1966 portant création d'un haut comité pour la défense et l'expansion de la langue française.

Le Président de la République, Sur le rapport du Premier ministre, Le conseil des ministres entendu,

Décrète:

Art. 1°. — Il est créé auprès du Premier ministre un haut comité pour la défense et l'expansion de la langue française.

Le haut comité a pour mission : D'étudier les mesures propres à assurer la défense et l'expan-

sion de la langue française; D'établir les liaisons nécessaires avec les organismes privés compétents, notamment en matière de coopération culturelle et technique;

De susciter ou d'encourager toutes initiatives se rapportant à la défense et à l'expansion de la langue française.

Figure 4. An excerpt of the first few lines of the decree of March 31, 1966, by President Charles de Gaulle (13).

As summarized by the notable French organic chemist, essayist, and historian of chemistry Pierre Laszlo (14),

General de Gaulle returned to power in 1958. Almost immediately, he realized the key importance of science and technology to France. The allocation of vastly increased funding, even more important the quality of the administrative bodies overseeing the French scientists and engineers, created a leap forward. This Gaullist policy of banking on science and technology connected with Les Trente Glorieuses: these 30 glorious years (1950-1980, roughly speaking) saw France participate in the general economic expansion and even take the lead in a few sectors.

The Gaullist activist effort translated itself into a cornucopia of breakthroughs: France became a nuclear power, its aerospace industry became competitive worldwide, the country infrastructure (freeways and railroads, telecommunications) was renovated, and scientists won Nobel prizes and Fields medals.

In addition, De Gaulle, with his lifelong will of independence from the Anglo-Saxons, wanted French scientists not to bow to the growing hegemony of the English language. He vowed, as he did in other areas, that French science would henceforth appear to the world in French. This became official policy. If a French scientist got funding to attend a conference abroad, the paper would by fiat be delivered in French.

In 1975, Philippe Meyer discussed in a rather thoughtful and emotionally open and honest fashion "A Problem for the Non-Anglo-Saxon Scientific Community," that problem being "The English Language". He asked, what should the French government's position be regarding the use of English in teaching science in France? And how should French scientists communicate with their non-French peers within the broad international scientific community? Meyer wrote (15),

I am thus about to express my deep regrets and to discuss the vast problem raised by the feeling that I speak a dying language ...

Most of the best French contributions in science and medicine are [now] published in English ... all French research of quality is presented in English in international scientific meetings ... French scientists and doctors are informed of the important advances in their fields by books and reviews published in English.

Meyer pondered whether the solution was "in rendering the French scientific community completely bilingual" (15)?

In 1976, Eugene Garfield, the American information scientist, linguist, and founder of the Institute for Scientific Information and innovator of such publications as *Current Contents* and the *Science Citation Index*, published a then-highly controversial article entitled "La science française est-elle trop provinciale?" ("Is French science too provincial?") in *La Recherche*. Using bibliometrics and scientometrics, Garfield examined the role of French in science and the tendency of eminent French scientists to publish in English. Garfield concluded that English was becoming the *de facto* language of science. Some of Garfield's conclusions are (16):

By publishing the results of their research exclusively in the French language, French researchers prevent their findings from being casually read by the rest of the world's scientific community.

The data also indicate that the French themselves are the greatest citers of the French.

. . .

A careful examination of the citation data for many highly ranked French scientists has clearly shown that these scientists all share one characteristic: each publishes in English or in international journals outside of France.

The nature of Garfield's statistics notwithstanding, his article in *La Recherche* produced some strong counterarguments (17), especially from French scientists (18). There is much evidence that these issues flowed from the highest levels of government and the most sophisticated intellectual circles in France right into the laboratories of practicing chemists. Pierre Laszlo recollects two incidents relevant to our discussion, first, an interaction within a French Department of Chemistry (14).

I was Paul Schleyer's first post-doc at Princeton, during the 1962-63 academic year. I then returned home, to France. Guy Ourisson was professor of organic chemistry in Strasbourg. During the winter of 1963-64, he invited me to his Institute, to present a seminar on the topic "Should One Publish in English?" ("Doit-on publier en anglais?") After my year in Princeton, I felt strongly that French chemists ought to do so, if they wanted their work to be known.

It was an evening seminar. It was lively, just this side of hectic. The only reason I emerged unmolested from the uproar I had set up was my obvious sincerity.

The interesting question is: why did Ourisson have me do this? Despite the many intervening years—in the meanwhile, Ourisson became a personal friend of mine—the answer remains ambiguous. He was fluent in English, he had learned the language from his first wife who was British. Hence, publishing in English was no problem to him. At the same time, he was a cultured Frenchman, a member of the elite, who strongly believed in the importance of the French language and of Frenchmen showing the flag effectively. Moreover, Ourisson was a political animal: getting me to give this seminar allowed him to test the waters, with little risk that he would get splashed.

The second incident related by Laszlo involves a lecture he gave outside France:

In August 1965, I travelled to Copenhagen, with a grant by the French Foreign Ministry, to attend the IUPAC VIIIth European Congress on Molecular Spectroscopy. My paper dealt with some NMR applications to organic chemistry.

Forty to fifty people made the audience. Most were native English speakers. As I started giving my paper in the language of Molière, they looked bedazzled. Their eyes quickly glazed. This came as no surprise to me, I knew this would happen but I had my plan. After the introductory paragraph, in the midst of a

sentence I switched to English. Alertness immediately returned to the room.

After my talk was over and well received, a few English and American colleagues came to ask why I had sprung such a surprise on them. I told them of the official policy, I had been compelled to toe the party line, so to say. They were greatly appreciative that I had paid to it lip service only.

Even those among us who are non-French, or even non-French speaking, or even non-French reading, can empathize with the conflicting positions and feelings within the French scientific community. Fortunately, now nearly 50 years later, there is no sign that French (or German or Italian or any of the other national languages) is a dying language, even as English has become the universal scientific language.

Tetrahedron, Tetrahedron Letters, R. B. Woodward, and the Internationalism of Chemistry

In the second half of the 20th century, several language-in-science phenomena were happening simultaneously around the world. First, as described in the previous section, many in France were concerned about the decreasing use of French in scientific venues, not just in journals but at scientific meetings. Newspaper reports of these matters such as those shown in Figure 3 added general popular interest and perhaps political pressure to the already building discussions among scientists and various governmental agencies. Second, the push for the internationalism of chemistry was well in hand (19). In the mid-1950s, Sir Robert Robinson—who had just retired as Waynflete Professor at Oxford but continued to be a significant presence within the chemical community for 20 more years—used his considerable influence to found in 1957 the first international journal in chemistry, Tetrahedron (20), as well as the second international journal in chemistry, Tetrahedron Letters, shortly thereafter in 1959. Lastly, Tetrahedron and Tetrahedron Letters were published by a commercial publisher, not by a chemical society. These two journals were very early titles of Ian Robert Maxwell's Pergamon Press. Figure 5 shows Robinson proudly handing Maxwell the first issue of Tetrahedron.



Figure 5. Sir Robert Robinson (left) proudly celebrating the publication of the first issue of Tetrahedron with its publisher, Robert Maxwell, 1957. Photograph courtesy Royal Society (London).

Robinson served also as one of the two Co-Chairs of the Honorary Editorial Board for both Tetrahedron and Tetrahedron Letters. Woodward was chosen and agreed to serve as Co-Chairman of the Honorary Editorial Advisory Board for both Tetrahedron and Tetrahedron Letters from their inception. That Robinson endorsed if not actually selected Woodward to be Co-Chairman of the Honorary Editorial Advisory Board of Tetrahedron and Tetrahedron Letters demonstrates a remarkable U-turn in the relationship between these two giants of chemistry. Their rivalry in a number of areas—the structure of penicillin (21), the structure of strychnine (22), and the synthesis of steroids (23)—is well documented. Indeed, the picture of the two of them together in the early 1950s (Figure 6) illustrates a frosty relationship better than words can describe. That only a few years after this picture was taken, they would work closely together on a project near and dear to the heart of Robinson, the formation of an international journal of organic chemistry—in spite of reservations by Woodward (see below)—speaks to the power of Robinson's goal of collegiality and to the power of a good idea over his own individual pride (24). More details of the founding of Tetrahedron and Tetrahedron Letters will be reported by one of us (JIS) separately.

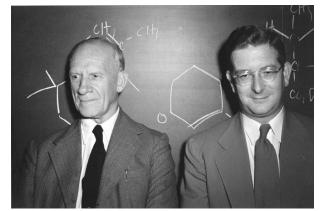


Figure 6. Sir Robert Robinson and R. B. Woodward, 1951. This photograph was taken before the two great men overcame their competitive issues and became friends. Clearly, they are not particularly comfortable standing next to each other. The structures on the blackboard were written by Robinson. Photograph courtesy J. D. Roberts.

Several factors made Tetrahedron and Tetrahedron Letters notable for their time, but rather prosaic today (25). The overriding goal of Tetrahedron and Tetrahedron Letters was to form a successful international journal. This goal of inclusivity was stated clearly on the front cover of these journals (Figure 7), in their mastheads (Figure 8), and in Robinson's essay in the first issue of *Tetrahedron* (20). These two journals immediately boasted an international team of editors and a very large international assembly of members of their advisory boards, from "Europe ... American Continents ... Far East," quite unique within the scientific milieu for the 1950s (26). Tetrahedron and Tetrahedron Letters accepted manuscripts for publication in the then-most-prominent science languages, English, German and French, though not in Russian. (See the Notes for Contributors from the first issue of Tetrahedron (27), Figure 8.) Indeed, articles from "the U.S.S.R. and Eastern Europe" were to be submitted to Professor A. N. Nesmeyanov in Moscow but with unspecified language.

Articles appeared in English, German and French in *Tetrahedron* for many years. In some early issues of *Tetrahedron*, abstracts for some articles published in either German or French appeared in that language as well as in English. Articles in English had only abstracts in English. In the first years of publication of *Tetrahedron Letters*, abstracts for articles that had appeared in *Tetrahedron* were published, and as in *Tetrahedron*, abstracts in either German or French appeared also in English but not the converse. In fact, it was only 50 years later in 2007 that the "Guide for Authors" in *Tetrahedron* specified that "Manuscripts must be written in English

TETRAHEDRON

THE INTERNATIONAL JOURNAL OF ORGANIC CHEMISTRY

FOUNDED BY SIR ROBERT ROBINSON

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Figure 7. Front cover of the first issue of Tetrahedron, January 1957. Note the international representation of Honorary Regional Editors and Honorary Editorial Advisory Board members, a remarkable organizational scheme for a journal in the 1950s. Sir Robert Robinson and R. B. Woodward served as Co-Chairman of the Honorary Editorial Advisory Board while the journal itself was founded by Robinson.

..." (28). In 2006, the "Instructions to Contributors" said, "The language of submission is English, but articles in French or German will be considered" (29).

Letters within the Robert Burns Woodward collection at the Harvard Archives provide clear evidence that Woodward took seriously his role as Co-Chairman of Tetrahedron and Tetrahedron Letters until his death in 1979. Woodward was quite involved in the setting of policy and developing and maintaining the goal of very high scientific standards for the papers published therein (30). Three themes recur over and over again in documents found within the Woodward collection: the international nature of *Tetrahedron* and *Tetrahedron Letters*, a commitment for exceptional quality of submissions and publications, and rapidity of publication.

Additional evidence for Woodward's commitment to the globalization of chemistry comes from an obituary

Submission of Papers

Original contributions submitted for publication should be sent to one of the following editors, as appropriate:

Professor H. Stephen, the Executive Editor, c/o Pergamon Press Ltd., 4 & 5 Fitzroy Square, London W.1.

Professor A. N. Nesmeyanov (for the U.S.S.R. and Eastern Europe), Akademiya Nauk SSSR, Bolshaya Kaluzhskaya 14, Moscow, U.S.S.R. Professor R. H. Martin (contributions in the French language), Laboratoires de Chimie Organique, Université Libre de Bruxelles, 50 Ave. F. D. Roosevelt, Brussels, Belgium.

Professor Dr. F. Weygand (contributions in the German language), Technische Universität, Berlin-Charlottenburg 2, Germany.

Figure 8. Excerpt from the "Notes for Contributors," the instructions to authors, published in the inside back cover of the first issue of Tetrahedron (27). That contributions in English, French and German were acceptable is clear from these instructions. A more concise but similar set of instructions appeared in the first issue of Tetrahedron Letters but was silent on the matter of language.

of Woodward written in 1981 by Derek Barton and Harry Wasserman (31). This obituary served as front matter for a special memorial issue of *Tetrahedron* honoring Woodward. After Robinson's death in 1975, Barton joined Woodward as Co-Chairman of the editorial board of Tetrahedron and Tetrahedron Letters. Upon Barton's passing in 1997, Wasserman succeeded him as Chair of the Board of Editors of these journals. Wasserman was also one of Woodward's first Ph.D. students, starting with him in the early 1940s and maintaining a close friendship for 40 years. Thus, when Barton and Wasserman jointly wrote the following commentary about Woodward's commitment to internationalism in chemistry, they based their conclusions on knowing him quite well (31):

His concern for these journals, particularly for their international influence, was of immense importance in establishing them as major publications in the world of organic chemistry.

By the early 1960s, Woodward had become a chemist of international fame and influence. Of course, his permanent academic position was at Harvard. In addition, he travelled to and lectured in Europe frequently, often visiting the United Kingdom (where his close friends included Barton and Alexander Todd) and Switzerland (where his close friends included Duilio Arigoni, Albert Eschenmoser, and Vladimir Prelog in Zürich). The Woodward Research Institute in Basel, Switzerland, was up and running in 1962 (32).

By 1965, Woodward also had a number of European postdoctoral fellows including the Frenchman Jean-Marie Lehn. Woodward had also published a number of papers with Barton, Prelog, Arigoni, Oskar Jeger, Hans Herloff Inhoffen, and other European scientists, the vast majority of which were written in the German language. Indeed, from 1934 to 1962, Woodward had 117 publications, 13 of which were written in the German language. Woodward well recognized and understood the tensions—the values and the shortcomings—regarding dissemination of his science in languages other than English. Thus, beyond knowing of the concern within both the scientific community and in non-English-speaking countries to preserve the use of their own national languages, Woodward himself had his own professional "investments" to protect as well. For example, in his March 5, 1956, letter to Robinson, Woodward wrote (33)

The proposal to publish an international journal for

organic chemistry is an intriguing one. My initial reactions are these ... Could the leading chemists in the various countries be induced to place their best material in the new journal? I am not sure, for example, that I could easily be induced to do so ...

In fact, in 1958 Woodward published his total synthesis of reserpine (34) in *Tetrahedron* and in 1963 he published the full account of his total synthesis of strychnine (35) in that journal (among seven other publications in *Tetrahedron* and four in *Tetrahedron Letters*).

"Woodward's La Marseillaise"

In April 1965, surely encouraged by the involvement of President

Charles de Gaulle in the matter of scientific communications, Woodward exercised his brilliance, prankishness, and mischievousness and provided us with an insight into these dimensions of his personality. On April 21, 1965, Woodward wrote about the French-English language controversy to Jean-Marie Lehn (Figure 9). Lehn had just recently returned to France after a postdoctoral term with Woodward and had taken up a position at the Université de Strasbourg where he remains today.

In addition to this witty and humorous letter, Woodward enclosed two newspaper clippings (Figure 3) and a one-page witticism which is reproduced in column 3 of Table 3 and which we refer to herein as "Woodward's La Marseillaise."

The newspaper clippings establish Woodward's awareness of the French-English language controversy.

Table 3 contains the first verse and the refrain of the

French national anthem La Marseillaise, "Woodward's La Marseillaise," and their translations into English. Woodward's lyrics were perhaps a lighthearted repartee, surely a play on words, on the French-English controversy using the first verse (from a total of seven verses) and the refrain of La Marseillaise. For the convenience of even those fluent in French, Table 3 presents a line-by-line comparison of La Marseillaise and "Woodward's La Marseillaise" along with the English translations of both. Our analysis of Woodward's key substitutions is found in Table 4. Woodward's cleverness is seen by his substitution of one word for another. Woodward transformed La Marseillaise's calling for resistance to foreign invasion to a call for resistance to the invasion of scientific communication in French by the English language.



Le Grand Charlie's cri de coeur, which has been widely publicized here in the camp of the enemy, suggests that a great cause is already in mortal danger. Apprised of this desperate situation, I have realized at once that what was needed was a rallying cry which, sweeping all before it, would reverse the melancholy trend. So I summonsed the Muse, and am glad to offer the accompanying modest result. Situated as you are in Strasbourg, you are in the most appropriate position to launch it on its triumphant march; perhaps you might even consider approaching the mayor of the city, whose distinguished predecessor performed a not dissimilar office on an earlier illustrious occasion--one hundred and seventy-three years ago this Saturday!

Best personal regards and good wishes.

Cordially,

ABurran

Should the rumor current here that you have become engaged be correct, please accept my warmest congratulations, and my hope that the state of euphoria undoubtedly induced by such a development will not interfere with your making proper use of the material accompanying this letter.

R. B. W.

Figure 9. R. B. Woodward's cover letter to Jean-Marie Lehn (36). Included with this letter were two newspaper clippings (Figure 3) and "Woodward's La Marseillaise" (column 3 of Table 3). The typographical error of "summonsed" instead of "summoned" is extraordinarily rare if not unique in Woodward's correspondence. Letter courtesy of Lehn.

Table 3. The third column is from Woodward (36, 37). The fourth column is our translation of "Woodward's La Marseillaise." The English translation of Woodward's "La Marseillaise" and of La Marseillaise is by one of the authors (JG). For a line-by-line analysis of the changes made by Woodward, see Table 4.

English translation of La Marseillaise Let's go, children of the fatherland, The day of glory has arrived! Against us is tyranny, The bloody banner is raised, The bloody banner is raised! Do you hear in the countryside The roar of these ferocious soldiers? They come right into your arms To kill your sons, your women!	La Marseillaise 1 Allons enfants de la Patrie, 2 Le jour de gloire est arrivé! 3 Contre nous de la tyrannie, 4 L'étendard sanglant est levé, 5 L'étendard sanglant est levé! 6 Entendez-vous dans les campagnes 7 Mugir ces féroces soldats? 8 Ils viennent jusque dans vos bras 9 Égorger vos fils, vos compagnes!	"Woodward's La Marseillaise" (36, 37) Parlons enfants de la Patrie, Le jour de gloire est arrivé! Contre nous de la taironnie, L'étendard anglais est levé, L'étendard anglais est levé! Entendez-vous dans cette campagne Mugir ces féroces savants? Ils viennent jusque dans nos bancs* Débaucher nos fils, nos compagnes!	"Woodward's La Marseillaise" in English Let's speak, children of the fatherland, The day of glory has arrived! Against us is not speaking The English banner is raised, The English banner is raised! Do you hear in this campaign The roar of these ferocious savants? They come right to our classrooms To corrupt our sons, our women!
To arms, citizens, Form your battalions, Let's march, let's march! So that an impure blood Will water our fields!	10 Aux armes, citoyens, 11 Formez vos bataillons, 12 Marchons, marchons! 13 Qu'un sang impur 14 Abreuve nos sillons!	Aux armes, citoyens, Formez vos bataillons, Parlons, parlons! Qu'une langue impure N'abreuve nos salons!	To arms, citizens, Form your battalions, Let's speak, let's speak! So that an impure language Will not flood our salons!

^{*}As can be seen in the typewritten text in Figure 10, Woodward did not change the word "bras", i.e., arms (limbs), in his first attempt at revising La Marseillaise. However, in the version shown in Figure 11 he replaced "bras" with "dents" (i.e., teeth). This appears to refer to the mouth, i.e., the organ of language, the implication being that the "enemy corrupts the language of our sons, our people". In a continuing evolution of "Woodward's La Marseillaise," in the text of the 3rd page found in the Harvard Archives (reproduced in column 3 above), the original "bras" (column 2) is changed to "bancs" (column 3), i.e., benches (which we render in context as laboratory benches or classrooms, see column 1 and entry line 8 in Table 4). Moreover, "bancs" is retained in the version Woodward sent to Jean-Marie Lehn, which is thus identical to the version shown in column 3 of this table.

La Marseillaise → "Woodward's La Marseillaise"

Analysis of Woodward's Revisions

Table 4. Listing and analysis of Woodward's revisions to the first verse and the refrain of La Marseillaise^a.

allons (let's go) → parlons (let's speak) Pseudo-homophones,^b two syllables tyrannie (tyranny) → taironnie (not speaking) Heterographsb, three syllables. There is no such word as "taironnie" in French; Woodward created this word by converting "tyrannie" to "taironnie," a word very similar in appearance and sound. "Taire" is a verb in French that means "to say nothing (about something);" in its reflexive form ("se taire"), it means "to be silent, to hold one's tongue," i.e., not to speak. Thus, "taironnie" fits in form and meaning "Woodward's La Marseillaise" and expresses the French-vs.-English language debate in communicating science.

- 4 & 5 sanglant (bloody) \rightarrow anglais (English)
 - Same number of syllables and some close similarity in sounds, i.e., the syllables, "sang" and "ang".
- dans les campagnes (in the countryside) → dans cette campagne (in this campaign)
 - The former refers to a battle with weapons, the latter to a conversation—it could be a debate—with words, in science.
- 7 soldats (soldiers) → savants (savants, scholarly persons) Similar letters, same number of syllables.
- jusque dans vos bras (right into your arms) → jusque dans nos bancsc (right to our classrooms)

 Note the two changes within this one phrase: "arms" is changed to "benches," or, by implication, "laboratory benches" or "classrooms," and "your" is changed to "our." "Classrooms" refers to the location where either French or English would be used in teaching or lecturing.
- 9 Égorger (literally, to cut the throat; figuratively, to kill) → débaucher (literally, to entice, to lead astray; figuratively, to corrupt)
 - Woodward expresses the intent of the "enemy of the French language" to corrupt the language of "our young, our country." Égorger and débaucher have the same number of syllables and are pronounced sufficiently similarly so that the new version retains the overall flavor of the original.
- 9 $vos \rightarrow nos$

Line

- "Vos" and "nos" are very similar in pronunciation. Woodward is now speaking of "our" sons and women, presumably students at all educational levels.
- Marchons, marchons (let's march, let's march) → Parlons, parlons (let's speak, let's speak)
 Similar sounds, poetic license
- 13-14 Qu'un sang impur Abreuve nos sillons (so that an impure blood will water our fields) → Qu'une langue impure N'abreuve nos salons (so that an impure language will not flood our salons)

 "Sillons" and "salons" are very similar in pronunciation. The latter is a substitution that is particularly noteworthy, as its several meanings all fit Woodward's lark. "Salon" can mean "a sitting room, drawing room," and, by extension, "a meeting place for fine conversation," as well as a lounge where alcoholic refreshments may be served. To "not flood our salons" in Woodward's text seems to refer to watering-down or reducing the effectiveness of a discussion, and, more specifically in the present context, to "drowning out our French language." The phrase could however also refer to diluting the percentage of alcohol in a drink. Woodward's text fits the overall context of his addressing the French/ English language debate; moreover, the interpretations also relate well to Woodward's personality, as he was a keen participant in the art of debate and he was certainly known to enjoy alcoholic beverages.

^a The analysis provided in this table is for the "definitive" version of "Woodward's La Marseillaise," i.e., that appearing in column 3 of Table 3 (36, 37).

^b Homophones are words that are pronounced the same but differ in meaning and may differ in spelling. Heterographs are two words with different meanings and different spellings but with the same pronunciations. Actually, these are loose heterographs, as they have either the same or almost the same pronunciation.

^c The appearance of "bancs" and its predecessors in the earlier versions of "Woodward's La Marseillaise" is discussed in Table 3 and in the captions to Figure 10 and Figure 11.

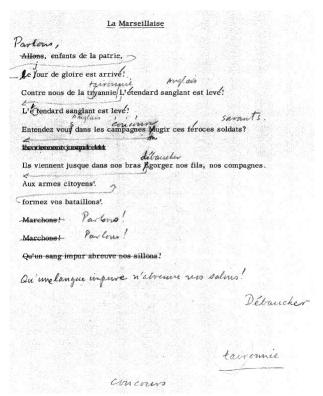


Figure 10. The first verse and refrain of "Woodward's La Marseillaise," a page from the Woodward Archives at Harvard University (37). Woodward apparently had "Woodward's La Marseillaise" typed by his administrative assistant, Dolores Dyer, as the typeset (font) matches Woodward's letters and manuscripts of the 1960s. The handwriting is Woodward's. Woodward wrote "concours" as a potential replacement for "campagnes." "Concours" in French has several meanings, but it appears that Woodward proposed it in the sense of "concourse," "gathering of people" (i.e., scientific conferences where the "roar" of English was heard). In fact, he chose not to use it in his definitive version (column 3 in Table 3). Note also that at the bottom of his "corrections" Woodward wrote "Débaucher," "concours," and "taironnie." These may have been notes of his during the construction of this first draft. Also, in the typewritten "original" of La Marseillaise in the figure, "nos" (i.e., our) in "nos bras, nos fils, nos compagnes" incorrectly appears rather than "vos [your] bras, vos fils, vos compagnes." The correct words are used in Table 3, column 2. See also Figure 11 and Table 4 for discussions of the changes introduced by Woodward.

La Marseillaise was written by Claude Joseph Rouget de Lisle in Strasbourg in 1792 at the request of the mayor of Strasbourg for the Army of the Rhine following France's declaration of war on Austria. La Marseillaise was a patriotic song of the French Revolution, a chant of the revolutionary war calling for mobilization and resistance to foreign invasion and tyranny. La Marseillaise was first adopted as France's national anthem on

July 14th, 1795. In 1830, Berlioz arranged it for orchestra and chorus.

It is these events, especially the fact that La Marseillaise was written at the request of the mayor of Strasbourg, to which Woodward refers in his letter to Lehn (Figure 9) (36),

Le Grand Charlie's cri de coeur ... Situated as you are in Strasbourg, you are in the most appropriate position to launch it [a "cri de cœur," a cry from the heart, a rallying cry, to retain the use of French in chemical communications] on its triumphant march; perhaps you might even consider approaching the mayor of the city ..."

Within the Woodward collection of documents held in the Harvard Archives resides a set of three pages which speak to the origin of "Woodward's La Marseillaise." Figure 10 and Figure 11 show two of these three pages; the third page of this set is reproduced in column 3 of Table 3 (37).

There are several slight changes throughout the several Woodward drafts. We comment upon these briefly, primarily to be complete and also for the benefit scholars of Woodward (32, 38) or La Marseillaise. The trend in these drafts provides insight into Woodward's

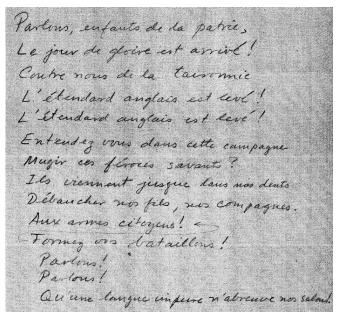


Figure 11. Woodward's handwritten draft of "Woodward's La Marseillaise" (37). Note that "concours," proposed in the version shown in Figure 10, is not used in this draft. Also noteworthy is the appearance in this draft of "dents" (i.e., teeth) in "jusque dans nos dents," i.e., "right to our teeth." In what appears to be the "definitive" version (column 3, Table 3), however, "dents" is replaced by "bancs" (i.e., benches; see the explanation in the caption of Table 3).

development of his play on La Marseillaise. The hand-written portion of Figure 10 shows what appears to be Woodward's initial trial at creating a linguistic twist of the original text. A very slightly different version appears in Figure 11, and column 3 of Table 3 contains a version yet slightly different from that. The various changes Woodward introduced are discussed in Table 4 and in the captions to Table 3 and Figure 10-11.

Woodward's letter to Lehn (Figure 9) displays Woodward's superb and subtle sense of humor, and also shows more evidence of his high-level knowledge of French. For example, Woodward used the very French expression "cri de cœur" (a cry from the heart). He also showed a detailed knowledge of the history of La Marseillaise (before the days of easy searching for historical details via Wikipedia!), referring to the mayor of Strasbourg in 1792, Frédéric de Dietrich, and referencing the 173rd anniversary of the writing of the lyrics the Saturday following the day Woodward's letter was written.

We speculate that four factors led Woodward to have fun with Jean-Marie Lehn and La Marseillaise. Indeed, his very choice of the French national anthem is an indication of the versatility of this man of letters and the proclivity of his subtlety. These factors are: (i) Woodward had a serious commitment to science as an international adventure. (ii) He was aware of the stirring controversies dealing with the movement to make English the universal language of chemistry. (iii) He had a keen sense of humor, loved intricate puzzles, had a vivid imagination, and enjoyed playfulness among his colleagues. (iv) He loved languages and, as we see herein, had an intimate knowledge of French.

The photograph of Woodward in Figure 12 illustrates several of these factors: Woodward and his visitor were playing some game or puzzle with matchsticks; and an issue of *Angewandte Chemie* is on Woodward's desk. That particular issue is not *Angewandte Chemie International Edition in English* but rather the Germanlanguage edition of that journal. In fact, the first issue of *Angewandte Chemie International Edition in English* was published in January 1962 and continues to be published, entirely in English, but its title has, for many years, been shortened to *Angewandte Chemie International Edition*.



Figure 12. R. B. Woodward and Paul Buchschacher, playing with what appear to be matchsticks in Woodward's Harvard office, June 21, 1960. Buchschacher received his doctorate working with Oskar Jeger before a postdoctoral experience with Woodward during the late stages of the chlorophyll synthesis. Woodward's tie is green rather than his typical blue. Likely this photograph was taken the day that the synthesis of chlorophyll was formally proclaimed (The JACS communication (39) was submitted on June 29, 1960.), thereby the celebratory color of Woodward's tie. Photograph from the Walter Lwowski Collection at New Mexico State University, courtesy William Maio.

It is worthy to note that *Angewandte Chemie* continues today to be published in its original German-only language edition, simultaneously with its English-language edition. That in 1962, the publisher of *Angewandte Chemie* decided to publish a second edition in English while the publisher of *Tetrahedron* (1957) and *Tetrahedron Letters* (in 1959) decided to publish multi-lingual journals are early steps in the trend toward globalization of communication within the chemical community. In a 2011 editorial celebrating the 50th anniversary of the publication of the English edition of *Angewandte Chemie*, the long-term Editor-in-Chief of this journal Peter Gölitz wrote (40)

A half-century ago, only a handful of contributions in *Angewandte Chemie* came from authors outside of German-speaking countries, and it was certainly a courageous step for the Editor-in-Chief at the time, Wilhelm Foerst, and his successor Helmut Grünewald, to start an English edition ... It hasn't been passed down whether they had the undivided support of the Editorial Board, which in 1961 was made up of Richard Kuhn, Otto Bayer, Wilhelm Klemm, Klaus Schäfer, and Karl Winnacker. But today's readers and authors, and of course also the editors, the publisher, and the GDCh [Gesellschaft Deutscher Chemiker], are most grateful to these pioneers for an internationalization of the chemical sciences.

Returning to Woodward and La Marseillaise, the eminent chemist and close friend of Woodward's, Duilio Arigoni wrote that, reading a draft of this manuscript (41)

reminded me that in September 1970, Bob and I (with my wife Carla) were participating in a meeting at St. Gervais organized by some French colleagues. On the occasion of a dinner party, Bob and I were challenged to address the audience in a duet. The choice of La Marseillaise was immediately obvious to the two of us, and the result has been immortalized visually (if not vocally) in several photographs. [See Figure 13.] The top of the party, however, was reached at midnight, when Bob defied Carla to take a midnight swim with him in the hotel pool. Carla, with her poker face, accepted right away, and I leave the hilarious consequences to your imagination.



Figure 13. Duilio Arigoni (left) and Woodward, singing La Marseillaise as a spontaneous duet as after-dinner entertainment, responding to a "challeng[e] to address the audience in a duet." The lady in the background is Irène Felkin, wife of Hugh Felkin. St. Gervais, France, September 1970. Photograph courtesy Duilio Arigoni.

Woodward's modification of La Marseillaise relies on the use of homophones and heterographs to produce altered text that retains the original sound and flavor but introduces meaningful new wording that is (falsely) related to the original. (For definitions of these terms, see footnote b in Table 4.) Such imaginative use of language is reminiscent of homophonic translation, which is another type of clever linguistic manipulation. In homophonic translation, text in one language is "translated" into another in such a manner that the translation, when read in the new language, reproduces (with a touch of foreign accent) the sounds of the text in the original language. Most such "translations" are, in fact, not translations and are nonsensical in the new language. An ingenious example of such homophonic translations is Mots d'Heures: Gousses, Rames: The d'Antin Manuscript (Mother Goose's Rhymes), English-to-French "translations" of English-language nursery rhymes, published in 1967 by Luis d'Antin van Rooten (42).

Woodward's Election as a Foreign Associate of the Académie des Sciences of the Institut de France

In early May 1978, Woodward received a handwritten letter from the eminent organic chemist Maurice-Marie Janot, then in the 74th and last year of his life. Janot wrote in French (43)

An hour ago you were elected foreign associate of the Académie des Sciences (founded December 22, 1666) of the Institut de France, that is to say, the highest distinction our country can bestow on a foreign scientist. By virtue of a proposal by Henri Normant, Marc Julia, Alain Horeau, and myself, you have just been elected with a so-called 'Maréchal,' that is, by unanimity. I congratulate you and am very happy for this result.

Woodward's response, dated June 2, 1978, to Janot, appears in Figure 14. In Woodward's elegant use of language—in English—he expresses his delight and joyfulness and even his inability to "find the words to express adequately my pleasure, and my appreciation". He further comments on his "admiration for the great traditions of French science". Lastly, and most relevant to the topic of this paper, Woodward says (44)

Forgive me that my capacity in your exquisite language does not extend to the expression of emotions as strong as those engendered by your news.

Woodward loved languages and, as we see in the examples above, he had an intimate knowledge of French. However, according to Elkan Blout, Woodward's close friend, eminent scientist, member of the U.S. National Academy of Sciences, recipient of the U.S. National Medal of Science, and biographer (See Ref. 38 (Blout).), Woodward apparently "was unwilling to speak [French] because he felt he was not perfect in [its] use" (45).

Woodward's policy not to speak French may well have implied to others—incorrectly, as it turns out—that he had little ability with that language. His statement to Janot to that effect was an understatement.

Marc Julia's congratulatory note said, in part, "We realize that it is only one line in the long list of honours that have been conferred upon you" (46). Woodward responded (47)

You are far too modest on behalf of France in your surmise that for me this distinction might count as only one of many honours. Very much to the contrary! My respect and admiration for the great traditions of French science is unalloyed, and that being the case, I can only regard this election as a most especial and singular honour, which will forever have a special place in the warmest recesses of my heart.

These communications further demonstrate Woodward's high regard for the French language and French science as well as his reluctance to use the French language—in these instances, in writing, where he could have expended various resources to assure himself of perfection.

Communications in the Chemical Community 1975-1985. The French Concerns

On September 22, 1981, Mr. Jean-Pierre Chevènement, French Minister for Research and Technology, emphasized the importance of the use of the French language. He suggested that (48)

- —researchers use French in meetings in France or in the French-speaking countries
- -they publish their work in French or at least in bilingual form
- conferences be provided equipment for simultaneous translation.

Shortly thereafter, on November 2nd, 1981, at a colloquium on "The Future of the French Language" in Montreal, Canada, Chevènement discussed several aspects of this issue, including (49)

- —the danger of disappearance of French from the language of science;
- —the responsibilities of scientists; and
- —the need for energetic policies to promote French as a language of science.

Chevenement also addressed more specifically some of the desirable measures in this domain, e.g.:

- —improvement of the quality and distribution of French-language scientific journals;
- —advancement and evaluation of researchers as a function of the imperative of the promotion of the French language;
- -efforts to promote translation; and
- —creation of a veritable francophone domain for science and technology.

In November 1982, the Académie published a report

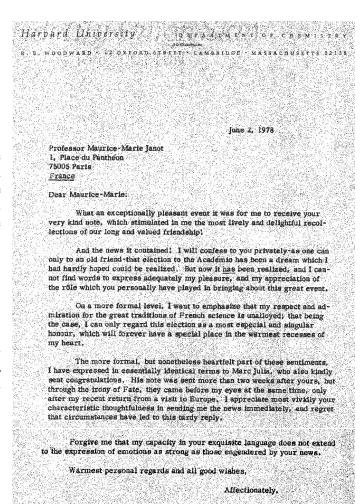


Figure 14. Woodward's letter of June 2, 1978, thanking M.-M. Janot for his note of congratulations on his election to the French Academy (44).

(50) on the matter of the emerging dominance of the English language and the diminishing use of French in scientific communication. An English translation of this report by one of us (JG) can be found in the Supplemental Material of the *Bulletin* and is available open-access with the gracious permission of the French Académie des Sciences. The report was the result of a "reflection" on and an examination of the issue by the Académie and was introduced by the statement

... given the national importance of what is at stake and the imminence of the decisions being prepared, the Académie decided to carry out a reflection on the subject and to publish its conclusions

The report contained an extensive scrutiny of the matter and included concrete proposals for potential remedies considered necessary for the safeguard of the French language. Excerpts on particularly important issues follow (50).

Our science needs to be examined, critiqued, and tested abroad; it must be compared to findings obtained elsewhere that are sometimes contradictory, sometimes complementary. Without such regular comparison, confrontation, testing, and without the international collaborations resulting from them, our science would become isolated and narrow and would at times lose its way, and, in the end, would decline, sooner or later. National independence, which we cherish, is neither possible nor desirable in the domain of pure science ...

The reasons for the decline of French in favor of English as a scientific language have often been pondered. The complexity and rigidity of French grammar and historical evolution have been cited. The principal reason, which deserves emphasis here, is the very high quality of scientific research in the English-speaking countries during the last decades. By contrast, it is observed, for example, that owing to the eminent position occupied by the French school of mathematics, there are still many mathematicians around the world who make use of French and are often even able to express themselves in French ...

All those who care about the future of our language, and in particular all the members and corresponding members of our Academy, are today greatly concerned about a triple threat that weighs at this moment on the destiny of the French language ... the influence exerted by all that comes to us from the US due to its scientific, industrial, and commercial power, to be sure, but also because of its cultural vitality ... the incapacity shown by our people to preserve its language in its traditional purity and accuracy ... with the development of distance-broadcasting, every French-speaking person, not only in France but also in Africa, will be able to receive directly in English an extraordinary collection of information, cultural riches, and entertainment ...

The proposals that will be made concern only the dissemination of French science and its connections to the influence of French culture and thereby the influence of the French language ...

- (a) USING ALL THE ASSETS OF FRENCH SCIENCE IN SUPPORT OF THE INFLUENCE OF FRENCH CULTURE AND LANGUAGE
- (b) DEVELOPING EXPRESSIONS OF FRENCH SCIENCE AND TECHNOLOGY IN THE SERVICE OF SCIENTIFIC TRAINING AND INFORMATION IN THE FRANCOPHONE COUNTRIES
- (c) ASSURING THE FRENCH PRESENCE IN HIGHLY SPECIALIZED SCIENTIFIC MEETINGS AND PUBLICATIONS. [emphasis in the original]

In 1983, Lehn—still four years prior to his receipt of the Nobel Prize in chemistry but nearly 20 years from being a postdoctoral student of Woodward's—participated in a colloquium entitled "Should the National Languages be Saved? The Role of Translation and Interpretation." The proceedings of the colloquium were published with the help of the High Committee of the French Language. Lehn's contribution was entitled "Language of Science or Science of Languages, The Point of View of a User." Highlights of Lehn's philosophical essay include (51):

Letters, words, symbols, structural representations, formulas, equations, the vocabulary, the grammar, and the syntax of chemistry are universal. With [the languages of] numbers, musical notes, alphabets, and gestures, the chemical language is a fifth language. In fact, it functions both as a system of signs [implied by the word "langue" in the original] and as expression of thoughts [from the word "langage" in the original] ...

The question therefore remains: which language to use in written and spoken science? I would answer: not a single language, but that which is understood by the majority of the audience, on condition to be sure that one is able to use it appropriately. Because it is above all a matter of communicating. The first obligation of the language is to serve the dissemination of science; it is not the role of science to defend the language ...

[The most] effective way to defend and spread a language and a culture of a country in parallel with its science is through collaboration programs and international exchanges. My experience with the fifty or so researchers who trained in my laboratory has convinced me that encouraging international exchanges is without a doubt one of the most effective ways to publicize the activities of French laboratories, to promote the French language and culture, to establish personal or professional relationships that will further amplify the effects of the exchanges. French scientific renown is due first of all to the research carried out in France ... The best method for a scientist to participate in the defense and display of his language and culture is to do the best science possible and to communicate it to the largest audience, regardless of languages or cultures

Lehn then provided eight recommendations to foster and improve the progress in chemistry, the ambiance within the chemical community, and the interactions between scientists and the broader population (51). An English translation of this publication by one of us (JG) can be found in the Supplemental Material of the *Bulletin*.

Communications in the Chemical Community: Current Status

In Europe and in Asia, over the past 20 years, numerous chemical journals once published in their national language have merged into multi-national single-disciplinary journals *published in English*. Such prestigious journals as *Liebigs Annalen*, *Chemische Berichte*, and *Bulletin de la Société Chimique de France* have been folded into these new international journals. As shown in Table 2, recent years have also witnessed the formation of new multi-national single-subdisciplinary journals *published in English*.

This evolution of journals is a remarkable transformation with much consequence to all the stakeholders: the publishers, professional societies, funding agencies, users (authors, reviewers, and readers), institutional subscribers, and individual subscribers. The driving force in the formation of these new international journals surely was for maximum inclusivity, rapid distribution of research results, and financial stability for the publishers—issues that have been faced by publishers of scientific journals for several centuries. The forces that have melded this transformation have been highly interactive and flexible, both responding to the stimuli and being the stimuli.

We conclude: There is no denying the trend today to English as the international language of chemistry. But who can tell of the future?

We also note that not all diversity has been lost! The venerable *Angewandte Chemie* continues to be published in German along with its English version *Angewandte Chemie International Edition*.

The concern of substituting English, or any language, for French in the scientific literature has, to some limited extent, persisted, somewhat continuously if sporadically, to this day (15, 52). We shall cite just several examples. In 1994, the Toubon Law was passed in France, mandating the use of the French language in many venues. For example, it said in Article 11 (53),

The language of instruction, examinations and competitive examinations, as well as theses and dissertations in State and private educational institutions shall be in French

In 2002, Gingras published a lengthy discussion that illustrates the continuing depth of the feelings in this matter (54). His article summarized the Garfield "provocation" (16), the French reaction, and the evolution of the

situation over the previous three or more decades. More recently, in 2013, there has been an eruption in France regarding these very issues. In May and June of 2013, the following headlines appeared:

From *The Guardian*, May 10, 2013 (55):

French academy in war of words over a plan to teach in English"

The global spread of the English language has long been a sore point in Paris politics ... teaching and lecturing in a foreign language at French universities has been banned by law, except in the case of language courses or visiting professors

From U.S. National Public Radio, June 14, 2013 (56):

War of Words: France Debates Teaching Courses in English

Will teaching in English at France's universities undermine the French language? That's up for debate in the country now, and the argument is heated.

From The New York Times, June 14, 2013 (57):

Bid in France to Add Courses in English Raises Fear for Language

The reaction was loud, swift and fierce this week to a proposed law that would require French universities to teach more of their courses in English, a measure that a well-known scholar had called a "suicidal project" that would lead to France's sacrificing its language to "Americanization disguised as globalization."

Nonetheless, the trend toward English as the universal language of science continues. As shown in Figure 15, ChemPubSoc Europe published the first issue in February 2012 of an English-only, open-access journal (58). On the other side of the coin, a very serious and not solely academic discussion on these matters continues throughout the academic literature (59) as well as in the popular press. Dahl concluded that "national culture will be more important [governing the pattern of metatext in economics and linguistics] than in medicine" and likely than in the physical sciences including chemistry "where the IMRD (Introduction-Method-Results-Discussion) structure is globally implemented and the research data to a greater extent are given outside the text" (60). In 2001, Ammon published a book on the effect of English dominance as the language of science on other languages and language communities (61). Indeed, criticism has recently been leveled against Germany's highly regarded Duden dictionary "for contributing to the decline of German by importing too many English words" (62).



Figure 15. A black and white version of the front cover of the first issue of the journal ChemistryOpen, published by ChemPubSoc Europe. This is an entirely English-language, open-access journal first published in February 2012 (58).

Conclusions

This paper encompasses both the serious and the ingeniously clever.

For serious: in 1965 the Académie wrote to the President of the French Republic "express[ing] its wish for a firm intervention by the [French] state to assure from now on the respect of the French language in the scientific domain." President Charles de Gaulle and Prime Minister Georges Pompidou responded affirmatively. In the 1980s, additional serious discussions and considerations regarding safeguarding the French language in scientific communications were made by the Académie and by the French Minister for Research and Technology. In 1994, French law (the "Toubon Law") banned the teaching and lecturing in a foreign language at French-government financed schools (53).

For ingeniously clever: R. B. Woodward's letter to Jean-Marie Lehn and "Woodward's La Marseillaise."

Thus, this paper reveals the interplay between the very public French national trauma about the possible loss of language on the one hand and Woodward's private

play with language in the context of a scientific debate on the other hand. From the words of Woodward, the French Académie, and the French government, there is a clear display of a private/public-simultaneous match and contrast.

Nearly 50 years after the English-French language-of-chemistry debate became acute, English has in fact become the dominant means of scientific communication as judged by the rise in number and strength of English-only international chemical journals. Despite this fact, the concern about the decreasing use of certain national languages continues—at least in France—as is well documented in recent media headlines. Will instruction in English in French universities, especially in disciplines like science—continue to be against French law?

The past 50 years is just a slice in the continuing evolution of communication within self-selected scientific communities, one being the chemical communities throughout the world. In our view, the net effect of these transitions has been more positive than negative—in the dissemination of knowledge, in the internationalism of science, in shared cultural experiences, and in economic terms. Indeed, today some in France are accepting this trend and proposing that teaching at French universities can be in English when appropriate for the subject, e.g., in chemistry. The serious and mindful efforts by the most influential among us to make readily available the research results of all within our community deserve praise as does the understanding and flexibility of those who place country-pride at high priority.

The evolution in the communication within the chemical community continues. Not only has the journals' choice of language changed over the decades but the very nature of chemical publication has changed. Several journals—and Chemical Abstracts—publish only electronic editions and in many others, subscription trends have moved away from paper and to "virtual" media. The manner of browsing, reading, searching and managing the chemical literature has certainly changed. New online-only, open-access journals have made their presence felt, especially with the increased number of journals and the number of pages published each year. Surely the matter of open-access publications has risen to a very high level of concern among publishers, learned societies, governmental funding agencies, organizational subscribers and individual scientists. The inclusivity and effectiveness of communication within the scientific community is central to the progress of science and to the pleasure of those doing science. The controversy about language was once a localized phenomenon; today, open

communication is more than a goal, it is a necessity. It is interesting to consider what the scientific literature will look like and how it will be accessed in another 50 years.

In this paper, we have focused primarily on events in the 1965-1985 time period. We discussed the founding and role of the first international chemical journals, Tetrahedron and Tetrahedron Letters. We did point out that in the 19th Century, Russian chemists published their research in the French and German languages in the Russian journal Bulletin scientifique publié par l'Académie Impériale des Sciences de Saint-Pétersbourg. In the 20th Century, the journal Russian Chemical Reviews was also published in English. Evidently, Russian chemists for several centuries wanted their research to be read by non-Russian reading scientists. To the extent that there were still "national" components to these journals and that chemistry was not truly a worldwide enterprise, the descriptor "international" rather than "global" was and is more accurate.

It is clear that the desire to have one's research read and valued is a powerful motivating force to communicate in whatever language will best serve that purpose,

over and above one's language-patriotism (63). Furthermore, financial imperatives have begun to squeeze national chemical societies and forced them to merge their journals into new, international journals.

Indeed, for many of the reasons and conclusions discussed herein, in a book published after the acceptance of this paper for publication, Scott L. Montgomery concludes, "yes" to the question asked as the title of his book, *Does Science Need a Global Language* (64). Henning Hopf, in the opening paragraph of his review of this book, responded to Montgomery's question (65)

The answer to the title of the book is straightforward: not necessarily, but it would be advantageous. An option is easy to find, as it already exists: namely English.

Robert Buntrock's review of this book (73) concluded that (66)

The trend toward English as the *lingua franca* of science has been very rapid ... The advantages ... include education and collaboration in research on an international basis.

According to a recent report, at the 94th Annual Meeting of the Chemical Society of Japan (CSJ) in March 2014 (67)

Although most of the events and presentations were in Japanese, there was an international program in-

cluded in the symposium and—for the first time—a 36 page guide for all presentations was provided in English. The CSJ discussed if the official language should be changed to English from 2015.

Lastly, it is obvious but worth saying: all of these changes affect people, the chemists themselves; and these changes affect national education, culture, and economics. Almost 50 years ago, the quite remarkable R. B. Woodward considered these matters and exercised his brain in a poetic yet fun fashion. In this instance, Woodward actualized his abilities to meld wit with seriousness, thereby inherently bridging the language barrier and the human tensions of the situation. Woodward's high-level use of French, his plays on words, and his knowledge of the nuances of French vocabulary and French history are stunning in their sophistication, originality, and ingenious cleverness.

May there always be celebration of the languages of the world. We note that the degree of appreciation of the wonders of "Woodward's La Marseillaise" is related to one's fluency in French. Nonetheless, all of us can understand the cleverness of Woodward's design as well as—in the broader sense—appreciate the tensions between protectionism and worldwide community, empathize with the intensity of the issues, and value the humor and intellectualism which is part of the human experience.

Acknowledgements

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Supplemental Material

English translations of the Rapport de l'Académie des Sciences sur la langue française et le rayonnement de la science française (Report by the Academy of Sciences on the French Language and the Influence of French Science) (50) and of Jean-Marie Lehn's paper "Langue de la science et science des langues: Multilinguisme ou langue unique? Le point de vue d'un utilisateur," ("The Language of Science and Science of Languages: Multilingualism or Single Language? The Point of View of a User") (51) can be found in the Supplemental Material for the Bulletin for the History of Chemistry at the journal's website,

www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

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Joseph Gal has long been interested in the history of French chemistry and the language of chemistry, and has published a number of articles on these topics. Jeffrey Seeman was Chair of HIST in 2005-2006. He has long been interested in Woodward as a chemist and a person.

BOOK REVIEWS

The Secrets of Alchemy, Lawrence M. Principe, University of Chicago Press, London and Chicago, 2013, vi+281 pp, ISBN 978-0-226-68295-2, \$25.

In his new survey of the history of alchemy, Lawrence Principe begins with the seemingly simple question, "what is alchemy?" Of course, the answer is not simple at all. As he states, Principe composed The Secrets of Alchemy, in part, because of the popular resurgence of interest in alchemy driven by fictional literature, television, and film. However, non-specialists who wish to dig deeper into the history of the field are often confronted by a labyrinth of contradictory sources composed by popular writers, occultists, and enthusiasts, who rely on cliché and gross historical misinterpretations. Concomitant with the growing popular interest, a scholarly resurgence of interest in alchemy, propelled by Principe and other historians, such as William Newman, Betty Jo Dobbs, Allen Debus, Bruce Moran and Pamela Smith, has overturned many of the common claims about alchemy found in popular sources. This revisionist work has recast medieval and early modern alchemy from an obtuse, obscurantist pseudo-science (which, in some interpretations, did not even attempt to study matter, but rather the psychological states of the alchemist) to a rational, experimentallybased form of natural philosophy aimed at producing and improving substances as well as understanding the principles behind these transformations. Principe's book offers the first synthetic view of this recent scholarly work and, strikingly, is the first such introductory survey of alchemy by a historian for almost sixty years.

The Secrets of Alchemy maps the history of the practices, theories, and cultural meanings of alchemy

from its ancient Egyptian origins through its almost two thousand year history. The book discusses the three traditional chronological/cultural periods of alchemy—the ancient Greco-Egyptian, the medieval Arabic, and the late medieval and early modern European. To these, he adds a fourth period spanning from the eighteenth century to the present, which focuses on revivals and reinterpretations of earlier alchemy.

Principe points out that he cannot discuss every alchemist and text in a book of this sort, so he focuses on main themes and a few key persons in each chapter to discuss in detail. Thus, he devotes a large section of Chapter 1 on Greco-Egyptian alchemy to Zosimus of Panopolis; Chapter 2 on Arabic alchemy focuses on Jābir ibn-Hayyān and the Jābirian Corpus; while Chapter 3 (the most diverse chapter) on medieval Latin alchemy examines the Summa Perfectionis, John of Rupecissa, the Lullian Corpus, and the development of *florilegia* and early alchemical emblems. In the final three chapters of the book (5-7), Principe discusses the "golden age" of alchemy of the 16th and 17th centuries. Here, he examines topics at the core of his own research and attempts to recreate the practical and conceptual world of the early modern alchemist. For example, in Chapter 5 he describes how one might have gone about making the Philosophers' Stone: deciphering a recipe from the various available texts, developing a theory of how it worked, collecting evidence that it worked, and then undertaking the work itself. In addition to making the Stone, Principe also reveals the wide breadth of alchemical projects, including the transmutation of metals via means other than the Stone, the making of alchemical medicines, the artificial generation of living things, palingenesis (the creation of a ghostly image from the ashes of a living thing), and the creation of the alkahest (universal solvent).

In effect, The Secrets of Alchemy presents a new model for the history of alchemy and establishes an interpretive framework, which explains and absorbs previous, competing depictions of alchemists and their activities. Building upon earlier work, in which he collaborated with William Newman, Principe shows that the image of alchemy as an occult art, psychological exercise, or irrational pseudo-science is largely the construction of 18th century and later reinterpretations of medieval and early modern alchemy (i.e., the work of the fourth period). In his book, he endeavors to peel away these later interpretations and place pre-modern alchemy within its proper historical context. To this end, he adroitly illustrates how changing ideas in and about alchemy and, notably, controversial practices, such as the emphasis on secrecy and use of allegorical language, were shaped by their contemporary philosophical, religious, literary, and political cultures. By taking this approach, Principe demonstrates the rationality of alchemical practices when interpreted according to culture and aims of alchemists themselves.

By historicizing modern psychological or occultist interpretations in the same way, Principe effectively subverts these approaches as viable models for understanding pre-nineteenth century alchemy. He effectively outlines the historical genesis of these approaches in Chapter 4. In the early 18th century, chemists at institutions, such as the académie royale des sciences, began to denounce the politically-problematic parts of their art, like the transmutation of metals, as fraudulent in order to improve their status among their peers and with their patrons. Although some chemists, including a few at the académie, continued to experiment with transmutation in secret, by the end of the 18th century, many authors lumped alchemy in with other "superstitious" beliefs, like magic and witchcraft. However, alchemy enjoyed a revival and reinterpretation in the hands and minds of Victorian occultists. In 1850 Mary Ann Atwood, a practitioner of Mesmeric healing and, later, Theosophy, first suggested that the true aim of alchemy was the spiritual perfection of the alchemist and not the pursuit of laboratory operations. This became a common interpretation among students of the occult and later, new age practitioners. Shaped by this view, the Swiss psychoanalyst, Carl Gustav Jung (1875-1961) argued that while some alchemists did perform experiments, the primary aim was the transformation of the psyche, and as such, the materials used in laboratory operations were of little concern; alchemical texts and emblems encoded "psychic" processes rather than chemical ones. Jung's interpretation of alchemy proved to be remarkably resilient, was adopted and expanded by a host of social scientists and other scholars, and shaped the popular perceptions of alchemy during the twentieth century.

A key difference, which distinguishes Principe's history of alchemy from the Jungian or occultist views, hinges on how one interprets alchemical texts. Secrecy was a central trope of alchemical writings, and alchemists obscured the meaning of their texts through the use of allegorical language, decknamen (false names), and techniques of dispersion (placing different parts of a process in different places in a text). Principe points out, however, that not all alchemical texts were written in this manner. For example, the very influential, 12th century Summa Perfectionis, composed by the Italian monk, Paul of Taranto, writing under the pseudonym, "Geber," was intended as a scholastic summation of alchemical knowledge and, as such, presented its material in a clear and orderly fashion. For those authors who utilized techniques of concealment, Principe argues that their allegorical language and decknamen encoded recipes, the identity of materials, and other theoretical and practical clues needed to undertake chemical processes. Thus, these texts were meant to be decoded by readers who could decipher their imagery and possessed enough practical knowledge of chemical operations and materials to interpret the clues correctly. As Principe asserts, these texts "not only ... conceal their knowledge, but also ... reveal it in a measured way" to those who had the talent and time to decipher them (152-3). Thus, the alchemist at work is both a scholar and chemical practitioner, one who by studying the texts deciphers recipes and processes, which he then tests experimentally in the laboratory.

Principe supports this interpretation of practical alchemy by discussing his own experimental work in replicating the processes encoded in several prominent alchemical texts. In Chapter 6 he discusses his work on the first three processes encoded in Basil Valentine's "twelve keys" (c. 1599), an allegorical presentation of a stepwise processes to make the Philosophers' Stone. He describes successful efforts to decipher the processes encoded in the texts (which, in later editions, also included emblems based on the texts) and, then, to test those processes in the laboratory. Similarly, he describes his efforts to create the "Philosopher's Tree" (a crystalline structure formed from an amalgam of gold and "philosophical" mercury) as described in Eirenaeus Philalethes' *Open Entrance to the Closed Palace of the King* (1667). As a result of these

trials, Principe argues that one cannot simply discount these texts out of hand, even if the deciphered recipes seem odd from the perspective of modern chemistry. Take, for example, Valentine's third key, which coded a process to make "volatile" gold, a substance that Valentine described as "the rose of our masters ... and the red dragon's blood." Principe's deciphered recipe called for dissolving a quantity of gold in acid, which was then distilled off and used again to re-dissolve the gold dregs. This process, called cohobation by 17th century chemists, was repeated over and over. As Principe points out, this process seems pointless at first, but after several cycles, ruby red crystals of gold chloride, which is normally unstable, begin to form in the distillation apparatus due to a buildup of chlorine gas (149-52).

Overall, this is an excellent introduction to the history of alchemy that corrects popular misconceptions,

makes the case for the current scholarly interpretations of the field, and also gives glimpses into the kind of contextualized work that historians of chemistry do. Principe's book provides solid and accessible ground for the novice, who seeks to navigate the labyrinthine literature on alchemy, but I must confess, it also provides a useful framework for scholars as well. As such, Principe aims for both audiences. He clearly explains technical terms and presents English translations for all titles and texts discussed, but also references all original source material in thorough footnotes and an excellent bibliography. Thus, I recommend this book for anyone with an interest in the history of alchemy or chemistry before 1800, tyro or adept.

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Dictionnaire de chimie: Une approche étymologique et historique, P. de Menten, De Boeck, Brussels, 2013, 395 pp, ISBN 978-2-8041-8175-8, \$45.88.

The reason for bringing this new foreign language chemical dictionary to the attention of historians of chemistry lies in its subtitle, since its author, Pierre de Menten, not only provides the usual definition of each chemical term but also attempts to trace both its linguistic etymology and, more importantly for historians of chemistry, the approximate date of its first appearance in the chemical literature. I can testify to the author's familiarity with early European chemical literature as I often corresponded with him concerning my bimonthly column "Ask the Historian" in the *Journal of Chemical Education*, and for which he would often provide highly relevant references I had overlooked.

The dictionary is richly illustrated with period woodcuts and historical diagrams, and also contains ap-

pendices devoted to synoptic historical charts and a list of chemical synonyms for the various entries. Though the formal entries themselves deal strictly with chemical terminology and apparatus and not with individual chemists, there is also an extensive index cross-referencing the names of important chemists with the various entries in which they are mentioned in passing.

About the only drawback to this ambitious project is the fact that de Menten's extensive historical footnotes, presumably referencing the various papers and books in which the terms are first used, are not included in the book itself but rather must be accessed via a supplementary website.

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Alexander Borodin: Composer, Scientist, Educator. A Biography. William Vijvers. Digital Printing Partners, Houten, Netherlands, 2013, 365 pp, ISBN 9789081226905.

The book is the result of long-term researches of the author dedicated to professional and personal life of Alexander Borodin (1833-1887), prominent Russian scientist and man of art of the second part of the 19th century. Thanks to researches in the field of organic and physiological chemistry conducted by Borodin in the period from 1858 to 1886 he became widely known both in Russia and abroad already during his lifetime. But in due course his musical fame as a composer outshone the activities of Borodin, scientist. The name of Borodin is met in many concert programs all over the world up to now.

Vijvers's research is developed on the basis of the published but not always readily accessible sources as well as considerable use of Borodin's letters published by Sergey Dianin in four volumes during the period 1927-1950 (The Letters of A. P. Borodin, in Russian). Wide quoting of personal correspondence not only substantiates the selection and angle of the factual material's presentation in the book but adds to it bright lively accents allowing reconstruction of the narration's character in more details. Simultaneously, detailed study of all biographical materials ever published about Borodin enabled the author not only to provide their comparative evaluation but also to make a critical revision of some information about this scientist given in several famous publications. In this respect, the heritage of Russian historians of science and art has been considerably reconsidered.

In the introductory note to this edition the author points out that music and science were intertwined in Borodin's life. Thus the book, consisting of 25 chapters, is built up in chronological order in correspondence with the professional and personal life of Alexander Borodin. The material related to his scientific activity and musical creative work is presented in chapters simultaneously: they show the longstanding tossing of the scientist between two of his life's hypostases. Three appendices and the list of quoted literature are added to the book. Appendix 1 contains information on musical works of Borodin, which includes description of two most prominent works: opera-farce "Bogatyri" ("The Athletes") and "Prince Igor" (based on the Russian epic "The Tale of Igor's Campaign") as well as his symphonic music. Appendix 2 provides an exhaustively reconciled list of scientific publications of Borodin, scientist. In particular, publications of the Soviet period did not provide a complete list.

Appendix 3 discusses different aspects of works about Borodin published before 2010, including their strengths and weaknesses. The author notes that the majority of published works "are one-sided:" they mainly reflect activity of Borodin as composer or "as an example of the unquestionable superiority of Russian art and science." In this respect, from my point of view, the main advantages of this book are exactly the well-balanced selection of the material touching upon both scientific and musical productivity of Borodin, the author's thoughtful and prudent analysis, and the attraction of a wide range of sources.

As is shown in Vijvers's work, the attention of the scientific community was primarily attracted by works of Borodin in the area of aldehydes, namely development of the general method of aldehyde condensation in the presence of sodium and potassium metal, analysis of the composition of products received on its basis, and discovery of the aldol reaction independently from Charles-Adolphe Wurtz. For the first time the book considers the genesis and detailed results of pioneer researches of the scientist in the area of fluorination of organic compounds, including material from his Italian publication dated 1862. As it turns out, some of Borodin's developments were applied in practice up to the mid of 20th century, for example, the analytical method (as well as the device) for determination of urea in the animal body (1876).

The main component of Borodin's activity was practical classes in chemistry arranged by him for students including their scientific researches within the framework of the Medical-Surgical Academy where he was a professor. The scientist regularly reported about results of his students' works at meetings of the Russian Physical-Chemical Society, promoting in such manner their further research activity. A separate chapter also illustrates Borodin's contribution in development of female education in Russia, his participation in arranging and teaching scientific courses for midwives at the Medical-Surgical Academy.

In spite of his serious attitude to composing, Borodin defined it as "a favorite leisure activity." This relationship with composing determined specific features of his creative development in music. His first symphony (in E flat major, completed in 1867) opened new horizons for Borodin, composer, having won his fame in Western Europe. In the circle of colleagues he took a special, independent position. Undoubtedly Borodin "has earned a

place among the "immortals," considers the author when evaluating his musical heritage.

Vijvers's book offers to readers a fascinating opportunity to plunge into the epoch of the social rise of Russia in the 1860s and post-reform time. On the one hand, one can become familiar with Borodin, liberal, who had become famous as a progressive social reformer

and outstanding pedagogue of female education. On the other hand, one can understand and accept new arguments in evaluation of his actual contributions to the development of chemistry and of new musical forms and musical language.

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Organic Chemistry Principles in Context: A Story Telling Historical Approach, Mark M. Green, New York, Science from Away, 2012, 452 pp, ISBN 978-0-615-70271-1, \$25.

In writing this textbook, Mark Green has completely overturned the accepted organization that has dominated organic chemistry textbooks for decades, rejecting the organization by functional group in favor of a contextualized, story-telling approach. Nearly all the basic information contained in traditional textbooks is present, but readers familiar with organic chemistry will need to immerse themselves in the book to find them, since Green has presented each one in a way that highlights a particular real-world chemical context in which it becomes relevant. The goal is to make organic chemistry less dry and more relevant to its everyday applications in polymers and biological systems. Every chapter mentions prominent chemists who were involved in some way with the chemical concepts discussed, and there are numerous portraits, several of which I had not seen before. Each chapter has problems for students, and there is a companion website with solutions to the problems and videos of Green lecturing on the material. In contrast to traditional textbooks, there are substantial amounts of unbroken narrative text and the chapters do not contain an overwhelming number of chemical reactions listed one after the other. This book appears to be self-published, and is clearly a labor of love, created after years of using this material in the classroom. Concepts are extensively cross-referenced by chapter and section.

The material is divided into twelve chapters that use either an industrial or biological example of organic chemistry. The first chapter uses the polymers of glucose-cellulose and starch-to illustrate principles of hybridization, stereochemistry and structure. Chapter two outlines mass spectrometry and IR and NMR spectroscopy. Chapter three uses galactosemia to introduce the conformational isomerism of six-membered rings, and carbocations are introduced in chapter four using the example zeolite catalysis of petroleum to increase octane levels of gasoline. Chapter five continues discussion of carbocations, using the biological synthesis of terpenes and lanosterol. The history of benzene and aromatic chemistry form chapter six, and carbonyl chemistry is treated in chapters seven and eight, using the metabolism of fatty acids and sugars. Acyl substitution and free radical reactions are introduced in the context of forming polyesters, nylon, polypropylene and low density polyethylene. Chapter ten begins with the industrial production of adipic acid and hexanediamine to explore kinetic and thermodynamic control of reactions, nucleophilic substitutions, and biological and non-biological reducing agents. Chapter eleven returns to polymer chemistry and elastomers, specifically the molecular structure of natural rubber and the synthesis of polycarbonates and spandex. The book concludes with a lengthy chapter on organic synthesis with two examples. Green first treats the highlights of R. B. Woodward's 1952 total synthesis of cholesterol, along the way explaining the Diels-Alder and Grignard reactions and more carbonyl chemistry. The second example is E. J. Corey's 1969 total synthesis

of prostaglandin $F_{2\alpha}$ that illustrates the Wittig reaction, hydroboration, and the use of protecting groups. Both examples are classic syntheses, and employ relatively simple chemical transformations that illustrate concepts of stereocontrol, functional group transformations, and synthetic planning.

Green's approach has a lot of potential, but I after examining this book, I came away with mixed feelings about it. I learned a great deal from the examples, and the radically different way of organizing the material certainly provides inspiration for different ways of teaching organic chemistry. Yet there are many disadvantages to the book as it is written. There are many convoluted sentences that are hard to follow. More often than not, those sentences are trying to pack in too much information on key concepts, and much of the presentation could be expanded to clarify the material for readers who have no knowledge of the subject. The text could use a good copy editor.

I admire Green's use of personalities throughout the text, but what is there is anecdotal and triumphalist, emphasizing who was right first, with little indication of contingency, disputes over methodology and ideas, or cultural and institutional influences on chemists' careers. The general assumption throughout the text is that the first publication of theories resembling our own are unproblematic and were immediately accepted by chemists as correct. Surprisingly, while discussing several of the historical examples, most notably Woodward's and Corey's syntheses, Green neglects even to mention a year in which they took place. There is more information about chemists than in a traditional textbook, but what is there is little more than expanded versions of the sideboxes found in other texts that are largely unconnected to the chemistry itself.

There are also some errors in the history. It repeats, for example, the myth that Friedrich Wöhler sounded the "death knell" for vitalism when he made urea in 1828. Archibald Couper was "scooped" by August Kekulé about the tetravalence of carbon and the self-linking of carbon atoms (p 33), because Adolphe Wurtz kept Couper from publishing his paper for a year until 1858, three months after Kekulé's paper, by which time Kekulé had "gained all the credit for the tetravalence of carbon." It's unclear where Green found this story, as it is not in the standard historical literature. Kekulé certainly had not gained sole credit for his theory in 1858, when he had

not publicized it, and when most chemists had not yet even accepted it or did not even know about it. Green also claims that Kekulé published his benzene theory in 1865, "sponsored by Wurtz," (p 169) when in 1865, Kekulé had been a professor in Ghent since 1858 and had left Wurtz's laboratory long ago in 1852. Linus Pauling did not win his Nobel Prize for proposing the structure of the alpha helix (p 10), but for his work on the nature of the chemical bond during the 1930s, a fact that is easily checked on the Internet. These fundamental errors are reason enough to suspect others throughout the book. What is perhaps most disappointing for a textbook that aims for historical context, however, is that there is no list of suggested readings or citations for more information about any of the historical information. The strength of Green's approach is therefore not in his use of history, but in his extensive use of specific real-world problems in organic chemistry, from increasing octane levels in gasoline, to understanding why cellulose is different from starch, to how and why chemists plan total syntheses of complex organic molecules.

Putting aside the problems with the presentation of history in the text, is this truly an introductory organic chemistry text, as Green claims? Can it be usefully adopted for a standard sophomore course in organic chemistry? Using this text in isolation would require a very steep learning curve: for example, the very first chemical structures that students encounter in the book are cellulose and starch polymers of glucose, drawn in line-bond formulas in the chair form, with no previous introduction to either structure or the various ways chemists draw structures. Stereoisomerism is introduced before structural isomerism, which seems to be putting the cart before the horse. There is very little on nomenclature, although students would absorb a great deal while working through the text. The chapter on spectroscopy is a good start, but it requires a great deal more explanation and examples of spectra for students to understand it from the text. Adopting this book would likely require instructors to add additional material, use it as a supplement to a more traditional text, or mine it for examples to use in lectures. Although Green has used the book in his own course, my sense is that in its present form, it would not work well at most schools without significant revision and/or expansion.

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UCL Chemistry Department 1828-1974, Alwyn Davies and Peter Garratt, Science Reviews 2000, St. Albans, UK, 2013, 287 pp., ISBN 978-1-900814-46-1, £12 (distributed by the UCL College Shop or its online store, onlinestore.ucl.ac.uk).

Before University College London was founded in 1826 as the University of London, there had been no new Universities in England for over 500 years. In contrast to Oxford and Cambridge, it taught modern technical subjects such as chemistry and had no requirement for affiliation with the established church; it was called "The Godless Institute in Gower Street." Faraday was offered the first Professorship of Chemistry, but he declined. Edward Turner took the post. An honors examination from this period is reproduced. There are 35 questions with the instructions that students may answer as many as they choose, but "the Examiners would prefer short and distinct Answers to a competent number of questions." This kind of detail is characteristic of the entire book.

The department has maintained an extraordinary archive of architectural plans, portraits, drawings, menus, and academic records many of which are reproduced throughout. Turner was succeeded by Thomas Graham, first president of The Chemical Society and famous for his work on diffusion. There are illustrations of his equipment.

Alexander Williamson (the Williamson ether synthesis) was made Professor of Chemistry in 1855. It was in 1863 that the remarkable story of the Japanese connection began. A group of five samurai smuggled themselves out of Edo Japan (at great risk; it was a capital crime to visit a foreign country) in order to study at UCL, the one institution in England that did not discriminate on the basis of race, religion, or nationality. The Williamson family welcomed them. In fact, three lived in the Williamson house. These arrangements continued: in 2004, out of 71 Japanese studying chemistry in Britain, 42 were enrolled at UCL.

William Ramsay, the discoverer of the noble gases, succeeded Williamson. There is a list of 30 of Ramsay's students who subsequently filled Chairs of Chemistry. Three of these were subsequently Nobel prize winners (Hahn, Heyrovsky, and Soddy) while two others became heads of Chemistry at UCL. The list includes Sir Stafford Cripps, who did not go on in chemistry but who was a member of Churchill's war cabinet. Later eminent Professors of Chemistry were Norman Collie, the mountain climber and originator of the polyketide motif in biosynthesis and Frederick Donnan (the Donnan equilibrium).

This brings us to the seventh chapter of the book (which is organized chronologically) and which details the disruptions due to World War II. The entire University has to be moved out of London. The Chemistry department, because of its size, was split in two between Bangor and Aberystwyth in Wales. The story of the dynasty of Sir Christopher Ingold and Edward Hughes begins in Chapter 8. While Ingold is best known for the invention of the terms nucleophile and electrophile and for establishing the mechanisms of SN₁ and SN₂ reactions, it is not generally appreciated in how many other areas he made fundamental discoveries, for example, using infra-red and Raman spectroscopy to establish the centrosymmetry of benzene. There are marvelous stories about the collaboration of Ingold and Hughes. I was struck by the skill with which Ingold staffed his department relying for the most part on his own students. This has the clear advantage of certainty about a candidate's abilities but also requires a judge with broad knowledge of all of chemistry. This Ingold possessed. A partial list of Ingold's choices: C. A. Bunton, K. Lonsdale, P. B. de la Mare, C. A. Vernon, R. S. Nyholm, J. H. Ridd, A. G. Davies, Y. Pocker, P. Pauling, D. V. Banthorpe, F. Sondheimer, T. Thirunamachandran. (See the story about his request for a grant of minus £13). There are many others with illuminating biographical details about all of them.

Nyholm who began his career at UCL in 1950 became head after the death of Hughes in 1963. His Inaugural lecture was titled "The Renaissance of Inorganic Chemistry" which reflects the shift in all research universities away from a purely descriptive view of this branch of chemistry. His tragically short tenure is described in chapter 10. The M.Sc. was the highest degree available in Australia at this time and so the reputation of Nyholm brought an influx of Australian inorganic chemists to UCL as described in chapter 11. There are sketches of the organic and physical staff at UCL in chapter 12 for the final time period of the book. The secretarial and technical staff are not omitted: they are the subject of the following chapter for the same time period. The final two chapters (14 and 15) deal with social matters (pubs and dinners) and with memories of former students. There are useful Appendices and a good index. My only complaint is that the binding is poor.

The authors are both Professors Emeritus of UCL.

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Pioneers of Quantum Chemistry, ACS Symposium Series 1122, E. Thomas Strom and Angela K. Wilson, Eds., Washington, DC, American Chemical Society (distributed by Oxford University Press), 2013, xi+330 pp, ISBN: 978-0-8412-2716-3, \$150 (hardback; e-book also available).

With the development of powerful desktop computers and commercial software packages, sophisticated quantum chemistry calculations have become accessible and relatively simple to perform so it is easy to forget the long struggle that brought us to this point. Thankfully, scholars are turning their attention to documenting the history of quantum chemistry. This collection of articles based on presentations at an ACS symposium held on March 28, 2011, in Anaheim, CA, is a welcome addition to that literature. The articles describe important early developments in quantum chemistry and profile the pioneers in the field and their accomplishments.

The lead article by Klaus Ruedenberg and W. H. Eugen Schwartz is a whirlwind tour of ideas about atoms and molecules from the Greeks to the present. This is followed by a survey of more modern developments. A particularly valuable section of the chapter by Istvan Hargittai is a discussion of the Soviet resonance controversy, an example of politics interfering with science. The remaining chapters mainly focus on the contributions of notable figures in the history of quantum chemistry, some of whom are nearly forgotten.

I found the chapter by E. Thomas Strom, one of the editors of the collection, on George W. Wheland to be particularly interesting. Originally from Chattanooga, Tennessee, where his father ran a foundry, Wheland had a stellar academic career, beginning with a bachelors degree from Dartmouth, a doctorate from Harvard where he worked with James Bryant Conant, and a postdoctoral stint at Caltech with Linus Pauling where he co-authored three seminal papers on resonance theory. He spent the remainder of his career at the University of Chicago where he wrote influential books on the theory of resonance and advanced organic chemistry. Wheland suffered from multiple sclerosis and became unable to function as a faculty member at about age 50 in the early 1960s, cutting short a brilliant career. There are also chapters on other pioneers including Michael J. S. Dewar, H. C. Longuett-Higgins, and John Pople, all members of the so-called British School of Quantum Chemistry. Each provides the personal perspective of the author on the scientist and his contributions.

Quantum chemistry came into its own with the development of the high speed digital computer and the requisite software to perform calculations. Some of those developments are highlighted in chapters entitled, "The Golden Years at LMSS and IBM San Jose," and "Quantum Chemistry Program Exchange, Facilitator of Theoretical and Computational Chemistry in Pre-Internet History." The first of these is a history of two important research groups, the Laboratory of Molecular Structure and Spectra at the University of Chicago presided over by R. S. Mulliken and C. C. J. Roothan, and the ALCHEMY project at IBM San Jose headed by Enrico Clementi, where talented scientists took advantage of developing computer technology to develop programs to carry out high-level (for the time) quantum chemistry calculations. While the San Jose group had access to the latest IBM mainframe computers, before 1960, members of the Chicago group had to fly to Dayton, OH, to use the computer at Wright-Patterson Air Force base. In the early 1960s, they obtained permission to use the IBM 704 computer at Argonne National Laboratory. Eventually, the University of Chicago got its own computer, an IBM 7090. The 7090 was the first transistorized computer and cost several million dollars. Results were checked by hand using electric desk calculators. This chapter reminds the reader that in the early 1960s, the calculation of a square root was not routine. The first electronic desk calculators became available in the late 1960s. Only the most expensive of them could automatically calculate a square root.

The Quantum Chemistry Program Exchange (QCPE) which was housed at Indiana University is a distant memory, but in its heyday it was a repository for the latest in software for computational chemistry. Individual researchers would contribute their source code, usually written in FORTRAN, and for a nominal fee, anyone could obtain a copy to use. Early on, if you wanted a program it would be shipped as boxes of IBM cards. Later, magnetic tape was used. QCPE also organized workshops to introduce researchers to computational methods and published a regular newsletter. QCPE was a remarkable example of scientific cooperation. The programs were all donated by the developers. The whole operation was run on a shoestring from an office or two in Bloomington, but it had an enormous impact. At its zenith, QCPE distributed as many as 2500 programs per year. With the development of commercial packages, such as Gaussian, and the ability to download software quickly from the internet, QCPE became irrelevant and disappeared so it was a pleasure to read this history and remember a gentler time.

Because of the nature of this volume as a collection of articles, it is not a systematic history of quantum chemistry. Such histories are being written, for example, *Neither Physics nor Chemistry: A History of Quantum Chemistry*, by Kostas Gavroglu and Ana Simões (1), but the individual contributions in this book do add to our knowledge of the history of this important area of contemporary science. *Pioneers of Quantum Chemistry* is enriched by a large number of historical photographs: George Wheland in his Baylor Military School uniform, Robert Mulliken working at his messy desk at the LMSS, and Linus Pauling lecturing at Moscow State University

in 1984, for example. Historians of chemistry will certainly want to peruse this book although its rather high price may mean that it will not find its way into a large number of personal libraries.

(1) Kostas Gavroglu and Ana Simões, *Neither Physics nor Chemistry: A History of Quantum Chemistry*, MIT Press, Cambridge, MA, 2012. Reviewed in *Bull*. *Hist. Chem.*, **2012**, *37*, 103.

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A Festival of Chemistry Entertainments, Jack Stocker and Natalie Foster, Eds., ACS Symposium Series 1153, Washington, DC, American Chemical Society (distributed by Oxford University Press), 2013, xiii+118 pp, ISBN: 978-0-8412-2716-3, \$150 (hardback; e-book also available).

If the phrase "chemistry entertainments" strikes you as an oxymoron, then this book is not for you. I suspect, however, that the phrase makes perfect sense to many readers of the *Bulletin*, as well as to readers of the "Newscripts" column of *Chemical and Engineering News*, collectors of chemistry trivia, and aficionados of science-themed songs, verse, and puzzles. The authors and editors of this volume have all shown the capacity to be entertained by chemistry and they endeavor here to entertain other like-minded chemists, chemistry students, and chemistry fans.

The book is based on a symposium organized by Jack Stocker at the 235th National meeting of ACS in New Orleans in April 2008. Stocker was a long-time professor of chemistry at the University of New Orleans and an extraordinary collector of chemistry memorabilia. As an ACS tour speaker, Stocker was willing to travel anywhere to share his collection, which he called "chemage" (a portmanteau of chemistry and garbage). He gathered quite an assembly of raconteurs, collectors, aficionados, and composers of puzzle and verse to share their enthusiasm for the whimsical in chemistry. This volume is one result of that occasion.

For those who were there, the symposium (and by extension the volume) evokes two bittersweet impressions. One is of resilience, as ACS met in New Orleans for the first time since Katrina. Stocker had lost much of his collection, but he was still sharing it with others as well as sharing his enthusiasm for chemistry and for his city. The other is of loss, for Stocker passed away the following year at the age of 85. One need not have been at the symposium or known Stocker, though, to appreciate the book, which stands on its own as a miscellaneous collection of metachemical fun.

One of the book's chapters has "history" in the title: "ACS History in Personal Debates, Both 'political' and 'Political." Former ACS President Mary Good writes about some of the politics within and outside ACS during her long years of service to the organization. She touches on matters ranging from the small-scale diplomacy of arranging for scientists who did not get along well to share the same stage, to some scientific fallout from the large-scale geopolitics of the Cold War. Her chapter makes for both interesting reading and raw material for further historical inquiry.

Another chapter that is rich in personal recollection is Mary Virginia Orna's, "Always a Cross(ed) Word." It is a delightful memoir that describes the development of her love for Latin and chemistry in high school. The latter became her career, while the former turned into a serious avocation in crossword puzzles. As a puzzle constructor, Orna has published in the *New York Times*,

among other places. The chapter explains some of the challenges and constraints of constructing a crossword puzzle. It recounts how her interests in crosswords and chemistry eventually combined. And it illustrates the text with several examples of published puzzles (including solutions at the back of the chapter).

Wordplay and reminiscence, combined with a large dose of humor, are front and center in Howard Shapiro's contribution, "Curriculum Witty." The chapter is mostly in verse, much of it singable to the tune of Gilbert and Sullivan's patter song about the modern major-general. The text notes that most of his talk was delivered in song with guitar accompaniment (which obviously loses something in print). Shapiro has delivered scientific papers in song before, including one on flow cytometry. This chapter includes pieces of his own and others' settings of science to verse and music, including an addendum to Tom Lehrer's song, "The Elements."

The book's opening chapter, by William Carroll Jr. (another former ACS President), revisits the "Newscripts" column of *Chemical and Engineering News*. It focuses on the Ken Reese years of that *C&EN* feature, although it also includes assorted examples of whimsy from *C&EN* from before Reese's tenure. The selection of examples displays Carroll's dry sense of humor—which, naturally, was more apparent in person than it is in text and illustrations alone.

Humor is also the theme of the contribution by the volume's co-editor, Natalie Foster. Her chapter describes several examples of the infiltration of satire or hoax into the more or less formal chemical literature. They include a letter by Alonzo S. Smith on the "hat" and "raft" conformations of $\mathrm{Fe_6H_8}$, a biographical article about Claude Emile Jean-Baptiste Litre, and the first and last issue of the Berichte der durstigen chemischen Gesellschaft. The letter (note the author's initials) was published in Chemistry in Industry in the 1950s and subsequently abstracted

in the *Chemisches Zentralblatt*. The pseudo-biographical article on Litre was published in the late 1970s as a joke in the newsletter *Chem 13 News*, then reported seriously in a couple of IUPAC publications, an encyclopedia, and even *C&EN*. Finally, this issue of the *Berichte* was published in the 1880s in the style of the better known *Berichte der deutschen chemischen Gesellschaft*. Its title translates as *Reports of the Thirsty Chemical Society* rather than the German Chemical Society. The issue contains several spoofs, including a depiction of Kekulé's structure of benzene using monkeys.

Kathryn Meloche, Janice Mears, and Roger Schenck contributed a chapter on oddities from the databases of their employer, the Chemical Abstracts Service. This chapter is like a cabinet of curiosities, displaying for the reader superlative items from the databases such as the shortest abstract, the longest name (of an author and of a substance), and the compound with the greatest number of elements. The article also treats strange structures, weird patents and the occasional cameo by chemist who would go on to be a head of state or government.

That brings me back to Jack Stocker, whose chapter finishes the book. It is also a collection of curiosities, not from CAS but from his own collection of memorabilia or "chemage" titled "Absurd Items That Survived Katrina: A Small Cornucopia of Miscellaneous Whimsy." These include visual puns in the form of chemical structures and equations, whimsical names, felicitous acronyms, and an apparatus diagram containing a superfluous surprise.

The volume contains groaners, to be sure, but each chapter has something to bring a glint of pleasure to the eye of anyone capable of entertainment by chemistry.

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