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A vial of phenylhydrazine from the lab of Emil Fischer.
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BULLETIN FOR THE HISTORY OF CHEMISTRY

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The Cover … A vial of phenylhydrazine from the lab of Emil Fischer. Copyright Deutsches Museum, Munich
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ADDENDUM TO "ON THE DISCOVERY AND HISTORY OF PRUSSIAN BLUE"

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In my 2008 article "On the Discovery and History of Prussian Blue" (1) I reported the story of the invention of Prussian Blue by Johann Jacob Diesbach (about 1670-1748) (2) and Johann Konrad Dippel (1673-1734) in Berlin in 1706 as told by Georg Ernst Stahl (1659-1734) in his book *Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae* from 1731 (3).

According to Stahl, Dippel produced his later "infamous" animal oil ("oleum Empyrevmaticum animale") in Berlin. For the rectification of the animal oil he mixed it with potash ("Sale Tartari"). After repeated distillation, the remaining potash was stored away in a glass container. This potash was contaminated with cyanide and/or hexacyanoferrate, which led to the precipitation of Prussian Blue when this source of potash was used by Diesbach for the production his red Florentine lake.

Meanwhile, an additional historical source has begun to speak: the diary of Johann Christian Senckenberg which is currently being transcribed and published online (4). Senckenberg (1707-1772) was a German physician, naturalist and collector based in Frankfurt am Main. As a young man he was a friend and admirer of Dippel, who was more than 30 years his senior. In 1732 Senckenberg visited Dippel twice in Berleburg, Dippel's last place of residence. In his diary, which includes entries from 1730 until 1772, Senckenberg also reported on his travels to Berleburg, including accounts of many stories which were told to him by Dippel. On August 22, 1732, Dippel reported to Senckenberg, among many other things, that once during his time in Berlin (1704-1707) he was preparing a large amount of a "sal volatile" by dry distillation of calcined sal tartari (potash) and dried ox blood. The remaining mixture of about six pounds of mixed sal alcali tartari and sal sanguine was not thrown away as Dippel would have done, but collected and stored away by Dippel's young assistant Rößer (5). However, on the label, Rößer had only written "Sal tartari" and not "ex Sale alcali tartari constans et sale sanguinis." A "Lieutenant dießbach" was working in Dippel's lab on the preparation of Florentine lake and other pigments. In need of sal tartari, he used the wrongly labeled previously heated mixture of calcined sal tartari and dried ox blood for the preparation of Florentine lake. A blue color "caeruleum Berolinense" (Prussian Blue) resulted. Without informing Dippel, Dießbach drew up a contract with some painters for the delivery of the new blue pigment. But he could not produce this material anymore after the source of contaminated sal tartari was finished. Therefore, he came to Dippel and reported his problem. Dippel told him to use sal tartari and bovine blood and it did work out.

So this is what Dippel himself reported to a friend about the invention of Prussian Blue. It differs somewhat from the story told by Stahl. Most important was the fact that the accidental formation of hexacyanoferrate was not a result of animal oil production but of the preparation of a sal volatile. Since Dippel was one of original inventors we should consider his story more to be credible than Stahl's.

Other newly discovered sources contain two recipes for Prussian Blue's preparation which circulated in Germany before the first printed publication (6) of a

Prussian Blue recipe in 1724. The first of these recipes was found in Dresden in a collection of papers (7) which most probably were in the possession of Johann Friedrich Böttger (1682-1719). The second recipe was sent in 1722 in a letter from a Hamburg merchant, Detlef Klefeker (1675-1750), to Johann Friedrich Henckel (1678-1744) a physician, mineralogist and chemist in the mining town of Freiberg in Saxony, Germany (8). Both recipes are very similar.

According to Klefeker's recipe, dried ox blood was mixed with potash. The mixture was then calcinated and treated with water to produce a first solution. A second red-colored aqueous solution was prepared from alum and ground cochineal insects. A third aqueous solution was made from alum and iron sulfate. All three solutions were then combined. The resulting blue precipitate was washed with water and dried.

Obviously, it was not so easy to successfully repeat this experiment. In 1723 Henckel, an experienced chemist, reported in an article in a scientific journal published in Silesia that he was in the possession of a Prussian Blue recipe (perhaps the one sent to him by Klefeker) that used blood, potash, alum, vitriol of iron and water, but he was not able "to get the blue down from heaven" (9).

Both recipes were written up in German, and included the unnecessary preparation of a red cochineal dye (carminic acid) solution, which was mixed with the blood lye and the iron sulfate solution during the precipitation of Prussian Blue. Therefore, they differ from the first officially printed recipe from 1724 in which cochineal was no longer used (10).

References and Notes

1. A. Kraft, "On the Discovery and History of Prussian Blue," *Bull. Hist. Chem.*, **2008**, *33,* 61-67.
2. Information on Diesbach can be found in parish registers of three churches in Berlin: the New Church and the Jerusalem Church in the Friedrichstadt neighborhood and the Church at the Köpenick Gate in the Köllnische Vorstadt suburb. In all these records his name is always written as Johann Jacob von Diesbach. In 1708 his marriage with Eleonora Dorothea Müller, daughter of Conrad Müller is recorded. In this record Diesbach is described as former Lieutenant of the English army. In the same year two sons (the twins Johann Jacob and Conrad Gottlieb) were born. Diesbach's wife Eleonora Dorothea died in 1721. In 1732 a second marriage of a Johann Jacob von Diesbach is recorded. It is not clear if he is the inventor of Prussian Blue or his son. The wife was Maria Elisabeth Leuen, daughter of Johann Michael Leuen. In the same year a daughter (Maria Dorothea Henriette) was born to the new married couple. The inventor of Prussian Blue died from a stroke in 1748 in Berlin at the age of 78 years. Therefore, it can be concluded that he was born about 1670.
3. G. E. Stahl, *Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae*, Ambrosius Haude, Berlin, 1731, pp 280-283.
4. Universitätsbibliothek Johann Christian Senckenberg, Goethe Universität Frankfurt am Main, J. C. Senckenberg (1707-1772) – Diaries, Vol. 2, p 406, entry for Aug. 22, 1732, transcribed and edited by Vera Faßhauer http://senckenberg.ub.uni-frankfurt.de/p/5381590 (accessed July 22, 2016).
5. According to Senckenberg's notes on Dippel's report, Rößer (whose first name is not known) later became a physician and resided in Hamburg.
6. J. Woodward, "Praeparatio Caerulei Prussiaci ex Germania Missa ad Johannem Woodward," *Philos. Trans. R. Soc.*, **1724**, *33*, 15-17.
7. "Berliner Blau zu machen," *Verschiedene Rezepte und Konzepte*, Staatliche Kunstsammlung Dresden (SKD) Archive PS, ca. 1708-1719, pp 42-44. This recipe is published in: A. Loesch, Ed., *Sächsisch schwartz lacquirtes Porcelain*, Sandstein-Verlag, Dresden, 2013, pp 179-180.
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9. J. F. Henckel, "Von Herrn D. Joh. Fridr. Henckels, ..., aus Saltz-Kraut und Sode neu-erfundenen blauen Farbe," *Sammlung von Natur- und Medicin- wie auch hierzu gehörigen Kunst- und Literatur-Geschichten*, **1723** [for 1721], *18*, 421-427.
10. A. Kraft, "On Two Letters from Caspar Neumann to John Woodward Revealing the Secret Method for Preparation of Prussian Blue," *Bull. Hist. Chem.,* **2009**, *34*, 134-140.

About the Author

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KLAUS AT KAZAN: THE DISCOVERY OF RUTHENIUM (1)

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Ruthenium was once called the "little Benjamin" of the platinum group metals (2), referring to its lesser status compared to the other platinum metals. For much of the twentieth century there were, indeed, remarkably few papers dealing with this element and its compounds (3). Then things began to change, and we can illustrate this by noting that three Nobel laureates—Henry Taube, who studied electron transfer reactions in metal complexes, Robert Grubbs, whose work helped make olefin metathesis a major synthetic method, and Ryoji Noyori, who developed practical chiral catalytic hydrogenation catalysts—all used ruthenium as part of their prize-winning work. By the time that this paper is being written, ruthenium has, in many ways, become a modern "miracle" metal. Certainly, the number of papers published following the first half of the twentieth century dramatically increased—the number of papers appearing during the decade of the 1980s approximately doubled the output of the previous decade, and each subsequent decade has seen an approximately 50% increase in the number of published papers devoted to aspects of the chemistry of this remarkable element (3). While part of the increase may be attributed to the general proliferation of journals now available, this by no means accounts for more than a minority of the increase.

Ruthenium metal itself was first isolated pure (4) in 1844 by Karl Karlovich Klaus (Клаус Карл Карлович, Carl Ernst Claus, 1796-1864, Figure 1) (5), who was, at the time of its isolation, Extraordinary Professor of Chemistry at Kazan University. The university itself had been established forty years earlier by royal decree of Tsar Alexander 1, and was at the time the easternmost university in Russia. At the time of his discovery, Klaus was relatively unknown—certainly, he did not have the international reputation as a chemist that the discovery of ruthenium gave him, nor had the Kazan University School of Chemistry achieved the stature it would attain over the next half century as an important center for chemical research and education.

Figure 1. *Karl Karlovich Klaus (Клаус Карл Карлович, Carl Ernst Claus) in Dorpat (daguerreotype, ca. 1852).*

Klaus was born in Dorpat (now Tartu, in Estonia) to Carl Claus, a talented painter of Baltic German descent who christened his son Carl Ernst (Karl Karlovich; in Russia, the patronymic, "Karlovich" (son of Karl) displaces the middle name in German). It is perhaps fortunate that the son inherited some of his father's talent as an artist, because the arts allowed him a place to escape from the trauma of his childhood. His skill as an artist is evident from some of the illustrations in this paper, which are his work. Klaus' childhood was, indeed, traumatic. At age four, he lost his father, and his mother married again, becoming the wife of another artist; a scant two years later, Klaus' mother also died, and he was left an orphan—unloved and neglected—in the home of his "hated stepfather." Klaus received little support or love in this household, and this neglect of a lonely child may have been important in building his self-reliant and persistent character.

Figure 2. *"Saratow" by K. K. Klaus*

Although Klaus was enrolled in the Gymnasium at a young age, he did not have (or his stepfather did not give him) sufficient funds to enable to complete the course of study, and he had to begin supporting himself by the age of 14 years. Thus, in 1811 he left Dorpat for St. Petersburg, where he became the student of an apothecary.

Klaus was a voracious reader, and during his time as a student with the apothecary he was able to teach himself pharmacy, botany, and chemistry from the books that he read. So successful was Klaus at educating himself, that—despite his lack of a formal education—he was able to pass the examinations for Assistant Pharmacist, administered by the St. Petersburg Medical-Surgical Academy in 1815. As a result, he became the youngest qualified Assistant Pharmacist in Russia (6). In 1816, while still working at the pharmacy in St. Petersburg, he took the test at Dorpat University to qualify as Provisor in pharmacy (later, this title changed to kandidat in pharmacy (7)), which he passed. The next year, the Medical-Surgical Academy also conferred on him the title of Provisor, and he moved to Saratov (Figure 2) in that capacity, as a fully qualified pharmacist.

Klaus spent the next ten years in Saratov. During his time there, he married Ernestine Bate, whom he had known since childhood. The marriage was a happy one, and the couple eventually had four children: three daughters, born at Kazan, and a son born in Dorpat after Klaus had left Kazan. At Saratov, Klaus was successful enough to save the money required to move to Kazan (Figure 3) and establish his own pharmacy there. He did so in 1826.

Figure 3. *A view of the city of Kazan from the direction of Kaban Lake, 1828, by K. K. Klaus*

His attention to detail, his breadth of knowledge in general, and his wide knowledge of medicinal herbs in particular, quickly made his pharmacy the most respected in Kazan. This had the result of allowing Klaus to enter the intellectual circles of the city. At the same time, he also obtained an excellent reputation as a scientist, based on his studies of the Volga-Ural flora. In fact, there are several species of plants that bear his name (8).

While he was a pharmacist in Kazan, Klaus was approached by the Professor of Zoology, Eduard Aleksandrovich Eversman (Еверсман Едуард Александрович, Eduard Friedrich Eversman, 1794-1860, Figure 4) to accompany his expedition to study the flora and fauna of the Volga region. Given Klaus' interests in pharmacy and the use of natural herb medications at the time, it is not surprising that he accepted the invitation.

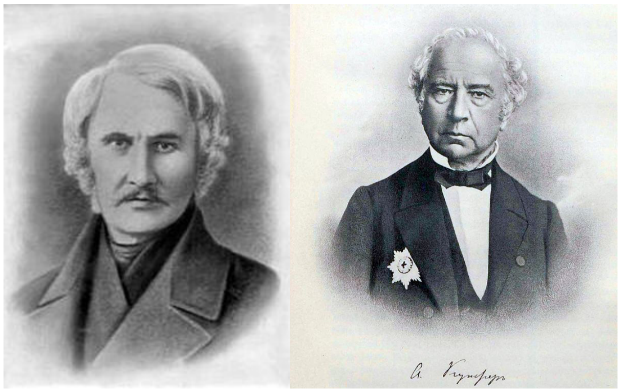

***Figure 4**. Eduard Friedrich Eversman (Еверсман Едуард Александрович, left) and Adolf Yakovlevich [Adolph Theodor] Kupfer (Купфер Адольф Яковлевич, right).*

The journey covered the area from Kazan to a number of places in the Orenburg district of Astrakhan province, as well as the shores of the Caspian Sea. This expedition, which took place during 1827, eventually led to Klaus' publication of the work in the German language (9). A year later, Klaus accompanied Adolf Yakovlevich Kupfer (Купфер Адольф Яковлевич, Adolph Theodor Kupfer, 1799-1865, Figure 4), the Professor of Chemistry and Physics at Kazan University, on his expedition to examine the placer deposits of platinum and gold in the Ural region (10). Kupfer asked Klaus to accompany him, and wrote later, "I was accompanied by Klaus, the Kazan pharmacist, an outstanding artist, whose paintings graced the appearance of that work" (11).

This expedition with Kupfer was a watershed moment in Klaus' life, because it spurred his interest in the chemistry of the platinum metals, and an eventual desire to complete his formal education in chemistry by returning to Dorpat to obtain his degree. Three years later, Klaus sold his pharmacy for what he felt was half its true worth, and he returned to Dorpat to obtain his degree in chemistry. From 1831-1837, he was an Assistant in Chemistry at Dorpat, serving for a time as the assistant to another Dorpat native, Gottfried Wilhelm Osann (Озанн Готтфрид Вильгельм, 1797-1866, Figure 5). At the time, Osann was Professor of Chemistry, and a recognized expert in the chemistry of the platinum metals. He was working on the residues from the platinum ores that he had obtained from the Finance Minister, Count Yegor Frantzevich Kankrin (Канкрин Егор Францевич, 1775-1845) (Figure 5), and it is almost certain that Klaus learned the techniques for analyzing platinum ores from Osann.

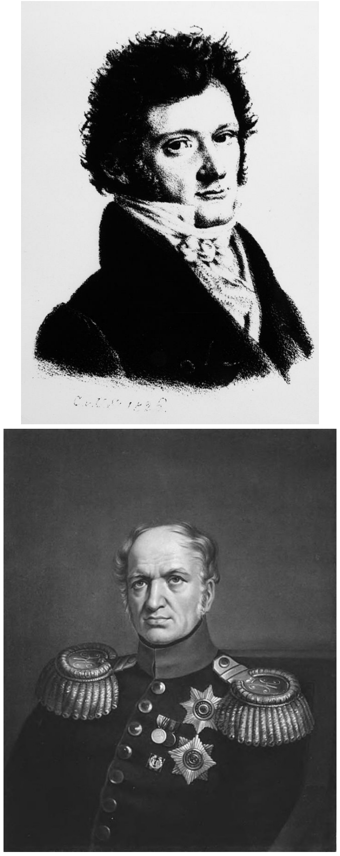

***Figure 5**. Gottfried Wilhelm Osann (Озанн Готтфрид Вильгельм, top) and Georg Ludwig, Graf von Cancrin (Граф Канкрин Егор Францевич, 1774-1845, bottom).*

At this time, Russia used platinum (which was known as "white gold") as a coinage metal, and Count Kankrin, who spearheaded the reforms of the Russian financial system during his twenty-year tenure as Finance Minister, was concerned that there were significant amounts of platinum still left in the residues from the process of refining. Consequently, he sought to determine how much platinum remained in the ore residues, and if methods for its extraction could be developed. As part of his efforts to determine the amount of platinum in the ores from the Urals, he sent samples of the ore to institutions within the Russian empire and abroad. Among those who received samples was the great Swedish chemist, Jöns Jacob Berzelius (1779-1848). Four pounds of the platinum ore were also sent to Dorpat, where they were analyzed by Osann.

Osann subjected the crude platinum to the standard methods of analysis of the day: the crude mass was dissolved in aqua regia, and the insoluble material was removed by filtration. The filtrate was then treated with ammonium chloride to precipitate the ammonium hexachloroplatinate (IV), along with the corresponding iridium (IV) complex. On heating, this salt decomposed to a platinum-iridium sponge that could be compressed into a malleable metal for minting coins (12). This crude platinum metal could be further treated by redissolving it in aqua regia; in this case, the iridium remains as an insoluble black solid.

In the course of his researches, Osann obtained what he considered to be three new elements, which he named ruthenium (L. *ruthenia*: Russia), pluranium (combining the initial letters of platinum and Urals), and polinium (Gk. polioς, grey); Osann later suggested that his polinium may, in fact, be impure iridium (13). He sent samples of his new elements to Berzelius, but the great chemist and mineralogist failed to confirm his discovery. Perhaps as a consequence of this, Osann withdrew his claims a year later (14). A later (1900) assessment of Osann's work (15) concluded that his polinium was impure iridium, perhaps containing some ruthenium, and that the red needles of ruthenium in his first report (13) may have been a mixture of osmium and ruthenium tetroxides; in 1845, Osann agreed with Berzelius that the crystals with a golden luster, to which he had transferred the identity as ruthenium, were probably a mixture of zirconium, iron, silicon and titanium oxides, but he vigorously defended the identity of his polinium with Klaus' ruthenium (16). The identity of pluranium has never been satisfactorily established. In a recent biographical account (17) containing a re-evaluation of his claims, Hödrejärv asserts that Osann had, in fact, obtained ruthenium as he had claimed, but he concedes that Osann's claims were undermined by the irreproducibility of his results. A succinct account of the "discovery" of the elements polinium and pluranium has recently been published (18).

Figure 6. Carl Christoph Traugott Friedemann Goebel (Гёбель Карл Христиан Траугот Фридеман, left) and Nikolai Nikolaevich Zinin (Зинин Николай Николаевич, right).

While a student at Dorpat, Klaus accompanied Professor Carl Christoph Traugott Friedemann Goebel (Гёбель Карл Христиан Траугот Фридеман, 1794-1851, Figure 6) in his expedition to the Volga steppes, in part because Klaus spoke and read Russian. Goebel wrote a report of this expedition (19) in two volumes on his return to Dorpat; the work received a lesser Demidov Prize (the smaller version of the most prestigious award conferred by the Academy of Sciences), although Klaus' share of this prize was never confirmed. In 1835, Klaus passed the examinations for the kandidat of philosophy degree at Dorpat University, and two years later, he submitted his dissertation (20), and passed the examinations—which included questions about the chemistry of the platinum metals—for the degree of Master of Philosophy. In May the same year, Klaus read the required sample lecture ("On a Rapid Method for Preparing Chemical and Pharmaceutical Products") at the St. Petersburg Medical-Surgical Academy, and in June, 1837, he was offered a position as Adjunct in Pharmacy at Kazan University.

Klaus took up his pharmacy appointment at Kazan in August 1837, during the time that the Adjunct in Chemistry, Nikolai Nikolaevich Zinin (Зинин Николай Николаевич, 1812-1880, Figure 6), was abroad on his *komandirovka*. At the same time, the chemistry laboratory was being moved into a new building, which was expanded in phases from 1837 to 1839 thanks to the efforts of the Trustee of the Kazan educational district, Count Mikhail Nikolaevich Musin-Pushkin (Граф Мусин-Пушкин Михаил Николаевич, 1795-1862, Figure 7). Musin-Pushkin had himself been a student at the university, and strongly supported it. One of his most significant acts was to secure the appointment of the mathematician, Nikolai Ivanovich Lobachevskii

(Лобачевский Николай Иванович, 1792-1856, Figure 7), as Rector of the university.

***Figure** 7. Count Mikhail Nikolaevich Musin-Pushkin (Граф Мусин-Пушкин Михаил Николаевич, top) and Nikolai Ivanovich Lobachevskii (Лобачевский Николай Иванович, bottom).*

The expansion of the chemistry building required someone to oversee the routine day-to-day work supervising the transfer to the new building. But the Adjunct, Zinin, was not available to do this, so Klaus was seconded to the *kafedra* of chemistry at the request of Professor Ivan Ivanovich Dunaev (Дунаев Иван Иванович, 1788-1840). This gave him the responsibility for fitting out and maintaining the chemistry laboratory, and for conducting experiments in inorganic and pharmaceutical chemistry. In order to obtain the rank of Extraordinary Professor of Chemistry, Klaus required the degree of *Dr. Filosofii*, which he obtained in 1839, with a dissertation (21) describing a study of the compounds in the mineral waters of the Sergievskii district. On graduating with this degree, he was appointed Extraordinary Professor of Chemistry.

In 1840, after receiving his appointment in chemistry, Klaus received an allotment of platinum residues from Count Kankrin, and began his analysis using the protocols that had been established by earlier workers in the field (especially Osann). He spent the next two years in completing the analysis of these residues for the known platinum metals, and was able to extract more platinum from these residues. His work had been fruitful enough for Count Kankrin to award him a further allotment of 8 kg of the residues, as well as 300 g of platinum metal. Unfortunately, this second batch of the spent ore contained much less platinum, and he was forced to inform Kankrin that the second batch of residues had so little platinum that it was of scientific interest only (22).

It is probably well here to dwell for a brief time on Klaus' laboratory practices. Some of his habits in the laboratory would certainly attract the serious attention of any modern chemical safety officer because of their likelihood of harming his health. Among other things, he tasted practically all his solutions: his colleagues recalled that on arriving in the laboratory early in the morning, Klaus often tasted solutions of substances with which he had to work that day. Thus, after dissolving platinum ore in aqua regia, he determined the strength of unreacted acid by dipping a finger directly to the reaction mixture, and then touching it to his tongue. When he first isolated osmium tetroxide, he noted that it had a sharp and peppery taste, and reminiscing later about working with osmium compounds, he wrote, "... osmic acid belongs among the most harmful substances ... I suffered much from it ..." (23).

This assessment came at a painful price. At least twice, Klaus had generated enough osmium tetroxide to flood the laboratory with its vapors and cause serious injury: In April 1844, a release of the gas into the laboratory, generated while he was alloying 15 pounds of platinum residues with nitre, injured some retired soldiers who were not even inside the laboratory; it took them three days to recover, even though they were outside in the hall. The *Preparator*, Gelman, was inside the laboratory, and was therefore exposed longer; he suffered a dangerous inflammation of the lungs. Klaus escaped serious injury on this occasion by being able to exit from the laboratory quickly into the auditorium (24). A year later, he did not escape injury as he had in 1844, and the poison affected him so much that he was forced to stop his experiments for two weeks (25). As he was characterizing his new element, he tasted an ammonium complex of ruthenium. This left him with a mouth so badly blistered that he was forced to take three weeks off from his research and teaching (5b). None of these incidents, however, was able to deter him from the practice of tasting his solutions; instead he impatiently endured these forced hiatuses, only to return to the research laboratory as soon as he had recovered.

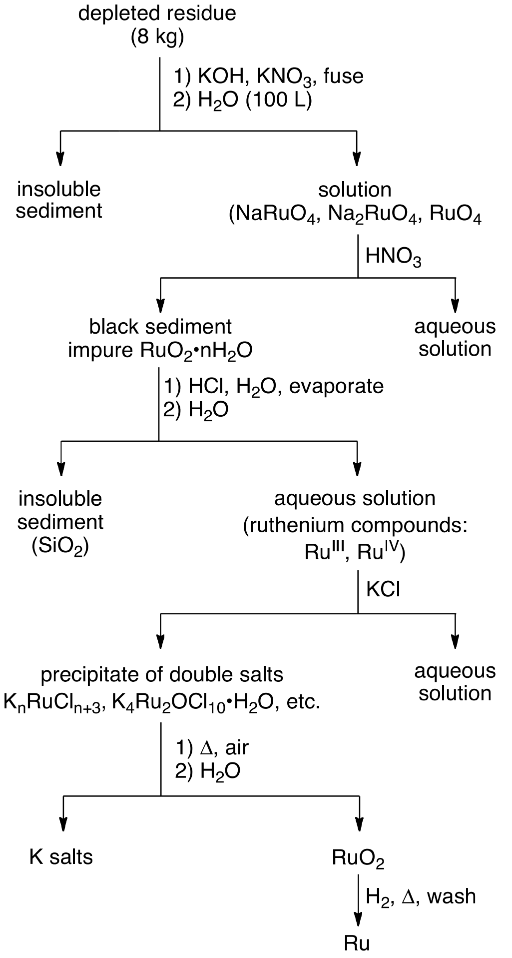

Figure 8. *Klaus' procedure for the isolation of metallic ruthenium from the poor platinum residues of the Ural placer platinum ores.*

Klaus now turned his attention to the metallic residue that was insoluble in aqua regia, and by means of the sequence of steps in Figure 8, he was able to obtain pure ruthenium metal for the first time. In Figure 8, the ruthenium compounds are identified as Klaus designated them. His procedure led him to believe that among the double salts precipitated with potassium chloride, he had isolated a hexachlororuthenate, K_2RuCl_6 analogous to the corresponding hexachloroplatinate salt, K_2PtCl_6. Fifty years later, Howe showed that this salt was, in fact, the nitrosopentachloro complex, K_2RuCl_5NO (26).

Klaus' habit of ignoring potential hazards to his health provides the clue to how he was able to track this new metal. As an inveterate taster of his solutions, he simply followed the "strange" taste in his metal solutions, and the associated acrid odor of ruthenium tetroxide. His senses of smell and taste were probably the most sensitive analytical tools available to him, even though the most hazardous to use.

Klaus first reported the isolation of his new metal in Russian in the *Uchenye Zapiskii Kazanskogo Universiteta* [*Scientific Notes of Kazan University*], taking one complete issue of the journal in 1844 to describe his results (4). The same year, he reported the discovery of ruthenium—now in German—in the *Bulletin de la Classe Physico-Mathématique de l'Académie Impériale des Sciences de St. Petersbourg* (27), and he was promoted to Ordinary Professor of Chemistry at Kazan. In 1845, Klaus reported his discovery in the *Gorny Zhurnal* [*Mining Journal*], one of the oldest journals in Russia. In this paper, he wrote (28), "At the very beginning of the work I noticed the presence of a new substance, but at first I could not find a way to separate it from impurities ... This new metal, which I have named ruthenium in honor of our Fatherland, certainly belongs among the most interesting materials." It is worth noting that Klaus considered Russia, and not Germany as his homeland, although he used the German term, "Fatherland," instead of "Motherland," or "Mother Russia."

Klaus is reported to have been an excellent lecturer, and to have spoken Russian with a "fair" accent. However, he is also reported to have lapsed into the German of his boyhood whenever he became excited or inspired (29). His choice of words here may reflect that although Dorpat was under the rule of the Tsar, it retained its German language and traditions until the late nineteenth century. As part of the University Statute of 1884, Alexander III promoted the Russification of all universities in the empire and repealed many of the reforms of his predecessor. This included establishing Russian as the official language of education (30).

The same year, reprints of his discovery appeared in a number of western European journals. The version of his paper in the *Bulletin* that was published in *Poggendorff's Annalen der Physik* drew an immediate response from Osann, who claimed that Klaus' ruthenium was actually his polinium (16); this, in turn, received an immediate response from Klaus defending his priority for the discovery of the metal. As part of this effort, he published a comparison of the properties of the new metal and iridium (31). In addition to publishing the work in

Russian, Klaus work was communicated to Paris by Germain Henri Hess (Гесс Герман Иванович, 1802-1850) (32). This paper, likewise, was reprinted in German and abstracted in English.

After obtaining his sample of ruthenium as a grey powder, Klaus sent samples of the new metal and some of its salts to Berzelius for authentication of his discovery. Predictably, perhaps (given his history with Osann's three "elements" from the same source), Berzelius was skeptical, and initially dismissed the claims. However, Klaus was dogged in his insistence that he had discovered a new metallic element. A year later, Berzelius wrote him a letter where he described the new element as being an impure form of iridium, and Klaus immediately replied that—respectfully—he could not agree with that assessment (33).

It appears that his letter crossed Berzelius' second letter in the post because just eight days after sending the letter with his initial negative assessment, Berzelius again wrote to Klaus, this time confirming his claims of the discovery of a new element, and praising the way in which Klaus had acknowledged the earlier work of Osann (34). This letter ended the doubts of at least some of the European skeptics of Klaus' discovery. Berzelius concluded this letter with the following: "I have taken the liberty of submitting an abstract of your article from the Academy of Sciences to the editor, who will print it in a report of this meeting." The report appeared in the *Jahresberichte* in 1846 (35).

This same year, Klaus received the Demidov Prize for his work in the chemistry of the platinum metals and the discovery of ruthenium. In 1847, by which time his priority as the discoverer of ruthenium had become generally accepted, Klaus published a summary of his contributions to the chemistry of the platinum metals, including the discovery of ruthenium (36).

In 1852, Klaus was offered the Chair of Pharmacy at Dorpat University. The reasons for this move were personal, and based mainly on family and financial considerations. His second daughter and her husband and son lived in Dorpat, and Klaus bemoaned the fact that his salary could not support his family both in Kazan and at Dorpat. The solution to the problem was to unify the family in one city, which set the two sides of Klaus' character in conflict with each other. Klaus, the patriarch of the family, was needed in Dorpat, while Klaus, the scientist, had strong ties to Kazan. As we know, his family concerns won, and he moved to Dorpat. One other thing that may have facilitated this move was the opportunity to occupy the Chair of Chemistry, which had been vacated by the death of Göbel. Klaus had written to Alexander Georg von Bunge (Бунге Александр Андреевич, 1803-1890), who had been at Kazan, and who taught botany at Dorpat, asking him to help facilitate his application. Although he did not receive the Chair in Chemistry he sought at Dorpat, he was appointed to the new Chair of Pharmacy.

Klaus left Kazan in 1852, but he did not completely break his ties there. In 1854 he wrote an account of the chemistry of the platinum metals as a *Festschrift* for the fiftieth anniversary of the founding of the University (37). This monograph was to define the field for the next century (5g). It had been Klaus' intention to complete a full monograph on the chemistry of the platinum metals, but he never accomplished this during his lifetime, and sections of his proposed manuscript were never completed. However, the parts of the manuscript that he did complete, were gathered by his student, Butlerov, and published after his death (38); the manuscript had languished among his papers for a decade, and parts of the manuscript had been lost during the decade between its writing and its publication.

Following his move to Dorpat, Klaus continued with his work on the platinum metals, and he continued to publish in the area. He traveled extensively, and received numerous honors throughout Europe; Pitchkov (5g) has provided an excellent synopsis of these travels and honors. In 1861, Klaus was elected as a Corresponding Member of the Russian Academy of Science. During his return from St. Petersburg to Dorpat after he had attended a meeting of the St. Petersburg Pharmaceutical Society as an honored guest, Claus caught a chill that failed to improve; how much this may have been due to the damage to his lungs from osmium and ruthenium tetroxides must remain conjecture, but it seems quite reasonable to propose that this may well have predisposed him to pneumonia. He died shortly after his return to Dorpat.

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I. S. Antipin for their support. I am also indebted to a reviewer for help with the series of references between 1844 and 1847, when Klaus announced the new element.

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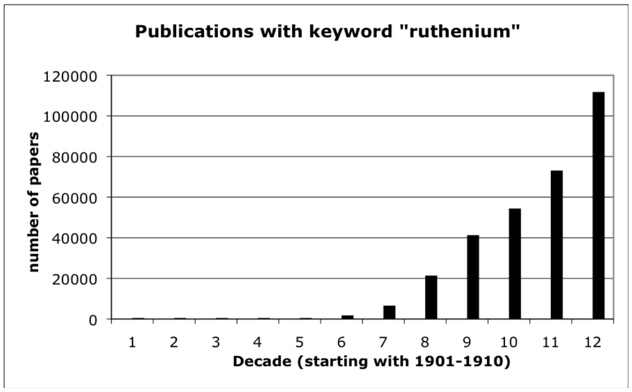

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EMIL FISCHER'S SAMPLE COLLECTION

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Much has been written about Hermann Emil Fischer's life and work (1-15). His investigations into substances derived from living organisms have influenced generations of chemists. His work led to an understanding of the molecular structures of many biologically important substances, provided numerous methods and laboratory techniques in synthetic organic chemistry, and laid the foundations of the field of biochemistry. His legacy touches every student and practitioner of organic chemistry and biochemistry.

His physical legacy—the actual collection of substances he prepared during his career—has received much less attention. The collection is housed in the Chemistry section of the Deutsches Museum in Munich. This location is particularly fitting because Fischer first attained his professorship less than three kilometers away at the University of Munich. Starting at the nascent Fischer lab, however, the collection would travel through six cities in four countries on two continents before arriving at the Deutsches Museum—a journey of several thousand miles spanning some 115 years.

The collection contains samples that represent work from all stages of Fischer's 45-year career. It is a tangible reminder of the remarkable scope of his work and the importance of the contributions he made in each of the areas of research that he pursued. As of this writing, the samples reside in two large crates and await formal cataloguing by the Deutsches Museum. A brief overview of Fischer's research will provide a sense of the content of the collection and the importance of the work it represents.

The Growth and Significance of the Collection

Conceptually, at least, the compound collection had its origin at the University of Strasbourg, where Fischer earned his doctorate in 1874 under Adolf von Baeyer (16). Continuing to work in von Baeyer's lab after obtaining his degree, Fischer investigated triarylmethane dyes and deduced the structure of phenylhydrazine (17, 18), which figured so prominently in his later work. He proposed the name hydrazine for the saturated nitrogen-nitrogen functional group (17).

In 1875 Fischer moved with von Baeyer to the University of Munich and continued studying organic dyes (19). By 1879 he had risen to the position of Associate Professor of Analytical Chemistry and had his own laboratory (16). Joined by his cousin Otto Fischer in 1876, he continued his work on organic hydrazines and, together with Otto, synthesized the dye pararosaniline from triphenylmethane (20). They then demonstrated that the other dyes in the rosaniline class, which at the time were depicted with a different structure, are actually congeners of triphenylmethane as well (21, 22). The Deutsches Museum has samples of phenylhydrazine and triphenylmethane that represent work from these early years.

The Emil Fischer lab moved in 1882 when Fischer took the position of Professor of Chemistry at the University of Erlangen. It was at Erlangen that Fischer first turned his attention to substances isolated from natural sources, the focus that would define his life's work, and the collection began to grow with new classes of compounds. Fischer showed that uric acid, xanthine, hypoxanthine, adenine, guanine, caffeine, theobromine, and theophylline, though derived from various plant and animal sources, all share a common chemical framework (23, 24). He called the framework "purine" (16, 24), a contraction of the Latin words "purum" and "uricum [acidum]" (8) and thus gave name to a class of compounds of great commercial importance; the immense biological significance of purines as components of nucleic acids, cofactors in metabolic processes, and components of signaling pathways would be recognized much later.

While at Erlangen Fischer also continued work with phenylhydrazine. After investigating its reactions with aldehydes and ketones (25) he discovered that phenylhydrazine reacts with sugars to form highly crystalline derivatives that were easily isolated (26). He called these derivatives osazones (8) and this discovery laid the foundation for his most famous work to come. In separate research he found that phenylhydrazine reacts with ketones to form the indole ring system and elucidated the indole synthesis that bears his name (27, 28).

The growing compound collection moved with the Fischer lab to the University of Würzburg when Fischer accepted the position of Professor of Chemistry in 1885 (29). At Würzburg Fischer focused his research on the sugars and produced the work for which he is best known. In 1888 Fischer reported the structure of mannose, a stereoisomer of glucose, which he obtained by oxidizing mannitol (30). By 1890 he had completed the formal syntheses of glucose, fructose, and mannose from glycerol (31, 32) and proposed a nomenclature to designate sugars—the "oses"—having different numbers of carbon atoms (33).

The theory of the tetrahedral atom, its implications for stereoisomerism, and its apparent relationship to optical activity had been put forward by van't Hoff (34) and Le Bel (35) in 1874 (36, 37). Van't Hoff further proposed that there would be 16 stereoisomeric aldohexoses and Fischer undertook to apply the theory to explain the differences between the isomeric sugars (38-40). Through logical application of the theory, Fischer determined the relative stereochemistry of all of the sugars known as of 1894, using D-glucose as a reference (7, 41-43). The diagrams that he developed to display and compare the stereoisomers of sugars are known to all organic chemists as "Fischer Projections" (41, 44). With no way of knowing the absolute stereochemistry of any atom, Fischer adopted the convention of putting the 2-hydroxyl group of D-glucose to the right in the projections (41, 42, 44, 45). With the establishment of this convention the collection became an invaluable source of reference compounds for anyone working in carbohydrate chemistry.

Figure 1. *A sample of synthetic glucose from the Emil Fischer compound collection. Copyright Deutsches Museum, Munich, Archive 67265.*

In 1892 Fischer became Chairman of Chemistry at the University of Berlin, succeeding A. W. von Hofmann, and his lab moved yet again. Fischer continued his work on sugars throughout the rest of his career (7, 46, 47); the presence of various synthetic sugars in the collection would attest to this. His modification and use of the Kiliani synthesis of sugars is one of the earliest and most important instances of stereoselective synthesis (1). He showed the relationship between pentoses, hexoses, and heptoses by degradation and synthesis (48). The exquisite selectivity shown by enzymes for stereoisomeric sugars and glucosides led him to draw the analogy of a lock and key to describe the complementarity between an enzyme and its substrate (49, 50). This is a concept that has informed enzymology and receptor research ever since (51).

In Berlin Fischer began his work on amino acids and peptones, the digestive products of proteins, and compounds from another major area of biological chemistry started entering the collection. From the hydrolysis of a variety of protein products he identified two new cyclic amino acids: α-pyrrolidinecarboxylic acid (52), which he later named proline (53), and hydroxy α-pyrrolidinecarboxylic acid (54).

By analogy with the saccharides, he coined the word peptide (55, 56) to describe chains of amino acids of discrete lengths to differentiate them from peptones, which are mixtures of amino acids and peptides of varying length. He explored methods of synthesizing peptides, founding a rich field of research (57-59). He prepared dipeptides, tripeptides, and numerous oligopeptides, the largest of which contained 18 amino acids (60). The preparation of the latter would be a respectable accomplishment even with today's techniques. The thermal instability of the amino acid esters used in his peptide syntheses led Fischer to develop the technique of vacuum fractional distillation, which allowed the separation of the compounds at lower temperatures (61).

Fischer's tenure in Berlin resulted in additional research in diverse areas, including the perfection of acid-catalyzed esterification (62), the synthesis of oxazoles (63), the synthesis of glucosides (64, 65), the synthesis of barbiturates (66, 67), and the synthesis of glycerides along with studies of their properties (68, 69). Later in his tenure at Berlin he studied the properties and syntheses of tannins and depsides (70-73). Some of the work on the depsides was undertaken with his son (74), Hermann Otto Laurenz Fischer, who joined the lab after earning his doctorate under Ludwig Knorr from the University of Jena (73, 75).

Fischer continued his work with the purines only briefly in Berlin (73) but he developed syntheses for numerous purine analogs, including adenine (Figure 2) and guanine (76), uric acid, and caffeine (77). By the time of his address to the Nobel Committee in 1902, Fischer knew of 146 natural and synthetic purines (24), a number of which are represented in the collection.

***Figure 2**. A sample of synthetic adenine from the Emil Fischer compound collection. Copyright Deutsches Museum, Munich, Archive 67267.*

The Collection After Fischer

Upon Emil Fischer's death in 1919, the stewardship of the sample collection fell to his son Hermann, who became an Assistant Professor in the Chemical Institute at the University of Berlin in 1924 (73). His distinguished career included ground-breaking work in the study of trioses, inositols, and glycerides (73, 75, 78). In addition to the compound collection, Hermann Fischer now looked after his father's library (3, 73 ,78) of some 4000 historic chemistry books, his laboratory notebooks and manuscripts, and a handsome, carved oaken laboratory stool that his father had inherited from A. W. von Hofmann in Berlin (3, 73, 78).

With the political climate in Germany deteriorating in the early 1930s, Hermann Fischer chose to accept a position at the University of Basel in Switzerland in 1932 and Emil Fischer's entire sample collection, his library, and laboratory stool began their international journey (73, 78).

As Europe moved towards war Hermann Fischer did not want his sons to serve in the army for a cause in which they and he did not believe (73). In 1937 Hermann Fischer accepted a position at the Banting Institute of the University of Toronto (73), and the Fischer lab moved once again, now crossing the Atlantic to North America.

In 1948 Hermann Fischer accepted the invitation of Wendell M. Stanley to join the Biochemistry and Virus Laboratory that he was organizing at the University of California at Berkeley, and the laboratory with its sample collection, library, and laboratory chair moved yet again (73, 78). At the official opening of the laboratory in 1952, Hermann Fischer donated his father's book collection to the university as the Emil Fischer Library (73).

The sample collection served as a reference for ongoing research and, according to Hermann Fischer, "made possible numerous identifications of interesting compounds" (73). It was used by Melvin Calvin to identify substances in his work on the carbon pathway in photosynthesis (79). With Emil Fischer's convention for the stereochemistry of sugars, this was one of the primary sources of stereochemical reference information. Fischer's convention stood for 60 years before being shown to be correct in 1951 (80).

A set of 30 peptide samples from Fischer's collection was analyzed in 1951, 50 years or so after their preparation. Paper chromatography showed that only three of these contained small amounts of one of their constituent amino acids in addition to the peptide; the other 27 samples were uncontaminated (81). Hydrolysis and analysis of small samples of several of these peptides showed only the described components (81). This is a remarkable testament to the caliber of work done by Fischer and to the integrity of the collection.

After Hermann Fischer's unexpected death in 1960, the care of the Fischer compound collection was assumed by Clinton Ballou, who had joined Hermann Fischer's lab in 1950. Ballou worked on numerous metabolic intermediates, and become Professor of Biochemistry at Berkeley in 1955 (82). Ballou continued to receive requests for reference samples from the collection, which he would honor as appropriate (83).

The compound collection and the laboratory stool were finally repatriated in 1983 when they were donated to the Deutsches Museum in Munich after a correspondence between Berkeley's Horace Barker and Ernst Otto Fischer at the Technical University at Munich (78, 84). The A. W. von Hofmann/Emil Fischer laboratory stool resided in Hermann Fischer's office until his death (78), after which it was displayed prominently in the Barker Hall Library at UC Berkeley (83). After its repatriation to Germany it found its way into the laboratories of Ernst Winnacker, a former postdoc of Barker's, in the Institute of Biochemistry at the University of Munich (79).

Emil Fischer's accumulated documents—his correspondence, laboratory notebooks, and manuscripts—were donated in 1970 to UC Berkeley's Bancroft Library by Mrs. Hermann Fischer (3, 85). Emil and Hermann Fischer's books moved in 1983 to the Marian Koshland Bioscience and Natural Resources Library in the Valley Life Sciences Building on the Berkeley campus, where they reside as of this writing (86, 87).

The compound collection contains some 9000 samples in vials and stoppered test tubes. The samples are carefully hand-labeled and packed in cigar boxes (Figure 3); this method of storage greatly simplified the samples' safe transport through so many moves (78). Each box is labeled with the name of the co-worker who collaborated on the work (78). Hermann Otto Laurence Fischer describes in his memoir the unique indexing system used for his father's collection: one looks up the compound to retrieve in the Collected Works of Emil Fischer (Emil Fischer Gesammelte Werke) (19, 29, 46, 47, 72, 77, 88, 89), finds the co-worker who did research on the compound, and then locates the cigar box that is labeled with

Figure 3. *A cigar box in Emil Fischer's compound collection with sealed test tubes containing compound samples prepared by Max Bergmann and Hans V. Neyman. Bergmann was a prominent member of the Fischer lab and did research on amino acids, sugars, and tannins; Neyman worked on furfural derivatives (3, 9). Photograph by Susanne Rehn-Taube. Copyright Deutsches Museum, Munich.*

that co-worker's name to retrieve the sample (73). One thus finds samples pertaining to innovative research that provided a wide array of techniques in organic chemistry, elucidated the structures of important classes of chemicals, and laid the groundwork for modern biochemistry.

After an improbable journey that lasted more than a century, Emil Fischer's compound collection has returned to its homeland near the institution where Fischer began his career. Residing in the Deutsches Museum in Munich, the collection contains samples from Fischer's work on dyes, purines, carbohydrates, peptides and proteins, glycerides, glycosides, tannins, and barbiturates—work that shaped major areas of biological chemistry. It endures as a tangible reminder of Emil Fischer's enormous contributions to chemistry.

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FROM CHEMICAL THEORY TO INDUSTRIAL CHEMISTRY: THE ECLECTIC CAREER OF GEOFFREY MARTIN

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Geoffrey Martin (Figure 1) was born on 29 January 1881 in Dover, England, one of several children of William and Grace (née Etheridge) Martin (1). At some point the family moved to Wales, where the father, a retired artillery officer who had served in India, began to develop mental problems that necessitated his confinement to the Joint Counties Lunatic Asylum in Carmarthen. The rest of the family then moved to nearby Haverfordwest, where Geoffrey received his secondary education at the local grammar school, followed in 1897 by his enrollment, at age 16, as a student at the Merchant Venturers' Technical College in Bristol.

By 1901 Martin had completed his undergraduate work at Bristol, which entitled him to a B.Sc. in chemistry with first class honors from the University of London, since at this time Merchant Venturers was not empowered to grant independent degrees of its own. This was followed by a four-year sojourn in Germany, where he spent the summer of 1902 at the University of Berlin attending the lectures of Warburg, Stark, Fock and Jahn. In the winter of 1902-1903 Martin transferred to the University of Kiel, where he attended the lectures of Martius, Stäckel, Pochhammer and Lenard, and where he met and married a German girl by the name of Anna Wentritt, by whom he would have two sons (2). Following a brief interlude at Leipzig, he finally landed at Rostock, where he remained until 1906, having received his Ph.D. in chemistry there in December of 1905 (3).

***Figure 1**. Geoffrey Martin (1881-1966).*

By 1907 Martin was back in England working as a Lecturer and Demonstrator at University College, Nottingham, and conducting research with Frederic Stanley Kipping on organosilicon chemistry. In 1910, after receiving a M.Sc. degree at Bristol, he moved to London, where he served as a Lecturer in Chemistry at Birkbeck College while simultaneously working on a D.Sc. degree at the University of London. This, his second doctoral degree, was granted in 1915, as well as yet a third, presumably external, doctorate from the University of Bristol the same year based on his published papers (4).

From this point on, Martin, at age 34, ceased to be associated with academia and instead embarked upon a bewilderingly diverse career as an industrial chemist—at least if we are to believe the numerous affiliations listed in his various books and papers and in his various entries in Poggendorff (5). Between 1915 and 1917, his list of industrial positions included Research Chemist with United Kingdom Chemical Products Co.; Managing Director of Abbey Chemical and Medical Supply Co. Ltd.; Research Chemist with Stockton-on-Trees Chemical Co., and Research Chemist with the Chemical Supply Co. in Barking. It is unclear whether all of these positions were held simultaneously or in rapid succession.

***Figure 2**. The original home the C.W.S. in Manchester as it looks today.*

In 1917 Martin became Director of Research for The Co-operative Wholesale Society or C.W.S. Ltd., of Manchester (Figure 2) (6, 7). This was one of several such societies born of the wholesale cooperative movement of the mid-19th century whose purpose was to obtain wholesale prices for food and other commodities for their members either by buying in bulk or establishing and running their own factories and farms (8). Martin was the first director of the C.W.S.'s newly established research and quality control laboratory that would eventually employ twenty-three university trained chemists and chemical engineers, and whose function was to ensure the quality of the co-operative's products and the purity of the raw materials used in their manufacture, as well as to develop new and improved methods of production. In a 1921 article describing the laboratory's operations, Martin reported that it was analyzing roughly 3000 samples per year and had issued an average of three patents per month on newly developed or improved techniques (9).

However, by late 1921 Martin was on the move once more and was now listing his employment as Director of Research for the British Portland Cement Association, followed in 1925 by Director of Research for Martin and Taylor Ltd. and Asheham Cement and Lime Co., as well as Technical Director for Hinde and Hardy Ltd, Silk, Dyers, Weavers, etc. in Norwich. Again it is not known whether these positions were held simultaneously or in rapid succession. However, the listing for Martin and Taylor Ltd. suggests that by the mid 1920s Martin may have gained some degree of stability by becoming part owner of his own business.

There is no entry for Martin in Poggendorff after 1938 and no listing of publications after 1931. This may simply be the result of a large lag time between submission of biographical data (1931) and actual publication (1938), coupled with the disruptions caused by the Second World War. The next volume of Poggendorff that would have contained Martin's name was not published until 1958 and by then Martin had almost certainly retired (he would have been 70 in 1951), though he did not die until 1966 at age 85 in his home borough of Brent in north London, having been predeceased by his wife the previous year.

Given the above barebones biography, why is Martin deserving of more historical attention than the average industrial chemist? The answer is that he was not only a prolific writer of papers and articles (Poggendorff lists at least 99 by 1931), he was also a prolific writer of books, of which he would author, coauthor, or edit at least 21. In addition, he also held well over 20 patents. As such, he is part of an almost uniquely 20th-century British tradition of prolific writers of chemical textbooks, monographs and reference works that includes such names as Joseph William Mellor (1869-1938), James Riddick Partington (1886-1965), Samuel Glasstone (1897-1986) and, more recently, Peter Atkins. And it is to his various books and more interesting papers that we must now turn.

Chemical Affinity and the Periodic Table

Soon after his arrival in Germany in the summer of 1902, Martin must have begun an extensive reading program in the chemical literature, as he was soon generating a steady stream of publications dealing with such diverse topics as the theory of solubility and osmotic pressure, the periodic table, the nature of valence, and the measurement of chemical affinity and its relation to other chemical and physical properties. Most of these appeared as short notes in the *Chemical News*, though a few longer contributions were also sent to the *Journal of Physical Chemistry*. Curiously the list (see previous section) of German professors given at the end of his first doctoral thesis, whose lectures he had attended during his years in Germany, did not include a single chemist, but rather only the names of various mathematicians and a few physicists, so the program for theoretical chemistry which he now began to formulate must have been largely the product of self tuition and his extensive reading.

Two of these papers were of particular importance to Martin's final program. The first of these, entitled "On a Method of Representing the Properties of Elements Graphically by Means of Characteristic Surfaces," appeared in the 7 October 1904 issue of the *Chemical News* (10). Here Martin proposed that, instead of plotting the properties of the elements as a function of their atomic weights so as to produce a two-dimensional periodic curve like the famous plot of atomic [i.e. molar] volume versus atomic weight first given by Lothar Meyer in 1870 (11), one should instead employ the short form of the periodic table as a grid lying in the *xy* plane and plot the corresponding property for each element along the *z* axis directly above its position in the periodic table. The result would then be a characteristic three-dimensional surface, rather than a two-dimensional curve, for the property in question.

Moreover, Martin proposed that these plots be used, not for just any chemical or physical property of the elements, but rather to display the chemical affinity of a given element towards all of other elements in the periodic table as measured by the heat of formation per equivalent of its compounds with each of these elements (12). In other words, there would be a separate plot, and hence a separate characteristic affinity surface for, say Li versus F, each simultaneously displaying its respective chemical affinities for all other elements in the periodic table. Martin believed that the affinity relations of an element, as displayed in such a plot, would ultimately be found to also determine all of its other properties as well, such as the solubilities and volatility of its compounds, their thermal stability, etc.

The basic premise of Martin's program was that chemically similar elements should have similarly shaped affinity surfaces (Figure 3) and that, consequently, such surfaces could be used to measure the degree of chemical relatedness of various elements within the periodic table. He was also aware that, since most elements displayed a range of possible valence values (or oxidation states in modern parlance) and affinity varied with valence, complete characterization of an element would ultimately require the construction of a separate affinity surface for each possible valence state. He also recognized that the affinity surface of an element would be both temperature and pressure dependent, and speculated that, by manipulating these parameters, it should be possible to equalize the properties of any two elements that were initially found to be dissimilar under ambient conditions, thus creating a chemical version of "corresponding states."

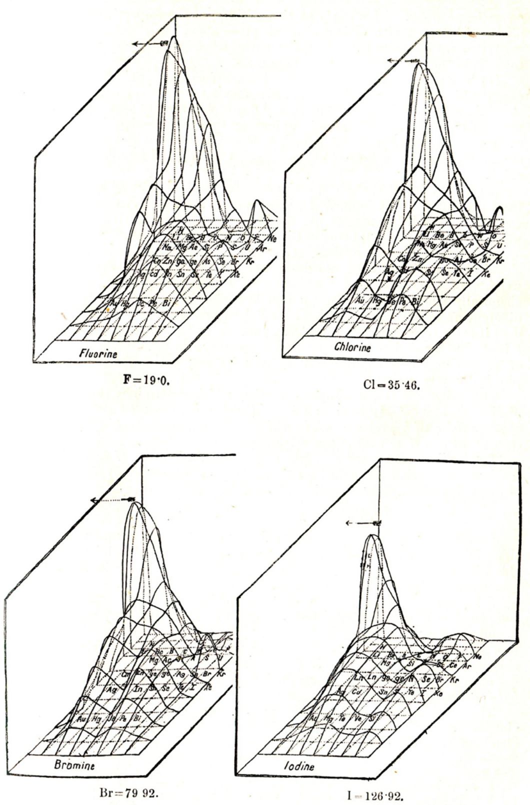

Figure 3*. Martin's characteristic affinity surfaces for the halogens F, Cl, Br, and I showing their similarity as members of the same group of the periodic table (13, p 17).*

The second paper, published in 1905 in the *Journal of Physical Chemistry*, was entitled "On the Condition which Determines the Chemical Similarity of Elements and Radicals" and proposed a more quantitative way of ascertaining how similar two elements were that went beyond a mere qualitative visual comparison of the shapes of their corresponding affinity surfaces (14). This involved calculating the ratio ($K_i = f_i/f_i'$) of their corresponding affinities values (f_i and f_i') towards a given third element *i*. If the two elements being compared really had identically shaped affinity surfaces, this ratio should be constant for the corresponding compounds of the two elements as one varied *i*. Thus, for example, if we wish to calculate how similar Cl and Br are, we would calculate the affinity ratios (K_i) for the formation of the chlorides and bromides of such metals as Ag, Li, Na, Hg, Sb, etc. If this ratio was approximately the same for all of the various metals, then the overall affinity surfaces of Cl and Br must also be approximately the same and the two elements rated as being chemically similar in their properties, whereas if the ratios varied widely in value then one must infer that the corresponding affinity surfaces have different shapes and that the two elements in question are chemically dissimilar.

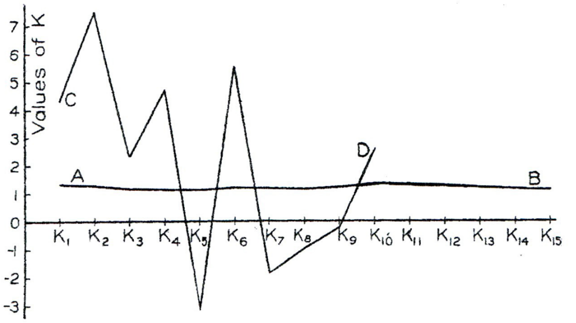

Figure 4*. Plots of the K ratios for various compounds of Cl and H (line CD) and for various compounds of Cl and Br (line AB) (14). The zigzag nature of the line for Cl and H indicates a lack of chemical similarity for these two elements whereas the nearly horizontal line for Cl and Br indicates a significant degree of chemical similarity.*

Martin illustrated this procedure using the graph in Figure 4 which shows a plot (CD) of the ratios obtained for various compounds of H and Cl versus the plot (AB) obtained for various compounds of Cl and Br. The widely varying values of K_i in the H/Cl plot show that these two elements are chemically dissimilar whereas the nearly constant values of K_i for the Cl/Br plot show that these two elements are chemically similar.

At the end of 1905 Martin expanded the results of these two papers, as well as several more minor points dealt with in some of his other notes to the *Chemical News*, into a 287-page book entitled *Researches on the Affinities of the Elements and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds* (15). In addition, in early 1906 he also submitted a brief summary of the book as his doctoral thesis at Rostock under the title of *Ueber das Affinitätsgesetz in dem periodischen System* (3). For lack of the necessary thermochemical data, Martin was able to construct the affinity surfaces under ambient conditions for only 34 elements. These he displayed in the form of a huge foldout chart tucked into a pocket inside the back cover of the book. In addition, many data points were missing even for the elements described, thus requiring some creative interpolation of the corresponding affinity surfaces.

Nevertheless, Martin's results, as may be seen from the affinity surfaces for the halogens in Figure 3, were truly impressive and allowed him to make some significant, and mostly correct, conclusions concerning the subject of chemical periodicity, which he summarized as follows:

1. The affinity surfaces of chemically similar elements are of a similar shape, and those of unlike elements of a dissimilar shape.

2. The form of the affinity surface of a metal is diametrically opposite that of a nonmetal.

3. The chemical inactivity of nitrogen is to a great extent only an apparent effect.

4. The affinity surface of hydrogen shows that it belongs to the alkali metals and not to the chlorine group of elements.

5. The point of maximum affinity shifts from F to Li as we pass from Li to F.

6. The chemical affinities of the heavy elements are in general much feebler than those of lighter elements.

Points 5 and 6 were based on Martin's observation that the maximum in the surfaces for the halogens occurred on the far left of the periodic table above the alkali metals, whereas that for the alkali metals occurred on the far right above the halogens. In the case of elements lying between the alkali metals and the halogens, the maximum gradually moved from left to right across a each period of the table and progressively decreased in magnitude as one movse from the top to the bottom of the table (Figure 5). Since the plots looked like a rolling wave, Martin called this result the "wave law of affinity in the periodic table."

Most textbooks of the period characterized nitrogen as having little chemical affinity for other elements, but Martin's plots revealed that this was not the case. While true that it had little affinity for the elements on the far left and right of the table, the plots showed that it had a significant affinity for elements near the center of the table, such as B and P, whence point 3 in the above list.

Reception of the book varied widely. The reviews in the *Chemical News* and in the *Journal of Physical Chemistry* were noncommittal and simply summarized the book's contents (16, 17). On the other hand, a rather lengthy review in the *Zeitschrift fur physikalische Chemie*, by none other than Wilhelm Ostwald himself, was quite favorable (18):

> We are here dealing with a research which deserves the most serious attention and encouragement ... One must recognize that here a quite unusual scientific imagination, taking the word in its best sense, has been at work, which leads one to look for far greater achievements in the future.

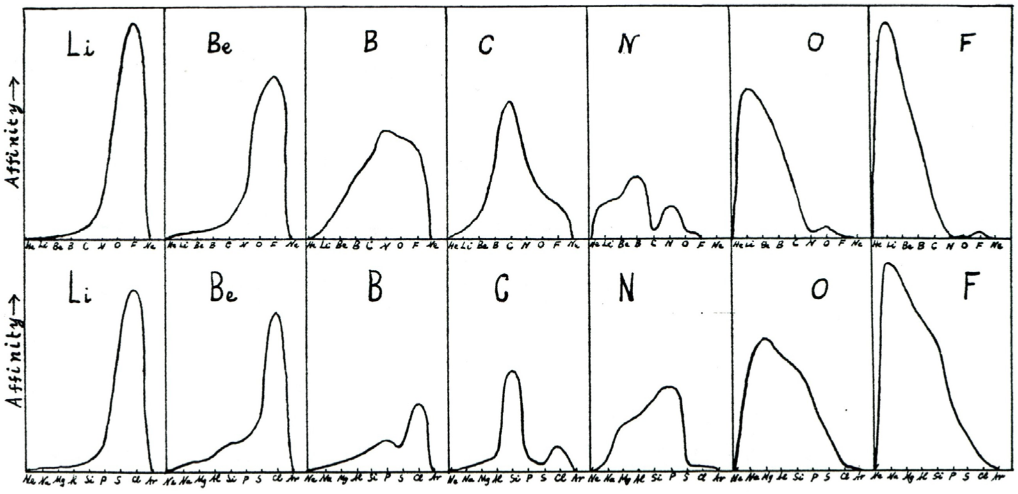

Figure 5. *Hand-drawn cross-sections through the affinity surfaces of the period 2 elements as shown in Martin's doctoral thesis of 1906 (3) showing their affinities for the other elements of period 2 and for the elements of period 3 and intended to illustrate Martin's wave law of chemical affinity.*

Similar positive comments occurred in the review in the *Philosophical Magazine* (19)

> This original and interesting work should strongly appeal to all interested in the wider generalizations of modern chemistry.

and in *The Oxford Magazine* (19)

> Chemists cannot fail to profit by reading it ... The great value of the book is that it puts things in a new way, and may help to change the textbook atmosphere which results in chemists seeing things, not as they are, but as they expect to find them.

Unhappily these favorable impressions were not shared by the book's anonymous reviewer for *Nature,* whose comments carried the suggestive title of "'Mathematics' Applied to Chemistry." The reasons for this title choice were spelled out in the first paragraph of the review which proceeded to attack Martin's preoccupation with mathematical formalisms (20):

> The word "mathematics" has been placed in the title of the review in inverted commas because, although the mathematical formulae employed appear formally correct, the application of mathematical formulae to the data in Mr. Martin's work appears to this reviewer to be unjustified.

After first summarizing Martin's mathematical analysis of the number of characteristic surfaces required to completely deal with all of the possible valence states of all of the known elements, the reviewer zeroed in on his primary objection (20):

> We have italicized the words "imagine a curved surface to be drawn through these points" because there lies the crux of Mr. Martin's attempt. Does he imagine that the interspaces are filled by an infinity of elements of all conceivable atomic weights between the known limits of 1 and 240? If not, then the whole system is discontinuous, and the characteristic surface is nonexistent.

Interestingly this mathematical objection is identical to that raised by Mendeleev 20 years earlier with respect to early attempts to reduce the periodic law to a mathematical function, as well as attempts to represent it using two-dimensional property-atomic weight plots like those of Lothar Meyer and later of Thomas Carnelley (21). It is, in many ways, spurious, since in most cases the purpose of the curves and surfaces connecting the discrete data points is merely to serve as a visual aid which allows the viewer to more easily see the variations in the actual data points. Even in cases where the authors attempted to represent this visual aid by means of an explicit continuous mathematical function (which Martin never did—his discussion of the curves is in very general mathematical terms and is largely concerned with the number of independent variables that would be necessary), the required "quantization," so to speak, comes not from the nature of the mathematical function itself, but rather from restrictions on the values of the independent variables that one is allowed to substitute into the function—a point which Martin also made in a brief answer to the review published the next month (22).

But this was not all. Following his criticism of Martin's overuse of mathematics, the reviewer proceeded to attack his use of heats of formation per equivalent as a measure of chemical affinity, and then concluded by criticizing the book's physical layout (20):

> A word in conclusion as to the "get up" of the book. The reviewer, in reading it, felt that he must act as a proof-reader. There is hardly a page on which a misprint does not occur; and such lapses as "The only data available is the following," the use of "uni-" and "tetra-valent" in one line, "to completely picture;" and the printing of almost every sentence as a paragraph, make the reader's task an ungrateful one.

Martin had no doubt rushed the book into print for fear he would be scooped by others, and having, at age 24, no colleagues or students of his own to burden with proof-reading the galleys, had done so himself—a procedure which every author soon discovers is fraught with danger, since one often sees what one intended to say rather than what is actually printed on the page.

Martin would later refer to this youthful work only once, in the introductory chapter of the volume on the chemistry of the halogens which he and Ernest Dancaster wrote in 1915 for the multivolume textbook of inorganic chemistry edited by J. Newton Friend (13). Here the affinity surfaces of the four nonradioactive halogens, shown earlier in Figure 3, were put to good use to provide a very insightful overview of the comparative chemistry of these elements. Beyond this, however, Martin's book and program for reformatting the descriptive inorganic chemistry of the elements seems to have almost immediately dropped out of sight. Since much of it concerned the use and extension of the periodic table, one would have thought that it would have at least been referenced in works on this subject. Unfortunately, though Martin referred to the periodic table in the title of his German doctoral thesis, no reference to it appears in the title of his book and thus no reference to it appears in either the 1909 monograph on the periodic table by Garrett (23) or the 1930 monograph by Rabinowitsch and Thilo (24). Nor does it appear in more modern histories of the periodic table, like that by van Spronsen (25).

The Rule of Eight

In May of 1902, while still at the University of Berlin, Martin published a short note in *The Chemical News* entitled "Note of the Mathematical Expression of the Valency Law of the Periodic Table, and the Necessity for Assuming that the Elements of its First Three Groups Are Polyvalent," in which he presented the graph in Figure 6 showing a plot of an element's highest (v_1) and lowest (v_2) valence values as a function of its group number (n) (26). All of the points on this graph were based on known valence values except those of the upper branch for groups 1-3 which are therefore distinguished using a dashed, rather than a solid line. Assuming that the predicted missing valence values on the dashed line segment would eventually be found to exist among the intermetallic compounds, Martin then derived a rather complex algebraic expression for the graph which he eventually reduced to the condition:

$$v_1 + v_2 = 8$$

and which he interpreted as implying that (26):

> ... the sum of the highest and lowest degrees of valence with which an element acts towards other elements is a constant whose value is 8.

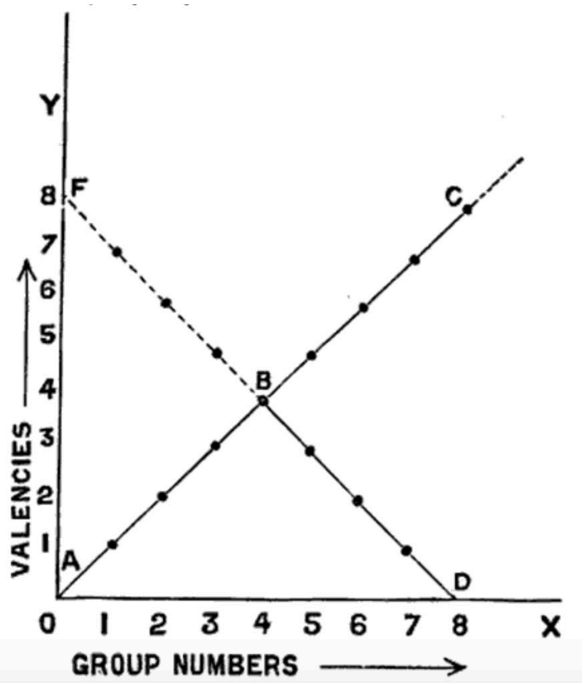

***Figure 6**. Martin's plot of the highest versus the lowest*

valence values of the elements in groups 1-8 of the periodic table (26). Those on line segment FB are hypothetical.

He then further elaborated on the significance of this result (26):

> This is a very remarkable relationship. It includes Mendeleev's observation that the total valency of an element both towards hydrogen and oxygen is 8. And for this reason: An element tends to act towards radicals of like electrical sign with its highest valence but towards radicals of opposite electrical sign with its lowest valence. Now hydrogen is electropositive and oxygen is electronegative. Therefore by observing the valence exhibited by any one element towards each of these two standard elements, we obtain at the same time the measure of its highest and lowest valence. Hence Mendeleev's law.

This is, of course, the well-known "Rule of Eight" usually attributed to the German chemist, Richard Abegg, who also first stated it in 1902 (27) and in much greater detail in 1904 (28). For many years the rule was a standard feature of inorganic textbooks, where it was always credited to Abegg alone, without any acknowledgement of Martin's presumably independent contribution (29, 30).

Electron Repulsion and Molecular Shape

The following year, after his move to Kiel, Martin published yet another note in the *Chemical News* with the rather cumbersome title of "Some Additional Remarks on the Connection Between Metals and Nonmetals and Its Bearing on the Valence Theory of Helmholtz and on Stereochemistry" (31). In his famous Faraday Lecture of 1881, Hermann von Helmholtz had proposed an electrical model of the atom in which valence was explained in terms of an excess of either mobile positive or mobile negative electrical particles (32). Though J. J. Thomson had characterized the electron in 1897, the Rutherford nuclear atom was still eight years away in 1903 and there continued to be much speculation as to where the necessary compensating positive charge resided in the atom. In short, what were essentially particulate versions of the older debate between the two-fluid versus the one-fluid theories of electricity were still going strong. Thus, as late as 1911, no less a luminary than Walther Nernst would opt, like Helmholtz before him, for the use of both positive and negative mobile electrons in his famous textbook on theoretical chemistry (33).

In this note Martin presented numerous arguments based on the transition between metals and nonmetals in support of the conclusion that only mobile negative electrons were involved in valence interactions and that the compensating positive charge had to reside somewhere in the interior of the atom and was itself nonmobile (31).

> We thus arrive at the conclusion that one, and only one, kind of electron causes the phenomenon of chemical valence. The electrons can cause an atom to appear either as electropositive [i.e. metallic] or electronegative [i.e. nonmetallic] in nature according as they are feebly or firmly held by the atom.

But what is of most interest is the manner in which Martin then used this conclusion to make some rather striking suggestions concerning the stereochemistry of various elements (31):

> This places us in a position to define the law of the special arrangement of the valence bonds on the surface of the atom. For electrons, being equally charged particles of like sign, repel each other with the same force. Therefore, in the case of a polyvalent spherical atom whereon several electrons are condensed by the attractive force of the material out of which the atom is composed, the mutual repulsions between the electrons will cause them to take up a position of equilibrium on the surface of the sphere such that each is as far removed as possible from its neighbor and, if possible, in a symmetrical position.
>
> Therefore the manner in which the electrons (and, consequently, valency bonds) distribute themselves over the surface of an atom depends only on the number of electrons and not at all on the nature of the material of which the atom is composed. The problem, therefore, of determining the shape of an atom of valency *n* is reduced to the problem of distributing *n* points as symmetrically as possible over the surface of a sphere.

Though Martin did not include an illustration of his model in his note, he did include a drawing (Figure 7) of what the model implied about the carbon atom in one of his later books (34).

Martin was neither the first nor the last to propose a repulsion model of molecular geometry (35), and in many ways his proposal was premature, since, at the time of his writing, only the inferred structures of organic chemistry, based on the van't Hoff tetrahedral carbon atom, and a few inferred octahedral and square-planar metal complexes, based on Werner's coordination theory, available for testing it. X-ray crystallography was still nearly a decade away and electron diffraction studies of discrete gas-phase molecules even further.

were

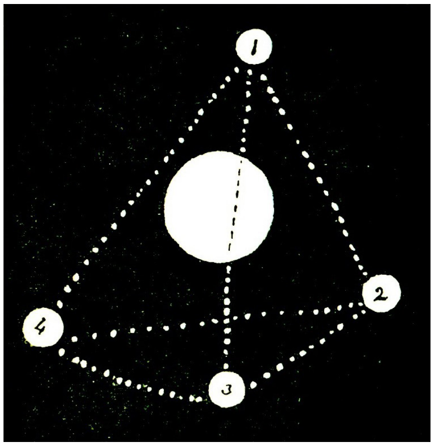

***Figure** 7. Martin's electron-repulsion model of the tetrahedral carbon atom (34, 1st ed., p 26).*

In addition, Martin had no idea of how many electrons were in a given atom, but was rather working backwards from classical valence values by inferring one electron per valence. This means he would have been unaware of the stereochemical consequences of nonbonding valence electrons so central to the final form of the successful Valence-Shell Electron-Pair Repulsion (VSEPR) model of molecular geometry finally proposed by Nyholm and Gillespie in 1957 (36).

Silicon as an Analog of Carbon

As noted earlier, Martin spent the first seven years (1907-1914) of his career in academia as a lecturer in introductory chemistry, first at University College, Nottingham and then at Birkbeck College in London, and during this time he published at least ten experimental papers on the chemistry of silicon in both the *Berichte* and in the *Journal of the Chemical Society* (37). Martin's interest in this subject actually went back to 1900 and his junior year as an undergraduate at Merchant Venturers' Technical College, when he had published a series of five articles in a popular journal called *Science Gossip* under the title of "Life Under Other Conditions" in which he speculated on the possibility of silicon life forms and which he reproduced as one of the appendices to his monograph of 1905 (38, 39).

As we have seen, one of the major premises of Martin's monograph was that the pattern of properties for the elements in the periodic table was pressure and temperature dependent and that it was possible to "equalize" the properties of two elements, especially if they were in the same group, by comparing them under widely different physical conditions. In particular, Martin postulated a "critical temperature and pressure" for each element's chemical compounds. This corresponded to an upper limit on their stabilities and represented the conditions under which they displayed a maximum in their reactivity. After first observing that carbon-based life was limited to a small temperature-pressure range, Martin wrote (38):

> I suggest that the temperature range of animal life is probably nothing more or less than the range of the critical temperature of decomposition of a series of certain very complex carbon compounds which are grouped together under the name "protoplasm," the external pressure of the atmosphere coinciding roughly with their critical pressures of decomposition.

Given this assumption, the next step was obvious (38):

> We are therefore justified in asking whether there is any other element which at some other temperature could play the part now played by carbon at ordinary temperatures in living organic matter?

as was Martin's answer to his rhetorical question (38):

> Silicon is such an element ... There probably exists for silicon, as well as for carbon, a transition or critical temperature range whereat a large number of unstable silicon compounds are capable of momentary existence, a higher temperature rendering their existence impossible, while a lower temperature would make the compounds stable. At this transitional temperature the complex compounds would be capable of a continual metathesis, and thus give rise to the phenomenon of life; only in this case all forms of life would have as the determining element not carbon, but silicon. Seeing that in the case of carbon this temperature occurs when many of its compounds are in a semi-fluid condition, and near their decomposing point, we should expect the corresponding temperature for silicon compounds to occur when they, too, are in a pasty or semi-fluid condition.

Last, but not least, Martin connected his speculations with the geological history of the earth, which he assumed had been formed via the gradual cooling of an originally molten mass (38):

> Have we any evidence which supports the view that living matter did not start originally with carbon, hydrogen, oxygen, and nitrogen as its fundamental elements, but started with elements of far higher atomic weights, such as silicon, phosphorus, and sulphur, of which only vestiges now remain in the protoplasm? It must be remembered that our evidence could only be indirect; such life could have thrilled to an enormous extent in the white hot molten siliceous matter which covered the earth's surface in by-gone ages, and yet

> have left no traces of its existence behind; for when such forms of life died, their bodies would but blend again into the molten rock, in the same way that a jelly-fish dies and blends into the ocean of salt water without leaving a vestige behind ...

In light of this interest, it is hardly surprising that Martin chose to move to University College, Nottingham, after his return from Germany in order to work with the British expert on silicon chemistry, Frederic Stanley Kipping (Figure 8). As early as 1899 Kipping had begun an intensive study of organosilicon compounds that would eventually span nearly four decades. Perhaps the most important contribution to come out of this work was Kipping's discovery of a new class of organosilicon oxygen derivatives known as the "silicones." Like his predecessors, Kipping, in his early work, naively assumed that analogous stoichiometry automatically implied analogous structure. Consequently, when he prepared a class of compounds having the general formula R_2SiO, he naturally thought that he had discovered the alkyl silane analogs of the ketones R_2SiO—whence his use of the name "silicones"—a term equaled in the annals of chemical nomenclature for its misleading implications only by Lavoisier's equally naive assumption that the composition of sugars and starches implied that they were literally hydrates of carbon.

Figure 8. *Frederic Stanley Kipping (1863-1949).*

However, by the time Kipping delivered his 1936 Bakerian Lecture on "Organic Derivatives of Silicon," summarizing his life's work, time and experience had considerably dampened his earlier enthusiasm for the possibility of a silicon-modified organic chemistry (40):

> Even after a very short experience, it was evident that corresponding derivatives of the two elements in question showed very considerable differences in their chemical properties; it may now be said that the principal, if not the only, case in which they exhibit a really close resemblance is that of the paraffins and those particular silicohydrocarbons containing a silicon atom directly united to four alkyl radicals. But of far greater importance in any general comparison of carbon compounds with the organic derivatives of silicon is the fact that many, if not most, of the more important types of the former are not represented among the latter. Apparently this is not merely a consequence of the insufficient experimental investigation of silicon derivatives but is due to the fundamental differences in the properties of the atoms of silicon and carbon ...

In other words, after 40 years of research, Kipping had come to the conclusion that even the weak form of the carbon-silicon analogy was defective, and subsequent work would soon show that his pessimism was fully justified.

Whether Martin experienced a similar sense of disillusionment is not known. In any case, his three-year sojourn with Kipping resulted in only one joint publication (41), as well as two authored by Martin alone, with the majority of Martin's work in this area being done after his move to London. There it served as the basis of his 1915 doctoral thesis at the University of London on *The Preparation of Silicon Tetrachloride and Disilicon Hexachloride* (4).

Textbooks and Popularizations

In addition to the numerous research papers mentioned in the previous section, Martin's brief sojourn in academia also led to the publication of four books between 1907 and 1915 dealing with various aspects of chemical education. The first of these, published in 1907 while he was at Nottingham, was a conventional laboratory manual entitled *Practical Chemistry for Army and Matriculation Candidates and for Use in Schools*. Its overly descriptive title no doubt reflected the kinds of students Martin was dealing with and, indeed, his introduction indicates that he did not think very highly of some of them (42):

> The average army candidate does not seem to possess the slightest idea of the necessity of care in carrying out experiments. He works in a mess and with a complete disregard of all the precautions necessary to ensure accuracy.

This was followed in 1914 by a short monograph on teaching aids entitled *Modern Chemical Lecture Diagrams* (43) showing the various lecture charts Martin had developed for use in his introductory chemistry course at Birkbeck.

Interspersed among these publications were two thick books of more than 350 pages each that attempted to popularize recent advances in chemistry for the general public: *Triumphs and Wonders of Modern Chemistry*, which appeared in 1911 (34), and *Modern Chemistry and Its Wonders*, which appeared in 1915 (44). During the first two decades of the 20th century chemistry was experiencing a veritable revolution, due in large part to the advent of the electronic theory of matter and all that it implied for the theory of valence and chemical bonding. It was the excitement of this revolution that Martin hoped to share with his lay audience (34):

> It has been my lot while lecturing on chemistry to have come into frequent contact with many thoughtful men and women, boys and girls, who have felt much interest in this new chemistry, which has arisen out of the old, and who have wished to know something more of the grand questions of the day touching the ultimate nature and constitution of the universe in which they live, and of the matter which surrounds them on every side in untold millions of tons, but who have neither the leisure nor the inclination to master the technicalities and enter into the minutiae of the regular textbooks of chemistry where such things are discussed.

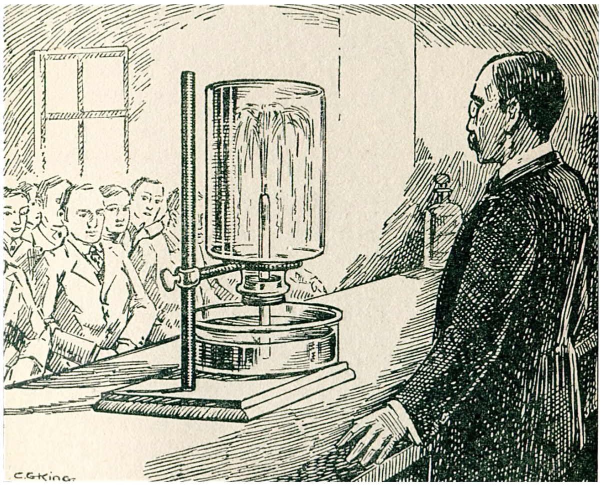

Figure 9. *An illustration from* Modern Chemistry and Its Wonders *(44) showing what is assumed to be Martin demonstrating the ammonia fountain to his class at Birkbeck College.*

The fact that this statement of intent was then followed by a trenchant criticism of the way in which chemistry was taught in Great Britain, suggests that Martin had found his years as a lecturer less than satisfying and may well explain his reasons for soon abandoning academia altogether (34):

> These textbooks, moreover, labor under the disadvantage that they are written for candidates for one or another of the innumerable examinations in which our university authorities take such keen delight, and which, combined with a complete lack of educational freedom, make an English university student's life a perfect nightmare to him (in sad contrast to that of a German or American student), and destroy rapidly and effectively any genuine interest in science he may have possessed at his entrance to the university, besides exercising a paralyzing effect on the university lecturers themselves, and diminishing greatly the output of research work in this country, to its incalculable material and moral harm.

In short, these two popular books apparently represented what Martin would have liked to tell his students but which he was unable to tell them in either his earlier laboratory manual or in his lectures, since he found himself trapped in a rigid system that reduced him to a mere drudge whose sole purpose was to cram enough predetermined rote information into his students to allow them to pass their qualifying examinations.

Both books were moderately successful. They were reprinted in the United States, translated into several foreign languages, and, via second editions, remained in print well into the 1920s. Both were also heavily illustrated with photographs and original line drawings, and several of the latter are still of interest to the historian. In the case of *Triumphs and Wonders*, these drawings include several speculative views of pre-Bohr and pre-Lewis atoms and molecules, of which the earlier drawing of the tetrahedral carbon atom (recall Figure 7) is an example, though most depicted flat solar system molecules with rotating swarms of peripheral atoms. In the case of *Modern Chemistry*, the drawings include several of a chemical lecturer performing various chemical demonstrations of which Figures 9 and 10 are typical examples. They all appear to depict the same lecture hall and a lecturer not unlike Martin in appearance, leading one to speculate whether the book's illustrator, C. G. King, might not have sat in on several of Martin's lectures in the old Breams building in Fetter Lane in order to make preliminary sketches for the book.

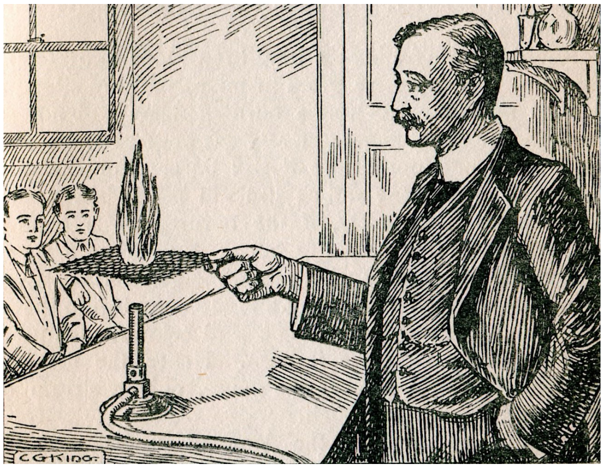

***Figure 10**. An illustration from* Modern Chemistry and Its Wonders *(44) showing what is assumed to be Martin demonstrating the principle of the Davy safety lamp to his class at Birkbeck College.*

Industrial Chemistry and Manufacturing Chemistry: Organic

In 1913, while he was still at Birkbeck, Martin's career as an author changed drastically when he published *Industrial and Manufacturing Chemistry. Organic. A Practical Treatise* with Crosby Lockwood & Co. of London, a massive tome of some 726 pages (45). This was only the beginning of a vast series of volumes relating to industrial chemistry. The inorganic volume of *Industrial and Manufacturing Chemistry* appeared belatedly in 1917 and both volumes went through several editions until the early 1950s. At the same time Crosby Lockwood produced a series of "Manuals of Chemical Technology" which would eventually run to nine volumes, eight of which were either authored or coauthored by Martin. This was not a stepwise process, fuelled by the success of the first volume, as it appears (as shown below) that the volumes were conceived at more or less the same time although their appearance was delayed mainly because of the First World War. While Martin was editor of these volumes, he also wrote much of the content as we will see, so their publication must have been a massive task.

How did this transformation in Martin's publications come about? Much depends on whether the initiative came from Martin or the publisher and without archival evidence we cannot be sure. However we can make an educated guess that the idea came from the publisher. The original firm had been founded by Mark Lockwood in the early nineteenth century and his son Crosby Lockwood took over the firm after his death in the 1850s (46). It published scientific and technical books ranging from advice for the general public to dense (and thick) engineering tomes. Martin's practical chemistry fitted well into the publisher's range. However in the first decade of the twentieth century, Crosby Lockwood was not publishing many chemistry books; only six appear in the online catalogue COPAC under the keyword "chemistry" between 1901 and 1910.

Given the time needed to produce the first volume of *Industrial and Manufacturing Chemistry*, the origins of the monograph and its associated series must have begun early in Martin's career at Birkbeck and may have even be precipitated by his newly found geographical proximity to the publisher in Ludgate Hill, only five minutes' walk from Fetter Lane. Furthermore most of the teaching at Birkbeck College was in the evening, leaving Martin free to visit the publisher and do research—possibly in the Patent Office Library off Chancery Lane, which would have been another five minute walk—and write.

In the preface to the first volume of *Industrial and Manufacturing Chemistry,* dealing with organic chemistry, Martin makes no reference to its gestation, but states (45):

> This book is a treatise on the applications of Organic Chemistry to the arts and manufactures. It embraces both British and American practice, and affords, so far as is ascertainable in view of the many secret processes employed, thoroughly up-to-date information regarding the various branches of chemical industry and of manufactures having a chemical basis.

As far as the intended audience, Martin aimed to cast his net as wide as possible (45):

> … the book will serve either as a text-book or as a work of reference; it is intended to meet the requirements of all business and practical men interested in chemical processes, of manufacturers, consulting chemists, chemical engineers, patent workers, inventors, technical lawyers, students in technical institutions, lecturers on technology, fire insurance inspectors, and others.

In the preface for the seventh edition in 1954, the new editor, Edward Cooke, tried to cast the net even further, "this book is thoroughly recommended to sixth-form and university students deciding on their future career, and to all who wish to know more of British Industry." In practice, the main market was probably libraries and larger chemical works. Students of industrial chemistry would have more likely have used a shorter book such as Frank Hall Thorp's *Outlines of Industrial Chemistry*

(47) which first appeared in 1898, although they would have probably consulted Martin's volume in the college library for additional details.

The organic chemical industry, as we understand it today, hardly existed in 1913 and most of the industrial sectors covered in this volume would hardly be considered to be organic chemicals nowadays. One finds not only aliphatic chemicals, coal tar chemicals, synthetic dyes, synthetic drugs and photographic chemicals, but also milk and cheese, sugar, wine and beer, paint and ink, and explosives. The text is entirely descriptive with an emphasis on the details of processes accompanied by drawings of the equipment used. There is no attempt to draw general principles from these processes or to teach industrial chemistry in a systematic way.

However there is a clear intention to be up-to-date as possible and an interesting example of this is the section of synthetic rubber. It was written by Martin himself and was clearly a late addition as the pagination for this segment is 366, then 366a-336h. The publishers obviously wished to capitalize on the upsurge of interest in synthetic rubber in 1912 following the work of Strange & Graham (collaborating with William Henry Perkin Jr and Chaim Weizmann), Fritz Hofmann at Bayer (collaborating with Carl Harries) and Ivan Kondakov in Russia (48).

Given the length of the volume (624 pages of text) and his lack of any direct experience of the chemical industry, one might have thought that Martin would have simply been the editor, but in fact he wrote much of it himself. He wrote 34% on his own and a further 29% with co-authors. The segments he wrote are rather random and one strongly suspects that he wrote those segments for which he could not find an expert author. This impression is reinforced by the fact that many of his segments are short, whereas the co-authored segments (and the segments by other authors) are usually longer. The average lengths of the 26 segments written solely by Martin is 8.1 pages, whereas the 15 segments written by others are an average of 15.3 pages long. The 13 segments co-authored by Martin are similar with an average of 13.9 pages.

How did Martin write his segments given his lack of industrial experience? He relied heavily on the published literature and his expert advisors, notably W. H. Stephens (49). Stephens was about the same age as Martin and a graduate of the Royal College of Science in 1903 (which became part of Imperial College four years later). He was a patent agent and Martin may have met him at the Patent Office Library. One thus gains the impression that much of the volume was based on the published literature rather than practical experience. It is striking that when Martin did not have an expert to fall back on or an established literature, his segments were very short, for example three pages for synthetic perfumes.

The main rival to the organic chemistry volume when it was published was Samuel Sadtler's *Industrial Organic Chemistry*, first published by J. B. Lippincott in 1892 with a fourth edition in 1912 (50). Sadtler was a leading consulting chemist in Philadelphia and a former professor of organic and industrial chemistry at the University of Pennsylvania (51). The two books are a similar size (559 pages of text compared with 624 for Martin) and discuss many of the same topics, such as fats, sugar, milk, textiles and dyes. Sadtler does not cover paint and ink or explosives and gives scant attention to rubber. More surprisingly he does not include synthetic drugs or photographic chemicals. By contrast, only the subject of "bread" is missing from Martin.

Industrial Organic Chemicals has a very regular structure in that every chapter deals with processes, products and analysis in turn. The addition of analysis would have made Sadtler's tome more useful to industrial chemists but the division of processes and products seems guaranteed to generate repetition. In their details and style, the two books are very similar. They are both aimed at the manufacturer and for reference rather than teaching.

Another competitor to Martin's book was *Industrial Chemistry: A Manual*, first published by van Nostrand in 1912 (52). Edited by Allen Rogers of the Pratt Institute, Brooklyn, and Alfred Aubert of the University of Maine, it had a large cast of authors, who in contrast to Martin, wrote most of the chapters. Once again, its coverage and style were very similar to Martin. The general structure of the chapters is in fact very close to *Industrial and Manufacturing Chemistry*, being a string of topics rather than Sadtler's more systematic approach. Like Martin, Rogers and Aubert cover explosives (but not drugs and photographic chemicals), but their treatment of inorganic chemicals is not as good. They do not devote a chapter to alkali manufacture for example (it is covered in "Commercial Chemicals"), but there are two chapters on white lead which is only covered by Martin briefly under pigments (in the organic volume no less!). Both books deal with construction materials and metallurgy. The most striking aspect is the wealth of illustrations which exceeds even the large number in Martin's volumes, whereas Sadtler's volume is relatively restrained in its use of illustrations.

The outbreak of the First World War in early August of 1914 soon showed the importance of the organic chemical industry and the dangerous reliance of the Allied countries on imports from Germany. This gave heightened importance to the development of the industry in Britain and it is perhaps not surprising that Crosby Lockwood quickly produced a second edition of the of the organic volume, although the inorganic volumes were yet to appear (53). The preface to the second edition, dated May 1915, curiously made no reference to the war and its impact on organic chemicals, but highlighted various improvements including a new section on rubber analysis (3 pages) by Martin's near namesake Gerald Martin, and a list of synthetic drugs and photographic developers. The section on rubber analysis was a new departure for *Industrial and Manufacturing Chemistry* which, in contrast to Sadtler, had hitherto not covered analysis.

However most of the changes were minor. For example, a new article on acetylene by Frank Gatehouse (54), the editor of journal *Acetylene Lighting and Welding*, was only a page longer than the section on acetylene in the previous edition and had little more to say about the burgeoning use of acetylene in the wartime chemical industry—in fact a prescient reference to the use of acetylene in synthetic rubber manufacture was dropped. The changes are so small in fact that the publisher did not change the pagination from the previous edition, using letters for new pages (e.g. 365a for a new half-page on rubber statistics). This slow evolution—amounting to little more than the updating of statistics and correction of errors—was to be an enduring feature of the later editions of *Industrial and Manufacturing Chemistry*.

Industrial Chemistry and Manufacturing Chemistry: Inorganic

It is a puzzling feature of *Industrial and Manufacturing Chemistry* that the less important branch of the industry was covered first, even if the subsequent war showed its importance. It was probably originally intended that the volume on the inorganic chemical industry be published at the same time as organic or at least shortly afterwards. For whatever reason the appearance of the inorganic volume was delayed and the outbreak of the war was a further complication as explained in the preface of December 1916 (55):

> The work which has been carried out on the lines of the previous treatise, has been written under very formidable difficulties, for not only have several years been spent in its compilation, but before its completion the great War broke out and dispersed many of the contributors in the fighting ranks throughout the world, one at least, the late Major L. Foucar, having been killed in action before his article could be completed. It is a great satisfaction to the Editor that he has been able to bring his task to a conclusion in spite of these obstacles.

Major Louis Foucar was killed in the Second Battle of Ypres on 8 May 1915 at the age of 32 but has no known grave; he is commemorated on the Menin Gate (56). This battle is of course best known for the first use of chlorine as a chemical weapon by the Germans under the direction of Fritz Haber (57). Ironically, liquid chlorine is the subject of one of the chapters in this volume, although it was written by Martin. Foucar wrote the sections about sulphur, sulphuric acid and sulphur dioxide (which were completed by Martin).

The inorganic section finally appeared in 1917 in two volumes (55). It covers a remarkably wide range of material, far beyond what we would consider to be the inorganic chemical industry today, but as we have seen this was true of other books on the chemical industry in this period. Hence it covers fuels, furnaces, building materials (including lutes), ceramics, glass, asbestos and matches. A particular feature of the second volume is the material on minor elements such as zirconium, tantalum and the radioactive elements, which were also hived off as one of the manuals of chemical technology under the editorship of Sydney Johnstone. Of course all the standard branches of the inorganic chemical industry were covered, such as the major acids, alkalis, industrial gases, chlorine, ammonia and nitrates, and industrial fertilizers. It is interesting to note that antiseptics and disinfectants are covered in the second inorganic volume despite the fact that many of them were organic. Martin apologized for this mismatch, noting that "the removal of them [i.e. organic antiseptics] from such sections would largely destroy their value." One suspects, however, that antiseptics and disinfectants were added once the war had demonstrated their importance. Insecticides and fungicides are also in this volume but they were almost solely inorganic compounds in this period. Needless to say, the style is identical to the organic volume, namely a series of well-illustrated descriptions of processes and products.

Manuals of Chemical Technology

The manuals of chemical technology began to appear in 1915, two years before the inorganic volumes of *Industrial and Manufacturing Chemistry* were published (58). It might be thought that they were produced to capitalize on the sudden interest in chemical technology as a result of the First World War breaking out. Certainly some of the titles seem to address that interest, namely dyestuffs, nitrogen products and industrial gases, even one on chlorine. The preface to the dyestuffs volume said that (58a):

> The lack of an English book on the subject, the sudden stoppage of the supply of German fine chemicals, and the preparations of the British Government for the establishment on a large scale of the synthetic dye industry in this country, all combine to provide opportunity and justification for the appearance of the present volume.

However publications take time to be produced and the series was probably conceived at the same time as the main volumes and the reason why they first appeared in 1915 was the delayed publication of the inorganic volume of the main work.

These manuals were not additions to the main book but extracts from it. Clearly the publisher aimed to sell the expensive and large *Industrial and Manufacturing Chemistry* to libraries and the larger manufacturers while producing the shorter manuals for smaller more specialized firms and individual chemists. The title page of the dyestuffs volume refers to "additions" which seem to be entirely restricted, as far as we can determine, to an updating of the figures for synthetic indigo production from 1910 to 1913. The reason for this is simple. If any significant updating or expansion of the text had taken place, the publisher would not have been able to use the same plates (as clearly they did) and this would have made the spin-offs uneconomic. Most of the manuals follow the same order as the original source, but the chapters were moved round in the dyestuffs volume (to its improvement, it has to be said) and the segment on saccharine (one page!) slotted in on page 116A, seemingly as an afterthought.

A Change of Career

The publications of these volumes also reflect a major change in Martin's career from 1915 onwards, as already mentioned in our earlier biographical summary. It is striking that in the organic volume, published when he was still at Birkbeck, he describes himself on the title page, first and foremost, as an "Industrial Chemist and Chemical Patent Expert" despite the fact that, at this point in his career, he had never worked in industry nor trained as a patent agent. One suspects that the latter title simply refers to his use of the Patent Office Library. By early 1917 (even before his move to C.W.S.), Martin was calling himself a "technological chemist and chemical engineer," perhaps reflecting his personal shift from academia and the Patent Office Library to the chemical industry and the general shift from industrial chemistry to chemical engineering which had been accelerated by the First World War. However his qualifications as a chemical engineer appear to be as equally tenuous as his claim to be a patent expert. Certainly his personal transformation into a chemical engineer is not reflected in any change of approach in *Industrial and Manufacturing Chemistry*.

It is interesting to reflect on whether his departure from academia was a consequence of his work on *Industrial and Manufacturing Chemistry* or his work on these volumes a reflection of his desire to leave academia. It is perhaps suggestive that Martin comments in his preface to the organic volume (45):

> Matters calling for industrial research have been specially emphasized by the editor; for he has recognised that the subject of chemical industry is not only one which is full of problems whose solution demands the highest technical skill, but also one that holds out prizes of very great value for the scientific worker.

Either way, his editorship of a major work on industrial chemistry would have strengthened his ability to find a post in industry. The urgent need to start producing chemicals formerly imported from Germany after the outbreak of war in August 1914 would have increased the value of his expertise (albeit mostly obtained from books) to chemical firms.

The Modern Soap and Detergent Industry

Martin's books written after the publication of *Industrial and Manufacturing Chemistry* were closely allied to his work and were authored solely by himself rather being co-authored by experts on specific topics. Soap manufacture was a major activity for the Co-operative Wholesale Society as it made its own soap in order to undercut the oligopolistic commercial soap producers, and especially Lever Brothers. So intense was the competition between the Co-op and Levers, that Lever Brothers took the alkali firm of Brunner Mond to court in 1924 for fraudulently selling alkali more cheaply to the Co-op (59). As a result, Brunner Mond had to pay Lever Brothers heavy damages and Roscoe Brunner, the disgraced chairman of Brunner Mond, committed suicide. Against this dramatic background, Martin published a three volume work on *The Modern Soap and Detergent Industry including Glycerol Manufacture* between 1924 and 1926 (60). In the preface, Martin noted that "[a]t the present time no complete work exists dealing with the soap and detergent industry in all its branches" and the book appears to have been popular as a second edition appeared in 1931, but curiously the third volume (on glycerol) was not republished and a revised version did not appear until 1956.

Cement Chemistry

In 1928, Martin published *A Treatise on Chemical Engineering*, but this was not directly an attempt to capitalize on the increasingly important discipline of chemical engineering as one might expect. In the preface, Martin writes (61):

> When in 1921 the author was appointed Director of Research to the British Portland Cement Research Association he found an almost unbelievable state of technical inefficiency in the cement industry, owing to the fact that much of the plant had been designed in ignorance of the laws regulating the flow of fluids. … It is the object of this work to remedy this state of affairs by providing the chemical and mechanical engineer and works chemist with scientific means for calculating the flow of fluids of all kinds, and practical methods for estimating their speeds and volumes, with a view to more efficient plant design.

On the title page of this book Martin no longer refers to himself as an industrial chemist or a Fellow of the Chemical Society (as he did only three years earlier), but as a Consulting Chemical Engineer and Works Contractor and a Fellow of the Physical Society. Two tables in this volume were spun out in the now customary manner as the monograph, *Volume and Weights of Industrial Gases,* in 1930 (which was republished in a revised and enlarged edition by Wilfred Francis in 1953) (62). Martin also published a more specialized volume on *Chemical Engineering and Thermodynamics Applied to The Cement Rotary Kiln* in 1932 which also clearly arose out of his earlier work at the British Portland Cement Research Association (63).

Later Reprints and Revisions

Having produced (or revised) a volume on industrial chemistry every few years from 1913 onwards, Martin did not publish any further books after 1932 and one must wonder why—though no obvious reason (apart from possible ill health) presents itself. The Technical Press (which we assume was a subsidiary of Crosby, Lockwood, as the latter existed until 1972) produced a seventh edition of the organic volume of *Industrial and Manufacturing Chemistry* in 1952 (64). This was edited by Edward Ingram Cooke, a chemist who appears to have been a writer and editor who also updated William Gardner's *Chemical Synonyms* from 1948 onwards (65). It is stated in the preface that the fuel-related sections had been updated, but the chapter on synthetic rubber, for example, barely reflected the development of the industry in the Second World War. Similarly the chapter on aliphatic chemicals was only updated with "slight additions." A sixth edition of the inorganic volume followed two years later, edited by Wilfrid Francis (66). Again the changes were largely a minor updating of the chapters.

This minimalist approach to updating is in sharp contrast to the radical revision of the sixth edition of Allen Rogers' *Industrial Chemistry* in 1942 by Clifford Cook Furnas of Yale University (67), who was a chemical engineer, as well as an Olympic athlete and a future Assistant Secretary of Defense under Eisenhower. The key to his revision was a complete new slate of authors for the chapters rather than the piecemeal tinkering of the Martin volumes. Seemingly lacking the resources or will for this scale of revision and facing competition from more modern American works such as the new version of Rogers, Emil Raymond Riegel's *Industrial Chemistry* which was first published in 1928 and completely updated in 1962 (68), and the *Kirk-Othmer Encyclopedia of Chemical Technology,* which first appeared in fifteen volumes between 1947 and 1956 (69), Crosby Lockwood never produced another edition of either part.

The last book to appear under Martin's name was *Glycerol*, published as a single volume in 1956 (70) rather than as part of *The Modern Soap and Detergents Industry* (the other two volumes had been republished under the editorship of Edward Cooke in 1950-1951) (71). Once again, the revision (even after a gap of thirty years) is only a modest updating of the chapters with no change to the structure of the book. In common with the other volumes published in the 1950s, the preface makes no mention of Martin, which is curious as Martin would have been 75 in 1956 and he lived for another ten years. Even if he was not able (or willing) to edit any volumes in the 1950s, it would have been customary to pay tribute to the founder of the series. This makes us wonder if there might have been a falling out between Martin and The Technical Press.

Some Conclusions

In reviewing the life and career of Geoffrey Martin, one is left with the impression that, despite his prolific publication record, he remained something of an outsider with regard to the early 20th-century chemical community. Aside from his brief association with Kipping at Nottingham, he seems to have had no academic mentors. His thesis at Rostock was based on his book on affinity surfaces and lists no doctoral advisor. Likewise no advisor is given for his doctoral degree from the University of London and his doctoral degree from Bristol, as already noted, was external and was based on his published papers. In short, all three degrees were based on his own independent ideas and research. Even his brief foray into silicon chemistry seems to have been driven more by his interest as an undergraduate in the possibility of silicon life forms than by an admiration for Kipping's work.

This apparent absence of influential contacts within the academic community doubtlessly played a role in condemning Martin to a series of low-paying, temporary, academic positions that eventually forced him to eke out a living as an industrial chemist. Both the fact that his major conceptual contribution to chemistry —the affinity surface—failed to attract any substantive interest among his fellow chemists, and the fact that by 1913 he also had a wife and two children to support, almost certainly contributed to his decision to change careers as well.

As for his many books and published papers, it is difficult to believe that the former were a source of any significant income and, with the exception of the volumes on industrial chemistry, most fell still-born from the press. In lieu of any significant social contacts, Martin appears to have instead used writing as his preferred medium for interacting with his fellow chemists. And here Martin's instincts were, in a sense, sound, for if he can be said to have left a chemical legacy, it is to be found in the form of his many books, and especially in those dealing with industrial chemistry.

In the final analysis, Martin's life and career illustrate many of the trials and tribulations facing an early 20th century chemist in Great Britain and are certainly worthy of being recorded for posterity.

A Personal Tribute

One of the authors (PM) has an emotional attachment to Martin's *Industrial and Manufacturing Chemistry*. His school had a policy of awarding some of its annual prizes by an essay competition and one year, when Morris was fifteen (hence 1971), the topic of the chemistry essay was an industrial chemistry one. He duly visited his local public reference library (which was still well stocked in these days of long ago), and in the basement he found a copy of *Industrial and Manufacturing Chemistry* (probably several editions as he recalls a run of several feet) which had clearly not been used for some considerable time. In amazement he read detailed accounts of bygone processes complete with numerous line drawings. The memory has always remained strong and is one of the motivations for this paper. Sadly, recent enquiries have (unsurprisingly) revealed that the volumes were probably thrown out a couple of decades ago at least.

References and Notes

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THE LEGACY OF TETRAETHYL LEAD

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Abstract

Accounts of lead exposure are sprinkled throughout human history. Lead poisoning remained a rare disorder, confined mostly to mine workers, until the early 20th century when lead found its way into the consumer market in the form of lead solder on food cans, paints, pesticides, toothpaste packaging and water stored in lead-lined tanks. However, it was the introduction of tetraethyl lead, a gasoline additive that prevents common engine knocking, that dramatically introduced lead into the Earth's biosphere. Tetraethyl lead increased lead levels in every inhabitant of earth, and years after the protracted battle to ban lead from gasoline, remains a legacy that is with us today and in our bodies.

Introduction

The first significant mining and refining of metallic lead is recorded around 3000 BCE. Hippocrates is credited with the first account of lead poisoning (370 BCE), but the first clinical account comes from the Greek physician Nicander (200 BCE), who describes the characteristic palsy and dull pallor associated with lead poisoning (1). In the ancient world, lead miners were the most likely to be exposed, but lead was also used in cooking utensils and added to food in the form of a sweet-tasting syrup called "sapa," containing a mixture of one gram of lead per liter of grapes (1, 2).

During the Middle Ages, lead was widely used by alchemists in their attempts to convert base metals to gold, and in a more insidious ways, it was sometimes used as a poison. In the New World, lead mining and smelting began almost as soon as the first colonists had settled. The low melting point of lead made it malleable, and it was also resistant to corrosion. During the 19th century lead made its way into the consumer market in the form of food cans sealed with lead solder and water stored in lead-lined tanks. By the time tetraethyl lead was introduced into gasoline, lead was already in many consumer items.

Biological Fate of Lead

Through most of history, lead poisoning was limited to individuals working with lead directly or those drinking wine out of contaminated containers (3). Charles Dickens writes of lead poisoning in his book the *Uncommercial Traveler* (4),

> The lead, Sur. Sure 'tis the lead-mills, where the women gets took on at eighteen-pence a day, Sur, when they makes applicaytion early enough, and is lucky and wanted; and 'tis lead-pisoned she is, Sur, and some of them gits lead-pisoned soon, and some of them gets lead-pisoned later, and some, but not many, niver; and 'tis all according to the constitooshun, Sur, and some constitooshuns is strong, and some is weak; and her constitooshunis lead-pisoned, bad as can be, Sur, and her brain is coming out at her ear,

> and it hurts her dreadful; and that's what it is, and niver no more, and niver no less, Sur.

Lead is a known inhibitor of protein function, and proteins that utilize a divalent cation such as Zn^{2+} and Fe^{2+} are particularly sensitive to inhibition from lead (5, 6). Lead enters the human body through ingestion, inhalation or dermally in the case of organic lead. Once in the human body, lead can be found in the blood, mineralizing tissues (bones) and soft tissue. In times of stress, like pregnancy or lactation, the body can mobilize lead and thereby increase blood levels. The human body accumulates lead over a lifetime and releases it slowly (7).

Lead is a neurotoxin, and the nervous system is the most sensitive target of lead exposure (8). It can produce irreparable damage to the nervous system and resulting symptoms are blindness, insomnia, kidney failure, hearing loss, palsies, convulsions and eventually death.

Children suffer neurological effects at much lower exposure levels. There is a large body of evidence that associates decreases in IQ performance and other neuropsychological defects with lead exposure (9, 10). Lead interferes with a hormonal form of vitamin D, which affects multiple processes in the body, including cell maturation and skeletal growth. Lead also interferes with the body's ability to make hemoglobin by interfering with several enzymatic steps in the heme pathway. Maternal blood lead from exogenous and endogenous sources can cross the placenta and put the fetus at risk (10).

Today lead levels in the environment are much higher than in the 19th century, and levels found today in most people are orders of magnitude greater than those of ancient times (11). The circumstance that significantly increased lead levels in the bodies of every animal on the food chain was the addition of tetraethyl lead to gasoline.

Invention of Leaded Gasoline: Tetraethyl Lead as a Gasoline Additive

Thomas Midgley (1889-1944) played a significant role in the introduction of tetraethyl lead into gasoline. Midgley majored in mechanical engineering at Cornell University, and in 1916 he joined Dayton Engineering where he was given the assignment to work on a way to prevent engine knock (12). Engine knock was the metal on metal pinging sound that occurred in an internal combustion engine and one cause of fuel inefficiency.

To eliminate this problem, Midgley first tried an oil-soluble dye with iodine, which proved too expensive. In 1921, he discovered several antiknock agents, but all had a terrible stench. Midgley noticed that almost every successful anti knock agent was made of heavier elements like tellurium or selenium, so lead seemed like a good candidate.

Carl Jacob Löwig was the first to report the preparation of an alkyl lead compound in 1853 (13). The field of organometallic chemistry had begun in earnest in 1849 when Edward Frankland reported preparing the ethyl radical (actually butane) by the action of metallic zinc on ethyl iodide (14). Several years later, George Bowdler Buckton isolated and characterized pure tetraethyl lead (Figure 1) (15).

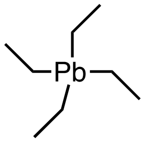

Figure 1. *Tetraethyl lead*

Midgley and his assistant Carroll Hochwalt turned to the procedure published more than 60 years prior, and in 1921, successfully prepared a tiny amount of tetraethyl lead in their laboratory (12). Midgley learned that 0.05% by volume of lead additive made fuel burn more slowly and prevented engine knock. Leaded gasoline gave greater power and better mileage. It appeared at the time that tetraethyl lead was the most effective and least expensive anti-knock compound.

As Midgley's laboratory developed tetraethyl lead, there were immediate health concerns. Physicians knew about acute lead poisoning among lead workers, and they understood that small amounts of lead accumulate in the body, but little was known about the long-term effects of low-level exposure to lead. At that time, there were no federal laws to require testing of new compounds for toxicity. The Environmental Protection Agency (EPA) and the National Institute of Occupational Safety and Health (NIOSH) were not created until 1970.

Although there were no federal regulations requiring him to do so, Midgley approached the US Bureau of Mines to examine the health hazards of exhaust from fuel burned with tetraethyl lead. He also devised his own experiments to find lead in automobile exhaust. At the time there were no instruments designed to detect small amounts of metals in the air, and he concluded that the exhaust contained no lead. However, after years of working with lead compounds both Midgley and his assistant developed symptoms of lead poisoning. As a precaution, he switched to using rubber gloves in the laboratory (12). Midgley was convinced that since lead was already contained in so many consumer products, the risk to the public was minimal and exposure in the laboratory could be avoided with proper precautions.

Gasoline containing tetraethyl lead went on sale to the public in 1923 and was given the name "Ethyl" (Figure 2). Car owners immediately noticed a difference. The additive stopped knocks, gave more power on hills and a cooler running engine. Ironically, it was already known that ethyl alcohol has a significantly higher heat of evaporation than gasoline providing a cooling effect, which helps reduce engine knock (16).

Midgley then turned his attention to solving the problem of modern refrigeration and developed chlorofluoromethanes for refrigeration and air-conditioning. These compounds were later linked to the destruction of the stratospheric ozone layer that protects earth from UV rays (17).

***Figure 2**. Early ad for gasoline containing tetraethyl lead (18), which first went on sale in 1923.*

Early Health Concerns about Tetraethyl Lead

During the first two years of leaded gasoline production, at least 15 tetraethyl lead workers died at different plants and dozens of others suffered the characteristic neurological symptoms of lead poisoning (19). The newspaper headlines called the fumes "Looney gas" when workers in a Du Pont factory became psychotic. During this time, the Bureau of Mines announced that the additive posed no peril (20).

Under pressure from scientists, activists and public health experts, the US Surgeon General convened a hearing in May of 1925 to examine possible public health consequences of the manufacture, distribution, or use of leaded gasoline (21). At the time, there was no data that examined how low-level chronic exposure to lead affects the human body (22). In January of 1926, the PHS (Public Health Service) committee released a report that found "no good grounds" for prohibiting Ethyl gasoline but recommended continued tests (23):

> It remains possible that, if the use of leaded gasoline becomes widespread, conditions may arise very different from those studied by us which would render its use more of a hazard than would appear to be the case from this investigation. Longer experience may show that even such slight storage of lead as was observed in these studies may lead eventually in susceptible individuals to recognizable lead poisoning or to chronic degenerative diseases of a less obvious character. In view of such possibilities the committee feels that the investigation begun under their direction must not be allowed to lapse…

By the 1960's tetraethyl lead was in 90% of fuel and was one of the most lucrative chemical enterprises in the United States.

The Age of the Earth and Lead-Contaminated Rock Samples

In 1948, in a seemingly unrelated area of science, a young geologist at the University of Chicago named Clair Patterson (1922-1995) began work on a project to determine the age of the earth. He was using a similar logic to that of Willard Libby who won the Nobel Prize for developing radiocarbon dating (24). Libby had been able to determine the age of organic remains by looking at the relative amounts of carbon-14 in samples using the half-life of 5,600 years. Patterson applied a similar technique, developed by Harrison Brown. The idea was to measure the decay rate of uranium to lead, calculate the age of rocks and ultimately determine the age of the earth. He assumed that the interior of meteorites, which were deposited during the formation of the earth, would have an unchanged interior chemistry, with the exception of radioactive decay (25).

Patterson immediately noticed unusually high lead contamination in his rock samples that were exposed to air. While at University of Chicago and later at California Institute of Technology, he devised a sterile laboratory to prevent contamination from environmental lead. In 1953, he announced at a meeting the age of the earth at 4,550 million years, a monumental breakthrough for which he was never awarded a Nobel Prize (26).

After completing his objective, he turned his attention to measuring lead in the atmosphere. Initially, Patterson collected samples and measured lead isotope ratios in oceans and ocean sediments. He measured lead on land, in layers of ocean water and sea floor sediments. Patterson secured funding through the American Petroleum Institute, which hoped that information about ocean sediments would locate oil.

Patterson and his postdoctoral fellow, Tsaihwa Chow, discovered a modern surge in the amount of lead flowing from rivers into the oceans. They compared lead to barium, which behaves like lead but is not heavily used in industry. Barium in terrestrial rocks and ocean sediment was essentially the control to compare with how lead should appear prior to industrialization. His conclusion: surface layers of the Pacific Ocean contained about 80 times more lead than expected in the natural erosion of igneous rocks on land. He also uncovered elevated lead levels in fresh snowfall, concluding that lead was airborne. The source was tetraethyl lead.

In 1963, Patterson published a paper in *Nature* describing industrial lead in snow and seawater (27). Representatives from the Ethyl Corporation immediately visited him. He carefully explained how their operations were poisoning the environment and people with lead, and one day this information would be used to shut down their operations. After that meeting the US Public Health Service refused to renew his research contract and the American Petroleum Institute discontinued funding. Lead industry officials pressed school trustees at California Institute of Technology to silence him or let him go (28).

To prove that atmospheric lead was caused by automobile exhaust, Patterson turned to ice-core samples. It was known at the time that snowfall in the Arctic accumulates into distinct layers with different colors for summer and winter. He was able to count through the layers and measure the amount of lead in each and essentially establish the concentration of lead in the atmosphere going back hundreds of years. This technique is also used in climate change studies to measure CO_2 levels since the industrial revolution. Patterson found that since 1923, when lead was introduced into gasoline, the level climbed steadily. He states, "…the average resident of the United States is being subjected to severe chronic lead insult" (29).

The Ethyl corporation believed that lead was hazardous only at high exposure levels and affected only careless factory workers or children who ingested lead paint chips. Patterson believed there was no clear line between what was obviously toxic and what was completely harmless. He was deeply troubled by the lack of objectivity in the health studies on lead (22).

In 1966, hearings on leaded gasoline began in the United States Senate and included testimony from scientists working for industry and Clair Patterson. Patterson told the committee (22)

> It is not just a mistake for public health agencies to cooperate and collaborate with industries in investigating and deciding whether public health is endangered—it is a direct abrogation and violation of the duties and responsibilities of those public health organizations.

The hearings, chaired by Sen. Edmund Muskie, led to an extended debate about the need for new regulatory agencies and new approaches to regulations. Most specifically lead could no longer be considered a one-time exposure hazard limited to factory workers, but rather an insidious airborne danger that accumulates over time and with exposure (22, 30).

During the 1960s the Centers for Disease control (CDC) considered 60 μg/dL of blood acceptable. By 1991 the number was lowered to 10 μg/dL and in 2012 dropped to 5 μg/dL. In children under 5 years, levels above 5 μg/dL require case management and levels above 45 μg/dL require chelation therapy (31).

In 1970 Congress passed the Clean Air Act of 1970. It did not ban leaded gasoline, but gave the EPA (Environmental Protection Agency) authority to ban harmful fuel additives (19, 32). In 1970 the General Motors Corporation began to equip its cars with catalytic converters, which oxidize certain pollutants using palladium, rhodium and platinum catalysts. Tetraethyl lead tends to clog up catalytic converters making the two incompatible. In 1972, the EPA announced that all gasoline stations were required to carry un-leaded gasoline to protect catalytic converters. The EPA delayed the standards until 1973 and was also sued by the Ethyl Corporation. The United States banned lead from indoor paint in 1978, years after many other countries (33).

Between 1975 and 1980, the sales of leaded gasoline dropped by from 160×10^3 tons/year to 60×10^3 tons/year. The ambient air lead concentration dropped correspondingly from 1.23 $\mu g/m^3$ to 0.45 $\mu g/m^3$. Children and adult blood levels also dropped. The average American child's blood lead level in 1976 was 13.7 μg/dL and by 1991 was 3.2 μg/dL (28). Lead settling on the polar ice cap also decreased and by 1989 was near pre-automobile levels.

Through the 1970s, Patterson examined lead levels in food chains. He and his assistant, Dorothy Settle, turned their attention to tuna, an animal at the top of the food chain. They found that fresh tuna contained 0.3 ng of lead per gram of fresh meat, but that canned tuna contained nearly 5000 times more lead because the containers were sealed with lead solder (34). This called into question lead levels in other canned products, many of which were marketed for children. Patterson was dismayed with the government agencies charged to protect the public and later offered to train government scientists in his clean (lead-free) laboratory techniques that he developed as a young scientist.

Looking Back

Clair Patterson's original research to determine the age of the earth led him to uncover massive lead contamination in the environment. Patterson then set out to educate and remove lead from gasoline and became a constant critic of the lead industry. Armed with the power of strong scientific inquiry, he played a crucial role in removing the lead additives from gasoline and lead solder from food containers. He uncovered a dramatic difference between preindustrial and post-industrial lead levels in the environment. He stimulated medical research on the effect of low-level lead pollution. He was a catalyst for lead remediation in homes and regular lead testing for young children as part of routine medical exams. Lead levels in our bodies have dramatically decreased as a result of his endeavors.

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About the Author

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Anderson Named President and CEO of CHF

The board of directors of the Chemical Heritage Foundation has voted unanimously to appoint Robert Anderson as the new president and CEO of the organization, effective January 9, 2017. Anderson is the former director of the British Museum, London, an internationally recognized historian of science, and a longtime CHF board member. He has been interim president since July 2016. After a very extensive search for a president, the board realized that the best choice was already in place.

MORE THAN MEETS THE EYE: CHEMICAL FOUNDATION INVESTMENTS IN THE JOURNAL OF CHEMICAL EDUCATION

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Abstract

During the 20th century, the discipline of chemistry in the United States changed dramatically. The discipline changed not only because of growth in the number of chemists and the volume of research they published, but also because of growing industrial and government support and heightened social acknowledgement of the health, economic, and defense benefits derived from having a strong discipline of chemistry. An active agent for change in American chemistry in the early 20th century was the Chemical Foundation, Incorporated. The Chemical Foundation, which simultaneously served as an advocate for both industrial interests and the public good, was able to invest in chemistry's infrastructure in significant and multi-faceted ways. One specific investment was directed towards the initial years of operation of the *Journal of Chemical Education*. In this paper the role of the Chemical Foundation is reconsidered with respect to investments made in the *Journal of Chemical Education* and the influence this had on the content of the journal from 1924-1950. This content analysis suggests that Chemical Foundation funding for the journal from 1924-1932 incubated the emphasis placed on publishing industrial-oriented articles in the otherwise education-oriented journal in the years during and after World War II. Industry, by publishing in the education journal, was able to make its needs and interests amenable simultaneously to chemists, the public, and government officials.

Introduction

The expansion in chemistry's infrastructure in the US that took place during the 20th century required significant funding and management. The catalysts for this expansion in the opening decades of the century were World War I (and its accompanying influx of government funding) and economic expansion (and its accompanying influx of industrial funding). The expansion in the research infrastructure in chemistry took the form of both expanded scale and more specialized scope. Helping chemistry meet this challenge was the Chemical Foundation, Incorporated. (CF). In chemistry, government officials, chemists, industrialists, and the public all interacted and shaped the CF's activities. The CF, in turn, invested in the *Journal of Chemical Education* (JCE) so as to orient the discipline of chemistry further to the needs of industry.

The JCE, although possessing by virtue of its title a pedagogical focus, published material whereby not only were the education needs of the public and many government officials met, but also those of industry. Within the JCE, industry had its affiliated authors publishing articles that reflected its research activities and motivations, packaged appropriately for students, teachers, and the larger profession. The objective was to have the practitioners of the discipline embrace the goals of industry and perceive the patron as a partner.

In American chemistry, the primary patrons at the turn of the century were industry and the government (1). In the United States, the industrial firms provided funding to researchers who were employees producing work whose benefits could be privately captured (2). As noted by Thackray et al. (1), the 1941 American Chemical Society (ACS) survey of membership indicated the growing dominance of industry for the employment of chemists in the interwar period.

Table 1. ACS members engaged in industrial research. Taken from Table 5.9 in Thackray et al. (Ref. 1), p 353.

Year	Respondents involved in industrial research
1926	16%
1929	19.3%
1932	18.7%
1934	19.7%
1937	23.2%
1938	23.3%
1939	23.5%
1940	24.4%
1941	25%

The chemists involved in industrial research did their work at the in-house laboratories that were being created with increased frequency. In 1921 there were 553 industrial research laboratories, and an average of 41 laboratories were created annually between 1922 and 1940 (with an astonishing 89 laboratories created in 1930) (3). The severity of the economic downturn in the 1930s did not translate into a curtailment of investment in industrial research.

The federal government in the United States provided research funding primarily to chemical researchers when there existed applications to agriculture and national defense. As noted by Thackray et al., the number of chemists employed by the government was less than 1000 through 1928 with nearly 50% employed by the Department of Agriculture and 20% or less employed by the Department of Defense (4). The government provided this funding to researchers whom they more often than not directly employed and who conducted their work in a laboratory typically owned and operated by the government (5). The federal government also realized the importance of industrial research and proposed the creation of a National Research Fund whereby industrial contributions would be collected to fund research that would benefit all corporations (6).

While World War I had created a wider appreciation of the value of research in chemistry and had contributed to a doubling of membership between 1915 and 1920 in the discipline's primary scholarly society, the ACS, the end of the war contributed to stagnation in membership (7). And although in the years leading up to and during the war there was an increase in domestic productive capacity in chemicals, demand for these domestically produced chemicals was weak as German chemical factories grew again and aggressively priced their products (8). The creation of meaningful and lasting growth in the discipline required investments in its infrastructure. One of the few actors willing to make such an investment in American chemistry's infrastructure with the intent of investing in education and increasing the role of industry was the CF.

This discussion begins with a consideration of the background of the CF with a focus on the organization's industrial philanthropist identity. This leads to a description of the contents of the JCE and the shift in who authored the content and what was published from 1924-1950. What is seen is that industry played an outsized but indirect role in the JCE via the CF. The role that education journals such as the JCE play in a discipline raises their importance within the infrastructure beyond that of research journals in that it serves to cultivate patronage relationships.

The Chemical Foundation, Incorporated

The CF was born out of a disposal of enemy property seized from the Germans during World War I (9). The Trading with the Enemy Act was enacted in 1917 and, after some amendments, it afforded the government the power to seize enemy-owned property. Alexander Mitchell Palmer served as the government's initial Alien Property Custodian (APC). Congress instructed the APC to manage the property in a manner that would conserve its value and empowered the APC to authorize the use of seized intellectual property by American companies when such use contributed to the war effort. During World War I, it became obvious that chemistry had national defense benefits and that the economic and social benefits from the discipline made it imperative that the country no longer be subservient to the Germans. As a result, the Trading with the Enemy Act became more encompassing: in March 1918 the Act was amended such that the APC was authorized to confiscate and sell enemy-owned physical property. Shortly before the armistice was signed the notion of property was amended to include intellectual property. And it was this last expansion in the definition of property that would give birth to the CF (10).

At the close of 1918, the APC argued that an institution needed to be created that would ensure that seized intellectual property was patriotically disposed of in such a way that a monopoly in the domestic chemical industry was avoided. The Manufacturing Chemists Association, a lobbying group that represented the interests of both large and small manufacturers, also supported the creation of such an institution. In 1919, a philanthropy by the name of the Research Corporation (RC) inquired several times of the APC as to whether they could manage and own the seized patents (11). The RC was ultimately rebuffed in its attempt to take ownership over the seized patents. With the RC serving as a model (two of the its directors being leaders in the chemical industry), the chemical industry provided the initial funding for the creation of the CF (12). Six of the corporations associated with the American Dyes Institute (the trade association for the dye industry) and five corporations associated with the Manufacturing Chemists Association provided a $500,000 loan to create the CF (13).

At the same time in June 1919 as RC was inquiring about the possibility of taking over the seized patents, Palmer was appointed Attorney General by President Wilson. The office of APC was subsequently presided over by Francis Garvan. With the loan from the Manufacturing Chemists Association, Garvan in February 1919 in his role as APC sold and transferred the seized German-owned chemical patents to himself in his President Wilson-appointed role as President of the CF. The CF had been formally incorporated in Delaware as a quasi-trustee corporation with the trustees managing the stock of the corporation for 17 years—the lifetime of the youngest patent seized. For the price of $269,850 Garvan purchased 4,764 patents, 283 patent applications (196 of which eventually became patents), 874 trademarks, 492 copyrights, and 56 pre-war contracts (14). The initial loan that funded the purchase of the patents was paid back as 158 different individuals, corporations, and organizations purchased ownership shares in the CF (15). This stock was divided into voting and non-voting shares. Approximately 80% of the stock was non-voting (almost entirely owned by industry) whereas 20% of the shares had voting rights. The transfer of the patents to the CF as well as the price paid by "shareholders" would be a topic disputed in the courts throughout the 1920s (16). The CF essentially had initial funding from industry in the form of payments for shares of the CF (shares that had no market value) and continuing financing from industry in the form of royalty payments for using the seized intellectual property owned by the CF.

Garvan, although focused on creating dominance of American firms in the global chemical industry, adamantly believed the CF would be an institutional device that could pursue philanthropic goals (17). Between 1919 and 1949, the period of time when the CF was most active, it earned $8.7 million in revenue as it granted non-exclusive licenses to companies that had at least 75% American ownership; licenses were granted free of charge to the federal government. Of the $9.7 million spent by the CF between 1919 and 1949, the CF devoted 62.5% to research and education activities with a blended industrial and philanthropic focus (18).

Given the source of its funding and the historical background of the organization, the CF had many similarities to a trade association as it championed industrial causes and built up public support around them. Given the government's role in creating it, the CF also had a strong public mission and provided research funding in areas such as medicine and agriculture. It served simultaneously as an advocate for industry and the public and consequently was able to provide funding and support in ways that other organizations with a singular focus were unwilling or unable to provide. Industrial patrons would have faced internal resistance and shareholder lawsuits had they provided funding that didn't directly translate into higher corporate profits. Government patrons would have similarly faced internal resistance from other government research agencies and from taxpayers had they provided funding for activities other than direct research that benefitted the public at large. And for Thackray et al., the CF was one of several "chemical boosters" who connected advances in chemistry to economic progress and national security with emphasis on economic advances (19). While many individual firms such as General Electric and du Pont played an outsized role in promoting chemistry advances, the coherence and force of the CF's boosterism was notable (20). The boosterism of the CF was more than mere promotion for temporary benefit. The investment the CF made in journals in chemistry set the stage for building an infrastructure capable of accommodating an expanded discipline after World War II.

The CF has been described in the past from several perspectives, each highlighting either the industrial or philanthropic motivations of the organization or the tension and controversy that accompanied the institution. John Servos was one of the earliest scholars to discuss the activities of the CF (21). In his discussion of the *Journal of Physical Chemistry*, Servos reveals the role played by the CF in funding a scholarly journal in a field of study that straddled the disciplines of chemistry and physics. Robert Kohler, in his discussion of the role played by philanthropies in the United States in the early 20th century, makes brief mention of the CF as involving itself with scholarly communities in the 1920s (22). David Rhees focuses on how the CF subsidized chemical education activities and created a public relations strategy to demonstrate the public and private benefits that come from research in chemistry (23). Kathryn Steen places the CF within a five-phase industrial policy of building up the organic chemical industry in the United States (24). Steen followed up her analysis with a discussion of the controversy over the disposal of the patents owned by Bayer, Inc., and the government's attempt to take ownership over the seized property—an attempt that culminated in the 1926 Supreme Court case of United States vs. Chemical Foundation (16). Each of these narratives of the CF to varying degrees highlights the dual industrial and philanthropic motivations, how its activities reflected this, and how the CF was a patron in areas such as the coverage of publication deficits and public relations when other patrons were unwilling or unable to. The present analysis contributes to an alternative understanding of the CF as an institution that invested in chemistry's infrastructure in such a way that industry had a prominent role in an education journal both during and after the interwar period.

The activities of the ACS were brought to the attention of the CF via Charles Herty (25). Herty had served as President of the ACS from 1915 to 1916 and had edited the industrial-oriented *Journal of Industrial and Engineering Chemistry* from 1917 to 1921. In 1921 Herty left his editorship to become President of the Synthetic Organic Chemical Manufacturers' Association. Herty's advocacy for the trade association and a pharmaceutical drug research institute had caught the attention of Garvan. Herty, upon leaving the Synthetic Organic Chemical Manufacturers' Association, was hired as a consultant to the CF. Akin to a program manager, Herty worked to identify and assess projects that the CF should support, promoted research, provided oversight of government policy, and expanded the CF's public education activities.

With the ACS in the interwar period unable to finance the needed size and scope of the scholarly communication process in chemistry, the CF provided significant financing to several journals to reduce publication backlogs. These journals included *Chemical Abstracts*, the *Journal of Industrial and Engineering Chemistry*, *Journal of the American Chemical Society*, *Analytical Edition*, and *Journal of Physical Chemistry* (26). There are at least three reasons why the CF made the investment in the scholarly journals published by the ACS. The first was that Herty had made the CF aware of the needed scholarly communication investment. Second, Garvan and William Buffum, business manager of the CF, were already active believers that scholarly communication was an under-invested component of the research process. As officers of the CF, they directed resources convinced that the full industrial and philanthropic potential of research could only realized if findings were published. The third reason was to implicitly provide industrial-affiliated researchers an opportunity to publish and make industrial applications known to and appreciated by other chemists and the public at large. To explore further this third motivation behind CF funding of journals our attention turns to the JCE. All told, the CF invested a total of $267,646.78 for the publication deficits and expansion of the JCE from 1924-1932 ($214,490.56) and for a smaller educational publication for high school teachers and students titled *Chemical Leaflet* ($53,156.22) (26). Ultimately, the CF invested in the JCE as a means to an end—an improvement in the state of chemical education that translated into the types of chemists that both industry and society needed (with the emphasis on the former).

The *Journal of Chemical Education*

Education journals in general and the JCE specifically can be seen in a narrow fashion as serving a pedagogical purpose. An education journal brings teaching ideas to teachers, provides opportunities to publish for teachers conducting teaching-based research, and exposes teachers and advanced students to applications within the chemistry discipline. Education journals can also serve to build up a discipline's infrastructure by shaping educational outcomes, create an outlet for patrons to the discipline to demonstrate to teachers and students what the goals of the discipline should be, and lend authority to certain pedagogical techniques and motivations.

The infrastructure for a discipline in the sciences has typically emphasized scholarly journals and laboratories (27). The journals and laboratories shape the research being done and the results published, and build the community of scholars into a particular form. The infrastructure, however, can be more widely conceived to also include patronage relationships and conferences. Scheiding (2009 and 2013) demonstrated how the industrial and government patrons of research in the discipline of physics also financed journals through the page charge pricing mechanism. The patron as a result created a particular kind of infrastructure in the second half of the 20th century whereby a well-financed journal operation was responsive to the needs of researchers (readers and authors) and patrons (28). Daemmrich and Shaper (2008) demonstrated the theoretical advancements in chemistry that emerged from the unique organizational structure of the Gordon Research Conferences (29). The Gordon Research Conferences were able to strengthen collaborations between those in similar research fields and provide an entry point for the industrial patron who helped finance both the conferences and research. Both Scheiding and Daemmrich and Shaper describe the indirect way that industry shaped the infrastructure in physics and chemistry respectively. In the discipline of chemistry, industry indirectly financed the discipline's infrastructure when the industrial philanthropist of the CF made investments in the JCE.

Although the title of the journal would suggest that the contents were pedagogically oriented, the contents were also capable of convincing educators, students, and others in high schools and in higher education of the value and role of industrial and government patronage. The JCE, besides providing teaching-focused knowledge, published articles that promoted government and industrial interests. The content served to communicate to educators and students what the needs and priorities were of industry and kept industry in tune with the training of future chemists. As the source and magnitude of financial, managerial, and editorial assistance changed, the size and contents of the journal changed as well.

The JCE was first published in 1924 and served as the primary publication for the Division of Chemical Education. The division was an official section of the ACS whose creation was spearheaded by Neil Gordon. With generous CF funding, the JCE was able to take on the implicit function of providing industry a platform for its research and gain the support of the profession (30). Garvan's foray into education started in 1923 when he provided his own funds for an ACS-administered prize essay contest for high school students (31). Garvan later created and financed a Chair of Chemical Education at Johns Hopkins University in 1928 and appointed Gordon to the position (32).

The financial and managerial support from the CF to the JCE—which continues to be published to this day—lasted from 1924 to 1932. In the eight years between 1925 and 1932 the journal published an average of 1,990 pages a year (33). By contrast, in the eight years between 1933 and 1940 the JCE published an average of 629 pages a year. In the eight years between 1925 and 1932 the journal contained 16.05% of industrial content. By contrast, in the eight years between 1933 and 1940, the journal contained 9.80% of industry content. It was in the first eight-year time period (1925-1932) when the CF provided significant funding and wielded influence. It was in the second time period (1933-1940) when the CF had withdrawn support. The significance of the CF funding is found in the fact that the JCE had in place an organizational structure and financial footing that could accommodate the publication of industrial content between 1941 and 1948 that represented 21.85% of the journal. The challenge in the 1940s was that a great deal of industrially oriented research was being generated from wartime mobilization, but not much of it was published. The JCE, courtesy of CF involvement almost a full decade earlier, met this challenge by being open to publishing more industrially-oriented research in an educational package.

During its early years, the JCE published articles of interest to professors such as "Starting the Small Chemistry Laboratory" (for teaching) and "The Use of Charts in Teaching General Chemists" and published articles of interest to college students such as "The Chemistry Profession: Preparation, Opportunities" and "How to Study Chemistry" (34). The JCE, over time, increasingly reflected the industrial agenda of the journal's primary patron—the CF. It published articles of interest to industrial chemists and chemists being trained for an industrial career such as "Colloids in Industry," "Chemistry of the Citrus Industry in California," "A Working Model By-Product Coke Plant: A Chemistry Project for a Student at the Secondary Level," and "Important Points in the Development of the Manufactured Gas Industry with Particular Regard to the Influence of Chemical Research" (35).

The JCE also frequently published articles directly aligned with the CF's philanthropic motivations. The CF, for instance, was a strong proponent of research in agriculture and the JCE published articles such as "Boyce Thompson Institute of Plant Research, Inc." (an organization to which CF would provide nearly $100,000 in the 1930s), and "Some Relations of Agricultural Chemical Research to National Prosperity" (36). Reflecting the interests of the dye industry (an initial financier of the CF), the JCE published "United States Institute for Textile Research" and "The Textile Foundation, Inc." (37). Reflecting the CF's interest in cancer research, the JCE published an article co-authored by a researcher at the Garvan Cancer Research Laboratory titled "Recent Work on the Cancer Problem" (38). Reflecting the $100,000 in start-up financing the CF provided for the National Institutes of Health in 1930, the JCE published "The National Institutes of Health: Uncle Sam's Organization for Medical Research" (39). Finally, reflecting the significant financing the CF provided for chemistry and economic development in the southern US, the JCE devoted an entire issue to the topic (40).

As evidenced in the previous paragraph, the contents of the JCE at times directly reflected the funding priorities and patronage interests of Garvan and the CF. The JCE however was the official publication of the ACS's Division of Chemical Education and it was the Division that exercised editorial control over the journal's contents. Early on, Garvan and the CF sought to become more involved with the JCE and inquired in 1925 whether funds could be donated directly to the Division. Gordon replied that since the Division of Chemical Education was an independent unit of the ACS, Garvan would be able to donate funds as he could for any independent organization (41). Although this donation never materialized, officers within the ACS expressed displeasure with what appeared to them to be an attempt by the Division to hoard patronage from the CF and an attempt by Garvan and the CF to impose more control over what the JCE published.

On October 8, 1932, after years of financial troubles for the Division of Chemical Education, the CF announced it would no longer manage the JCE after the December 1932 issue. Although the reason given was that the journal was not financially self-sustaining, few journals ever were (and the CF was well aware of this fact). Rather, it was more that the CF was frustrated with its lack of control over a journal it managed and financed but over which it did not exert editorial control (42). Mack Publishers, a long-time publisher of other ACS journals, agreed to take over the journal and was given exclusive control over the business management of the journal while the Division of Chemical Education retained editorial control (43). The CF certainly had significant financial concerns in the early 1930s (44), but correspondence between two industrial chemists, R. E. Rose of du Pont and William Hale of Dow, reveals that discontent remained between the ACS and CF over the imposition of an industrial agenda in the JCE. The correspondence between Rose and Hale reveals that industrial laboratory research managers did not agree on how best to integrate the activities of the scholarly society into the industrial laboratory setting (45). Thus the suggestion remains that persistent ill will between the ACS and the CF over control of the journal's editorial policy and content contributed to the elimination of CF support for the JCE.

As evidenced in the next section, the financial and organizational assistance provided to the CF influenced the journal beyond the publication of articles covering research already financed by the CF. An analysis of the contents of the JCE from 1924-1950 reveals that CF funding in the initial years was associated with the publication of industrial articles (articles either authored by someone with an industry affiliation or content that was of primary interest to those in industry) and provided key building blocks for an infrastructure that would be relied upon by industry during and after World War II.

Content Analysis of the *Journal of Chemical Education* (1924-1950)

Ogden and Pella published a content analysis of chemical education journals in 1974 (46). They reviewed six journals from 1918-1967 in an attempt to understand the objectives of chemical education (47). They sorted articles based on their content and motivation into ones concerned with knowledge (focused on the attainment of factual or conceptual material), process (focused on the understanding and application of knowledge), attitude and interest (focused on developing an appreciation of the material), and cultural awareness (focused on the connections between science and society and the cultural consequences of scientific advances). They also separated the time period of 1918-1967 into six subperiods: 1918-1933, 1932-1941, 1936-1946, 1945-1957, 1954-1967, and 1963-1967. Ogden and Pella concluded that the pressure of economic conditions, World War II, and the Cold War encouraged the initial emphasis on knowledge and process in chemical education journals. An emphasis on cultural awareness was prompted by the civil rights movement and political protests.

The content analysis carried out in the present article differs in that it is limited only to the JCE and only during the period 1924-1950. This content analysis is also solely focused on the quantity of content either authored by someone affiliated with industry or where the focus is on the needs and interests of industry. The contents of the JCE were analyzed using the archived version of the journal at http://pubs.acs.org/journal/jceda8. The archived version does not contain advertisements and some of the front and back matter in each issue is omitted. Each article's title and abstract was reviewed as was the author's affiliation. When either the title or abstract had a focus on industrial application or the author had a corporate affiliation, the article was defined for the purposes of this paper as "industrial." Articles that were authored by Science Service (48) were not part of the total article counts or considered "industrial," but were included as a part of the total page count for each journal issue. This content analysis demonstrates that CF investments in the JCE had a lasting impact to the extent that the journal was able to build up an infrastructure capable of and amenable to publishing a significant amount of industrial research in the years during and after World War II and create an identity with an industrial component.

Between 1924 and 1950 the JCE published 27,588 pages, nearly half in the journal's eight initial years. The annual breakdown in publication size is shown in Figure 1.

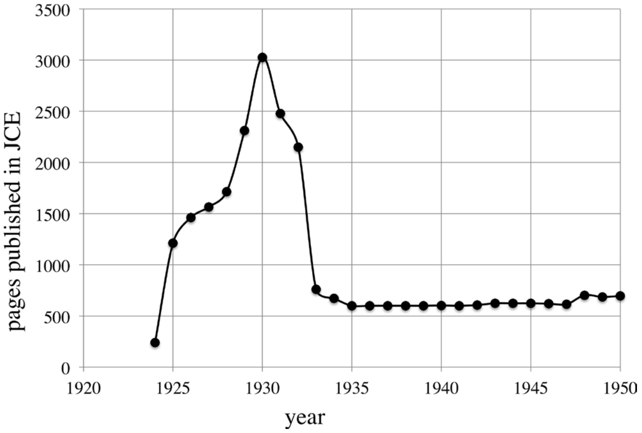

Figure 1. *Annual pages published in the JCE, 1924-1950. Data from http://pubs.acs.org/journal/jceda8.*

Between 1924 and 1950 there were essentially three different phases of ownership, editorial, and management. In subperiod 1, 1924-1927, the journal published a total of 4,478 pages over the four years. During this time, the journal was owned, edited and managed by the Division of Chemical Education, and a fair amount of influence was exerted by the CF which provided funding for the journal and directed resources to Gordon who served as the journal's creator and editor. In subperiod 2, 1928-1932, the journal published a total of 11,679 pages over five years. During this time the journal was described by many as "an organ of the CF." The CF assumed all financial responsibility for the journal and the Division still laid claim to exerting editorial influence (Gordon still serving as editor). While the Division during this subperiod continued to direct the journal's editorial policy, the CF's support previously extended to Gordon undoubtedly worked to the CF's favor. In subperiod 3, 1933-1950, the journal published 11,431 pages over 18 years. By this time the CF had withdrawn its support, and there was a change in the journal's editor within the Division of Chemical Education. Mack Publishing Company assumed responsibility for the finances and business management of the journal, and the Division continued to have sole control over choice of editor and the journal's editorial policy (and unlike periods one and two, these were choices were uninfluenced by the CF) (49).

In between each subperiod there were changes in the role of the CF, in what the journal published and in how much it published. The transition between subperiods 1 and 2 was the result of long-standing tension between the ACS and the CF and between the ACS and Division of Chemical Education over who would control and finance the journal (50). The transition between subperiods 2 and 3 was the result of the ACS asserting control over the journal and the CF subsequently ceasing financial assistance and involvement.

What follows is a more detailed description of the contents of the JCE across the three subperiods. The focus is on the level of industrial content across the time frame. The overall percentage of "industrial" articles between 1924 and 1950 is shown in Figure 2.

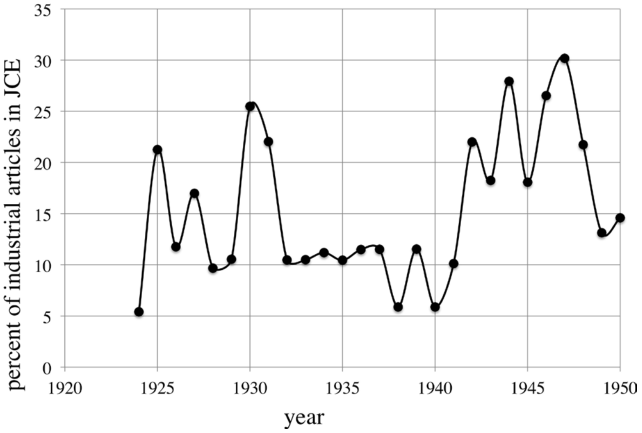

Figure 2. *Percent of articles in JCE with industrial authors or content, 1924-1950. Data from http://pubs.acs.org/journal/jceda8.*

Subperiod 1 (1924-1927)

During subperiod 1, the 4,478 pages published contained 509 articles, of which 81 (16%) were from industrially affiliated authors or were industrial in their focus. In the journal's initial year (volume 1, 1924), 37 articles were published. The focus was on pedagogical articles, with only two authored by industrially-affiliated chemists. The journal also published material from Science Service. The journal in 1925 (volume 2) grew by a factor of 4 in number of articles to 160. The number of published pages increased by a factor of 5 from 240 pages to 1212 pages. The journal grew in size to accommodate the publication of essays that had won an ACS essay contest (a prize that was funded by the CF) and to publish more Science Service content. Volume 2 had 26 industrial articles with issue 11 containing the article "The Application of Research to Industry" (51). In 1926 (volume 3), there was slight growth in the journal to 1461 pages, most of the growth coming from Science Service content. With 12% of the 153 articles being industrial in their nature (18 articles), there was a slight decline in industry articles. A fairly large number of the industrial articles dealt with the dye industry, an important source of industrial employment for chemists and an important industry to the CF. Finally, in 1927 (volume 4) while there was only a slight growth in the size of the publication to 1,565 pages and 159 articles, there was a significant increase in industrial articles (27 of them), and the publication of Science Service material remained a priority.

During subperiod 1, the 81 industrial articles along with the Science Service material helped establish within colleges, universities, and corporations an identity of the journal as one amenable to the needs of industry and aware of the importance of research to industrial profits. The journal had grown in size and prominence during subperiod 1 such that it took on a lead role in exposing teachers and students in the high school and college classrooms to applications of chemistry to industry. The growth trajectory started in subperiod 1 accelerated dramatically in subperiod 2 (1928-1932).

Subperiod 2 (1928-1932)

During subperiod 2, the journal published 1,137 articles over the course of 4 years across 11,679 pages, with 185 of the articles being industrially oriented. The percentage of industrially oriented articles over this subperiod increased by less than one half of one percent over the previous subperiod from 15.9% between 1924-1927 to 16.27% between 1928-1932. In 1928 (volume 5) the journal out of 186 total articles published 17 articles that were industrially oriented. The journal grew slightly in size to 1,714 pages with the Science Service material continuing to be published extensively. In 1929 (volume 6) the journal out of 237 articles over 2,311 pages published 25 industrially oriented articles. In that year the journal began to publish profiles of industrial research laboratories ("The General Electric Research Laboratory. What It Is and What It Has Accomplished") and of corporations ("The Story of Portland Cement") (52). In 1930 (volume 7) the journal grew dramatically in size to 3,026 pages in which 259 articles were published. These included 66 industrially oriented articles, more than doubling the fraction of industrially-oriented articles over the previous year. A fairly large source of this growth came from the fact that all of issue 10 was devoted to industrial topics. In 1931 (volume 8) there was a reduction in the size of the journal to 2,478 pages with 54 of the 245 articles being industrially oriented. Although there were no single issues devoted to industry as had been the case the previous year, the fraction of industrially oriented articles had decreased only slightly. In 1932 (volume 9) there was again a decrease in the number of pages (2,150) and in the number of articles (210) and an even greater decrease in the number of industrially oriented articles (to 22). The journal still published industrially oriented articles that had broad appeal such as "Chemical Research: A Factor of Prime Importance in American Industry" (53), but the decrease in industrially oriented articles was notable. This decrease would persist through the first half of subperiod 3 during the Great Depression.

Subperiod 3 (1933-1950)

Subperiod 3 represents a time when CF funding and influence was completely absent. This subperiod is perhaps best understood as consisting of two eras. In the first era from 1933-1941 the contraction in economic activity contributed to a decrease in industrially oriented articles with an average of 9.8% of the total number of articles. With the start of World War II , the second era from 1942-1950 saw a doubling of the proportion of industrially oriented articles with an average of 20.84% of the total number of articles. Throughout this entire subperiod there was dramatic curtailment in the size of the journal with an average of 635 pages published annually (compared to an average of 1,879 pages in subperiod 2 and 1,119 pages in subperiod 1). With the size of the journal constrained, the industrial nature of the journal became particularly pronounced in the 1940s. One possible explanation for the increase in industrial content then is that the CF assistance that had been provided to the journal in subperiod 1 and especially during subperiod 2 contributed to the journal's more secure financial footing and organizational structure. The JCE had no debt and had an editor whose editorial activities were compensated by the CF. Additionally the JCE had, under the CF, acquired an identity deemed friendly to industrial concerns. Fast forward to the 1940s and it is then hardly surprising the greater level of industrial research that would be accommodated by the journal.

In the first 9 years of this subperiod an average of 626 pages were published annually. Of the 1341 articles, 132 were industrially oriented. The latter 9 years of this subperiod had an average of 644 pages published annually, and 307 out of the 1473 articles were industrially oriented. Some of the curtailment in the size of the journal came from removing Science Service material. Although there were fewer industrially oriented articles in the first era of subperiod 3 than in subperiod 2, relevant articles continued to be published, including:

- "Class Exercises in the Industrial Chemistry Course," a six-part series over four issues in volumes 10 and 11.
- "What Training Industry Expects of Chemists and Chemical Engineers", volume 11.
- "Elements of the Quantum Theory," an eleven-part series of articles in volume 12 by industrial chemists at General Electric.
- "What Industry Wants of its Chemists," volume 14.
- "Industry's Challenge to Chemistry Education," volume 18.
- "Industry's Interest in the Professional Training of Chemists," volume 18.

In the second era of subperiod 3 the industrially oriented articles were more numerous. Articles were devoted to specific industries where chemistry was used such as glass, leather and ink (volume 19); to patenting industrial research (volume 20); to how to organize research (volume 22); to a revisiting of what industry expects of the chemistry graduate (volume 24); to the placement of chemists through industrial training programs (volume 25); and the nature of being a chemist at General Electric, Eastman Kodak, and du Pont (volume 27).

When analyzing the number of pages published across the three subperiods and the proportion of industrially-oriented articles in each subperiod, CF support allowed the journal to expand in size and by the end of subperiod 2, the level of CF support was correlated with the journal's contents being more industrially oriented. The journal's infrastructure was funded and organized with CF assistance and this contributed to the greater industrial content than would have been expected of a journal with a pedagogical focus or from a journal in chemistry when so many others struggled to survive.

The JCE was so much more than a publicity outlet for the CF as an organization. Simultaneously the JCE published articles covering the research activities of individuals and institutions that received CF funding and the JCE published a larger-than-expected amount of "industrial" material. When the JCE published industrial material the journal was promoting the domestic chemistry boosterism agenda of the CF. When CF funding ceased, the journal did publish fewer pages and the proportion of industrial content was reduced. However, the CF influenced the JCE in subperiod 1 in such a way that by the 1940s the journal published and repackaged for an educational audience a larger-than-expected amount of industrial content. Readers of the JCE had become accustomed to finding industrial content in the journal and industrial authors were accustomed to publishing their work in the journal.

Concluding Remarks

It was during the 20th century that world dominance in many academic disciplines was relocated from Europe to the United States. And while certainly World War II and the displacement of individuals and destruction of institutions in Europe played a role in this relocation process, the war did not single-handedly determine the timing and extent of the relocation. The relocation of the disciplines to the United States after World War II occurred with respect to the place where the majority of discipline's graduate students studied, the location where the vast majority of pre-eminent scholars in the discipline taught and conducted research, and where geographically authority in the discipline was located. This relocation process in many disciplines, including chemistry, began in the initial decades of the 20th century as government agencies and industrial firms financed more research and hired more researchers and newly emerging philanthropic organizations began to finance education and experiment with methods of giving to scholarly communities.

The discipline of chemistry was aided by the fact that it played a key role in defense, agriculture, medicine, and industry. Consequently, there was a widespread recognition of the fact that investments in chemical research and education were needed to create American dominance. However, all of the actors that served as patrons to research and education in chemistry, with one notable exception, were largely self-interested and focused in their giving. The government funded research primarily in its own laboratories conducted by researchers who were paid employees. It funded research in the areas of defense and agriculture where there were demonstrable public benefits. Corporations also funded research in their own laboratories primarily by researchers who were paid employees. They funded research to the extent that it improved the quality of existing products and led to the development of new products. Philanthropies funded research in more experimental fashions and engaged with academic researchers, but they did this with less resources and only after fulfilling massive financial commitments made to the National Academy of Sciences for graduate school fellowships (22).

While individual actors within the government and industry each aided chemistry to the extent that they benefitted, the discipline in the early 20th century needed an actor that had the goal of building up its infrastructure. Only a patron like the CF was capable of serving such a role because of the institution's identity as a boundary organization whose funding came from industry and whose identity was sanctioned by the government. From the perspective of industry, the CF ensured that new monopolies did not emerge and advocated for industrial needs (54). From the perspective of the government, the CF ensured that chemistry would be strong for defense and agricultural research. From the perspective of the public, the CF ensured that education, medicine, national defense, and economic growth would all be furthered with a strong discipline of chemistry.

The impact and legacy of the CF was significant given the organization's controversial founding, smaller amount of funding and leaner administrative structure with respect to other philanthropies and a mixed identity that straddled private profit and the public good. As a boundary organization, the CF invested in education, made commitments to specific research projects, and devoted financial and managerial support to scholarly societies and journals, including the JCE. The JCE was a publication that was designed with students and educators in mind and it published a large amount of pedagogical articles. The journal also published industrial research and articles authored by those in industry. The JCE was able to take on an industrial agenda to the extent CF financial and managerial assistance was present. The journal was viewed by those in industry as amenable to their need for trained researchers. And for educators and students, the needs of industry were revealed and their importance reinforced. Both industry and education, through the JCE, were able to see each other as partners. While the JCE, at times, looked like a public relations publication as it published results from CF-funded projects, most of the time the JCE was able to maintain an identity of advocating for the needs of education and industry by publishing articles of interest to both groups.

In the content analysis of the journal between 1924 and 1950 it becomes obvious that greater levels of CF assistance to the JCE were associated with both a larger journal and a journal that contained more industrial content. Once CF funding ceased in 1933 and up until World War II, the industrial content in the journal was dramatically reduced. This was despite the fact that industry maintained its research activity during the Great Depression. World War II represented a dramatic increase in industrial research which was combined with a patriotic and profit-infused recognition that industrial research was important. Although the JCE during and after the war did not increase in size, the fraction of industrial content returned to levels last seen when CF funding was present. The CF originally had invested in the JCE with the goal of strengthening the American chemical industry with targeted investments in the chemistry discipline's journals. The JCE, with its CF-inspired and CF-financed packaging of industrial content for an education audience, was able to meaningfully bring industrial and academic audiences closer. And in so doing, American chemistry was strengthened.

Acknowledgments

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3. Ref. 1, p 346.
4. Ref. 1, Table 5.4, p 362.
5. The research laboratory environment for the government chemist is described in Ref. 1, pp 129-134.
6. For a description of the National Research Fund see L. Davis and D. Kevles, "The National Research Fund: A Case Study in the Industrial Support of Academic Science," *Minerva*, **1974**, *12(2)*, 207-220.
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ETHICS OF CHEMICAL WEAPONS RESEARCH (1)

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Abstract

Throughout history the use of chemical weapons in warfare has been controversial. The morality of chemical weapons research is similarly controversial because several potentially conflicting obligations and codes of ethics impact the decision of the individual chemist as to whether to participate in such research. In this article I will discuss the complex ethical questions surrounding chemical weapons research. All chemists are members of a national community with the obligations of citizenship, but they are also professionals subject to a code of ethics. Of course, they are also members of the human community and consequently subject to the more or less universal common morality. Membership in a religious community might also add moral restraints. A key question for chemists is whether the current professional codes of ethics can provide adequate guidance in trying to deal with this complex issue.

Introduction

In the usual telling, the history of chemical warfare begins on April 22, 1915, near Ypres, Belgium, when the Germans under the command of the future Nobel Laureate Fritz Haber opened the stopcocks on 5,370 buried cylinders releasing 168 metric tons of chlorine gas. The attack had been delayed for several days because of unfavorable winds, but on that day the wind carried a large elongated cloud of toxic gas about 50 feet high across no-man's land and into the Allied trenches. The gas seared eyes and lungs, and hundreds of French and Algerian troops were left blinded and dying in the wake of the cloud.

The attack was militarily ineffective because the German generals, skeptical of this new weapon, were not prepared to follow-up with sufficient ground troops, but the psychological effects were enormous. In the bitter words of Wilfred Owen,

> But someone still was yelling out and stumbling,
> And flound'ring like a man in fire or lime . . .
> Dim, through the misty panes and thick green light,
> As under a green sea, I saw him drowning.
> In all my dreams, before my helpless sight,
> He plunges at me, gutting, choking, drowning.
> . . .
> The old Lie; Dulce et Decorum est
> Pro patria mori.

The Latin is from Horace: "It is sweet and right to die for one's country" (2).

Like many stories, the standard account of the beginning of chemical warfare is not quite correct. Earlier in World War I the Germans, and perhaps the French, had used grenades and artillery shells filled with various poisons, but with little effect. In fact, the use of chemical weapons, such as poisoned arrows and Greek fire, goes back to antiquity (3). The word toxic derives from the Greek word for an arrow: *toxon*.

The Hague Declaration of 1899 had specifically outlawed "the use of projectiles, the sole object of which is the diffusion of asphyxiating or deleterious gases." The Hague Declaration of 1907 had gone further and had prohibited "poison and poisoned arms." Disingenuously, the German High Command had focused on the 1899 Declaration and argued that their artillery shells also produced shrapnel and the release of chlorine from cylinders did not use projectiles (4). These are distinctions that a logician or lawyer might love, but they were little comfort to soldiers whose lungs were filled with hydrochloric acid.

It is not my purpose to recount the history of chemical warfare. That story is well told elsewhere (5), although I will refer to parts of that history as necessary. Instead, I want to examine the moral questions related to chemical weapons, particularly the question of whether scientists, especially chemists, may engage in chemical weapons research. The ethics of chemical weapons research is part of a larger question: the ethics of war-related research in general, about which I have written previously (6), but chemical weapons raise some specific issues which will be the focus of this article. These ethical questions involve the professional ethics of science, the relationship of science and society, the ethics of warfare, and in the end, our view of how we should treat our fellow humans, even when they are temporarily our enemies.

Science and engineering and the military have had a long, and often productive, mutual relationship. Beginning with World War II the U.S. Government has made huge investments in military-related research through the Department of Defense, the Department of Energy and other agencies. Many scientists and engineers are employed in industries that manufacture weapons and other war-related products. The scope of war-related research is broad, ranging from research on weapons, for example nuclear warheads, to improvements in radar, which have both civilian and military applications. In this article I leave aside these broader questions and concentrate on the ethical issues peculiar to chemical weapons development. Therefore, it is important to specify what I mean by the term chemical weapon.

The term chemical weapon usually refers to a lethal or toxic agent such as the nerve agent sarin, that is designed to kill or incapacitate. There are, however, other forms of chemical weapons. I will consider four classes:

1. Lethal or toxic agents such as chlorine, mustard, and sarin
2. Non-lethal or incapacitating agents such as tear gas and malodorants
3. Herbicides such as Agent Orange used in the Vietnam War
4. Incendiary agents such as napalm

The distinction between a lethal and a non-lethal agent is a bit arbitrary because toxicity depends both on dose and on individual reactions to the agent. A large dose of a so-called non-lethal agent might kill and a small dose of a lethal agent might only act as an incapacitating agent. Herbicides generally do not kill outright, but can inflict serious environmental damage and sometimes can cause chronic human diseases. Incendiary weapons can be used in ways that do not take lives directly, say by starting fires to slow troop movement, but when used on humans can cause terrible injury and death. In a strict sense one might also consider gunpowder and other explosives as chemical weapons, but since these agents generally do not kill in and of themselves, the discussion will be restricted to the four categories listed above.

The moral decision as to whether to engage in research on chemical weapons is complicated by the fact that all scientists are members of at least three distinct moral communities. Each of us is a citizen of a national society with a history, goals and ideals. With citizenship comes obligations. For example, Kenneth Kemp has argued that conducting scientific research for the military is a civic duty (7). On the other hand, Jonathan Glover has warned against a "nationalization of morality" in which questions of war and weapons, among others, are seen only through a narrow patriotic lens (8). Every scientist belongs to a professional community of scientists, and more specifically to the community of chemists or biologists or some other discipline, and is subject to the professional code of ethics of science in general and of the particular discipline. Chemists are subject to the Chemical Professional's Code of Conduct of the American Chemical Society (9) and similar codes adopted by other chemical societies. In addition, as members of the human community, scientists have the same moral obligations as all other people. Finally, the moral landscape might be further complicated by the scientist's religious beliefs and practices. Because science is a secular community, the influence of religious beliefs will not be considered explicitly, although such beliefs might play a large role in an individual scientist's thinking.

These moral communities are not independent, however. A profession makes a tacit agreement with society. In return for a monopoly on certain specialized knowledge and skills not easily attainable by the general population, the profession agrees to use that knowledge and those skills to serve society. In professions such as medicine, law and engineering, this agreement is part of the licensing procedure. In science, the agreement is less formal but it does imply that scientists have special obligations. For example, all U.S. federal grant applications require the principal investigator to discuss the broader impacts of the research for society. Guston and Kenniston characterize the bargain that has governed science in the U.S. since World War II as follows: "Government promises to fund the basic science that peer reviewers find most worthy of support, and scientists promise in return that the research will be performed well and honestly and will provide a steady stream of discoveries that can be translated into new products, medicines or weapons (10)." Historically, the emphasis on weapons resulted from the success of the Manhattan project and other wartime efforts, but military funding of research has continued unabated since World War II even after the end of the Cold War.

A second important consideration is the scientist's view of the morality of war (11). There are three general positions on this question. The first is realism. Realists express a strong suspicion about applying moral concepts, like justice, to international affairs. They view war as an inevitable part of an anarchical world system that should be resorted to when it is in a nation's self interest. When war begins, nations should do whatever is needed to win—no holds barred. In this view moral questions about any kind of weapons research are beside the point.

The second position, which is widely held, is based on just war theory which has a long and complex history. Just war theory does not suggest that wars themselves are just, but rather considers when a war is justified (*jus ad bellum)*, puts restraints on the conduct of the war (*jus in bello)*, and then outlines the components of a just peace after the war has ended (*jus post bellum*) (11). Those aspects of the just war theory particularly relevant to chemical weapons will be described in detail below.

The final position is pacifism. Pacifists object to killing, particularly mass killing for political reasons. They believe that there are no moral grounds that can justify war, so war is always wrong. As a result, for the pacifist, engaging in weapons research is always morally problematic and something to be avoided.

Chemical Weapons

To better specify the moral problem I will assume the general perspective of the just war theory, that there are times when warfare can be justified and that preparation for a national defense is a morally acceptable pursuit for a scientist or engineer although perhaps with limits. The moral questions arise because the just war theory places restrictions on the ways in which war can be conducted. The relevant provisions of *jus in bello* include (1) adhering to international conventions, (2) respecting noncombatant immunity, (3) using only proportionate force to achieve victory, and (4) not using methods or weapons that are "evil in themselves" (*mala in se*). These are restrictions on the decisions made by commanders and individual soldiers, but in my view, are also restrictions on those who develop weapons. Certainly, any tool, or weapon, can be misused, but I will argue that developing a weapon which is highly likely to break one of these restrictions is morally problematic.

The Chemical Weapons Convention (CWC), a multilateral treaty that bans chemical weapons and requires their destruction within a specified period of time, entered into force in 1997 (12). The CWC is far more comprehensive than the Geneva Protocol of 1925 that was developed after World War I. The Geneva Protocol had, in turn, strengthened the provisions of the Hague agreements that had been established in 1899 and 1907. One might conclude that because of the CWC and the restriction in the just war theory that all international agreements should be followed, that the issue of chemical weapons research would be simply resolved. This is not the case for several reasons.

First, the CWC prohibits the production and use of toxic agents which are defined a chemicals that "cause death, temporary incapacitation, or permanent harm to humans or animals." There is an exception, however. Toxic agents can be used for "law enforcement including domestic riot control." The United States has argued that the CWC does allow for the use of riot control agents, even in warfare, because these chemicals, such as tear gas, which produce sensory irritation or disabling physical effects, because these effects are not a form of temporary incapacitation and continues to pursue research on these non-lethal agents (13). Such research can raise moral questions for several reasons. First, these substances may not be as benign as advertised. As noted above, toxicity is a matter of dose and response, and incapacitating riot control agents do cause deaths, although at a much lower level than nerve agents, for example.

Second, even though the CWC only allows the use of these chemical agents for domestic reasons, once the weapon exists, there is the possibility of using it in war.

Although the CWC does not address the use of herbicides or incendiaries, Protocol III of the Convention on Certain Conventional Weapons of the United Nations, which came into force in 1983 and was finally ratified by the United States in 2008, states that incendiary attacks against concentrations of civilians should be considered as war crimes, which places a restriction on the use of agents such as napalm (14).

The just war theory makes a clear distinction between combatants and non-combatants. A combatant is someone, usually a soldier, who is engaged in harming. Soldiers are liable to attack, but those not engaged in harming, non-combatants, are not. But, the just war theory does provide a way to avoid this restriction, what is called the law of the double effect. Some kind of attacks, such as bombing, will inevitably harm some non-combatants who happen to be in the way. The current euphemism for this is collateral damage. Some harm to non-combatants can be morally justified from a consequentialist perspective if the ultimate result of an attack is to increase the chance of winning a just war.

Michael Walzer's doctrine of supreme emergency is a recent addition to the just war theory (15). Walzer argues that a nation can set aside the provisions of both *jus ad bellum* and *jus in bello* in cases where defeat is imminent and the aggressor will crush that nation's sovereignty and massacre and enslave its inhabitants. Walzer's only example of such an emergency is Nazi Germany, but there are recent examples of genocide and use of weapons of mass destruction that might also qualify. This exemption is quite controversial because, if accepted, it allows a nation to unilaterally declare a state of supreme emergency and then ignore all the restraints of the just war theory.

One of the strongest ethical arguments against the use of lethal, and non-lethal, agents is that they do not discriminate between combatants and non-combatants. Once a chemical weapon is released anyone in its path is likely to be harmed. A similar argument can be made against the widespread use of herbicides to "defoliate" the countryside. Whatever immediate or long term health effects there are will be shared by combatants and non-combatants alike (16). Another argument against the use of herbicides is that they can interrupt food production, which is a basic human need. A traditional law of warfare is that one may attack the soldier but not the human. Actions such as poisoning the water supply have always been regarded as unfair.

Just war theory requires that the amount of harm not be unnecessary or otherwise disproportionate to what can be achieved by the resort to violent force. This restriction bans weapons that are indiscriminate and whose destructiveness goes well beyond the rational military objective of neutralizing the enemy (17). There are two kinds of proportionality, horizontal and vertical. Horizontal proportionality involves the amount of harm and the number of people harmed. This aspect of proportionality overlaps with the principle of non-combatant immunity but also addresses the wholesale massacre of enemy soldiers. Vertical proportionality involves the severity of that harm.

Although some might argue to the contrary, a clear example of a weapon that violates the principle of horizontal proportionality is the thermonuclear warhead which indiscriminately kills combatants and non-combatants, destroys property and leaves behind radioactive wastes that contaminate the area. Many would argue that chemical weapons are similarly disproportionate. Toxic agents kill indiscriminately but do not ordinarily destroy property. Herbicides do not usually cause many immediate deaths but can cause serious long-term damage to the environment as well as chronic health problems among those humans and animals who have been exposed. Incendiaries kill indiscriminately particularly when used on cities.

On the other hand, one might argue that it is inappropriate to classify particular weapons as disproportionate for two reasons. First, it is possible to use these weapons in a way that is not indiscriminate. Second, conventional weapons can also be used indiscriminately. These are reasonable arguments, but some weapons are more likely to be used indiscriminately than others. Weapons that increase the physical and emotional distance between the attacker and the victim are more likely to be used indiscriminately. A rifle shoots bullets which are directed at particular targets, targets that shooters can see through their sights—one bullet, one victim. A bomb usually kills most if not all the people near where it lands whether they are combatants or non-combatants. I think there is a reasonable moral distinction between the two.

Vertical proportionality overlaps with the fourth restriction, that it is impermissible to use weapons that are evil in themselves (*mala in se*). Are there weapons that should be banned because they are just too horrible to use? Are there limits to harm, even in warfare? To approach this question we need to realize that the enemy soldier is also a human being and is part of the broader human community. This fact is something that wartime propaganda does its best to persuade us to forget. The enemy is portrayed as the "other." The goal is moral exclusion: increasing the psychological distance, viewing the enemy as non-entities undeserving of fairness, and destroying any sense of moral obligation. This allows one to approve of actions that would be unacceptable if performed on those who are within the sphere of justice. During World War II, as the Japanese became increasingly vilified in the American press, there were calls for the use of chemical weapons. Headlines appeared saying, "We should gas Japan" (18). Weapons that are evil in themselves are weapons that cause unnecessary suffering, not justified by military necessity. They are weapons that attack the human rather than the soldier.

What kinds of weapons should be considered evil in themselves? Based on the completely indiscriminate nature of their impact and the horrible deaths that result, nuclear weapons are certainly a prime candidate. Another candidate is incendiary weapons such as napalm. Death by fire is exceptionally cruel and fire is similarly indiscriminate. Nick Ut's iconic photo of Vietnamese children fleeing a napalm attack shows the horror (19). During World War II flame throwers loaded with napalm were used to attack and immolate Japanese soldiers hiding in caves. Napalm bombs dropped on Japanese cities during World War II killed more people than the two atomic bombs (14). Some other weapons that are considered exceptionally cruel are land mines, which are placed before a battle and are indiscriminate, harming combatants and non-combatants alike and causing horrible injury, and cluster bombs that send out hundreds, or thousands, of small bomblets or grenades over a large area. Another candidate is shells filled with glass. Once imbedded in the body, the glass shards are undetectable by X-rays, so they remain, causing long-term suffering.

There are those who argue that the category of weapons that are evil in themselves is meaningless in the context of war. Instruments are neutral; they can be used either for good or evil. A scalpel can be used to commit murder and a saber can be used to perform surgery. Conventional weapons, bullets and grenades, can also cause horrible injuries. For the soldiers going over the top during World War I, was there a qualitative difference in the horror between being mowed down by machine gun fire and being gassed? It is certainly true that as weapons become more familiar, the degree of revulsion decreases. For example, long ago the introduction of firearms was opposed by both practical and moral arguments. Some said that they must have issued from the devil himself, but eventually guns and cannons were accepted and even glorified (20).

But certain kinds of weapons continue to seem more repugnant than others, and chemical weapons certainly fit into this category. There are several reasons for this. First, in traditional warfare, poison was considered not to be honorable. War was a battle between men, essentially a duel, and poison was "sneaky." It subverted the traditional hierarchy of war between men of stature. It was a weapon resorted to by barbarians and others who could not win in a fair fight. Margaret Hallissy has argued that the negative image of poison results from men's fear that it could be used to upset the dominance of men. A "weaker" woman could use secret knowledge to compensate for her physical inferiority (21). Another reason is that chemical weapons fuse the roles of the doctor and the warrior and disrupt the normal social order (22). The warrior injures by deadly force while the doctor heals by providing medicines which we ingest. Chemical weapons use the methods of the doctor to injure or kill.

The experiences of World War I certainly contributed to the perceived horror of chemical weapons. At the 1921 Washington Conference on arms limitations, a report signed by General John J. Pershing, the U.S. commander during World War I, stated that "chemical warfare should be abolished among nations as abhorrent to civilization. It is a cruel, unfair and improper use of science. It is fraught with the gravest danger to noncombatants and demoralizes the better instincts of humanity" (23). An emotionally powerful literature, exemplified by the poem by Wilfred Owen quoted earlier, made a huge psychological impact and has contributed to a taboo on the use of these weapons (24). Chemical weapons were not used during World War II, although the Germans had developed and manufactured the nerve agents tabun and sarin. The history is complex, but moral considerations were important. Neither side was willing to introduce a controversial weapon, partly in fear of retaliation but also because of the moral opprobrium that would accompany the use of lethal chemical agents.

During the Vietnam War, the widespread use of napalm gained enormous public attention largely due to widely circulated photographs of victims, particularly children, but napalm, invented during World War II by the Harvard organic chemist Louis Fieser, had been used to devastating effect in both World War II and Korea. Napalm burns at a high temperature and because it is a gel it adheres to the skin causing horrible burns. Napalm bombs dropped on Tokyo caused conflagrations that killed approximately 100,000 people and destroyed fifteen square miles of the city. People were burned alive and those who sought refuge in pools or streams were boiled to death.

In deciding whether a weapon is evil in itself, the moral perspective that seems most relevant is that of Kant (25) who argued that the essence of morality was that human beings needed to be treated as ends in themselves and not as means. In the context of war, this means that even extremely hostile behavior towards others must be compatible with treating them as persons. Inside the enemy uniform is a human being. A weapon that is evil in itself is one that degrades the essential humanity of the person being attacked.

Making a Decision

Should a scientist, usually a chemist, engage in chemical weapons research? What are the moral considerations that should go into such a decision? This is a question that must be answered by individuals based on their own values but I will try to outline the issues that should be considered.

As noted earlier, I assume that it is morally permissible, and perhaps also an obligation for scientists who do not have personal philosophical or religious objections to participating in war to contribute to research related to the national defense, which might include weapons research.

Chemical weapons research, however, is morally problematic for several reasons. First, many chemical weapons are prohibited by the CWC, which represents an international consensus on the use of lethal agents. Arguments have been made that certain kinds of chemical agent such as riot control agents are permitted under this treaty, but there is good evidence that these so-called non-lethal agents are not as benign as hoped and, if used in war, can be quite destructive. If developed, such weapons are available for use by governments, insurgents and terrorist organizations that are not parties to the CWC. Recent history has shown that there are those who will use even banned chemical weapons (5). It has also shown that the use of non-lethal riot control agents can be deadly (13).

One might argue that it is morally permissible to develop chemical weapons as a deterrent. Similar arguments were made during the Cold War regarding nuclear weapons. This argument is easily countered. First, the CWC bans lethal chemical weapons independent of their proposed use. Second, once the weapon is developed it is available for use in a future war.

Second, although there are dangers associated with the manufacture of all weapons, chemical weapons pose more dangers than most. For example, in the manufacture of nerve agents, any leaks in the production system or in the filling of shells can be fatal. There are also serious problems in disposing of the toxic wastes from the manufacturing process.

Herbicides present different issues because they have legitimate peacetime uses in agriculture. The agents used in Vietnam, including the now infamous "Agent Orange," were commercial products, mainly 2,4-D and 2,4,5-T (T (2,4,-Dichlorophenoxyacetic acid and 2,4,5-Trichlorophenoxyacetic acid respectively). All herbicides are toxic to some degree and must be handled carefully. The major fear with 2,4,5-T is that it is inevitably contaminated with the very toxic dioxin. The moral question with herbicides is in their use during warfare, so research in the development of better herbicides, particularly those that are less toxic to humans is a legitimate enterprise.

Incendiaries such as napalm are also morally problematic. Napalm burns are enormously painful. Although Kim Phúc, the Vietnamese girl in the iconic photo mentioned above, did recover from her burns, a physician in the hospital where she was treated "compared the experience to being flayed alive: suffering so severe that it constituted a 'wound to the soul'" (26). The firestorms created when napalm bombs are dropped in a city destroy essentially everyone and everything in their paths (27).

The chemist trying to decide whether to engage in research on chemical weapons will get no help from the American Chemical Society's Chemical Professional's Code of Conduct. The code lists the responsibilities of chemists to various groups beginning with the responsibilities of chemists to the public (9).

> Chemists have a professional responsibility to serve the public interest and welfare and to further knowledge of the science. Chemists should actively be concerned with the health and welfare of coworkers, consumers and the community. Public comments on scientific matters should be made with care and precision, without unsubstantiated, exaggerated, or premature statements.

These are fine words, but the code does not help the chemist decide how to prioritize the various responsibilities. What does "active concern with health and welfare" mean in practical situations? The code is silent on the ethics of weapons research, leaving that decision to the individual. I have argued elsewhere that current codes of ethics for chemists should be revised to address contemporary ethical issues more fully (28).

In the end, I think the crucial question is not whether a weapon can be used in a way that is consistent with the restrictions of the just war theory and other moral considerations, but whether having a particular weapon, say napalm, in the arsenal makes it more likely that the conduct of the war will be escalated. Dwight Eisenhower observed that as war proceeds, both sides are pulled deeper and deeper into the business of killing. The history of war in the twentieth century is filled with examples of conflicts that violate the principles of the just war theory (8). The chemist needs to decide whether the particular chemical weapon being developed will make it easier to conduct war in an unjust manner, whether that weapon attacks the human rather than the soldier, whether it is evil in itself. No one can foresee all the possible uses of a discovery, but all chemists have a moral responsibility to consider the long-term negative consequences of their actions.

Acknowledgments

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About the Author

Jeffrey Kovac was educated at Reed College (B.A. 1970) and Yale University (M.Phil. 1972, Ph.D. 1974). After two years as a postdoctoral research associate at MIT he joined the faculty of the University of Tennessee where he is Professor of Chemistry and Director of College Scholars, the interdisciplinary honors program in the College of Arts and Sciences. Dr. Kovac has broad research interests ranging from statistical mechanics and thermodynamics to history and philosophy and is the author of nearly 100 articles and 6 books. He has written extensively about the ethics of science including the ethics of war-related research. As an historian he has written, *Refusing War, Affirming Peace: A History of Civilian Public Service Camp #21 at Cascade Locks* (Oregon State University Press, 2009).

2016 HIST Award

The History of Chemistry Division of the American Chemical Society is pleased to announce that Professor Doctor Ursula Klein of the Max Planck Institute for the History of Science in Berlin is the winner of the 2016 HIST Award for Outstanding Lifetime Achievement in the History of Chemistry. This international award has been granted since 1956 under sequential sponsorships by the Dexter Chemical Company, the Edelstein Foundation, the Chemical Heritage Foundation, and the History of Chemistry Division.

The award includes presentation of a monetary prize and a plaque, a symposium honoring the work of Professor Klein, and a lecture by the awardee; it took place on August 23, 2016, at the American Chemical Society's annual Fall meeting in Philadelphia, Pennsylvania. The symposium program was:

- Wolfgang Lefevre, "Methode de nomenclature chimique (1787): A document of transition"
- Michael Gordin, "Periodic table as scaffold and foundation: paper tools and demarcation"
- Alan J. Rocke, "Erlenmeyer as capitalist and entrepreneur: A case study of chemical enterprise in mid-19th- century Germany"
- Mary Jo Nye, "Stability and change in chemical problems and methodologies from the 1890s to the 1930s"
- Stephen J. Weininger, "Delayed reaction: The tardy embrace of physical organic chemistry by the German Chemical Community"
- Evan Hepler-Smith, "Paper tools, paper things and a third-order science of organization"

The symposium culminated with Prof. Dr. Klein's address on "Chemists for the common good."

ON THE ORIGIN OF "SYNTHETIC METALS": HERBERT MCCOY, ALFRED UBBELOHDE, AND THE DEVELOPMENT OF METALS FROM NONMETALLIC ELEMENTS

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Introduction

Unlike typical saturated organic polymers, conjugated polymers (Figure 1) are a class of organic semiconducting materials that exhibit enhanced electronic conductivity in their oxidized or reduced states (1, 2). As such, these materials combine the electronic properties of classical inorganic materials with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs. This combination of properties has led to considerable fundamental and technological interest, resulting in the current field of organic electronics and the development of a variety of modern technological applications. Common applications include sensors, electrochromic devices, organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and field effect transistors (FETs) (1-7). In addition, the flexible, plastic nature of the organic materials used as the active layers in such electronic devices has led to the realistic promise of flexible electronics in the near future (4-7).

Typical discussions of the history of these materials generally begin in the mid-to-late 1970s with the collaborative work of Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger on conducting polyacetylene (8-11). In 2000, the Nobel Prize in Chemistry was awarded to these investigators for their early contributions to the field of conjugated organic polymers and the language of the award further reinforces the common view of the historical origins of these materials, which states that the award is "for the discovery and development of electrically conductive polymers" (12). It is only somewhat recently that reports have begun to present a more complete account of the early history of these materials, with particular attention given to highlighting efforts that predate the commonly cited polyactylene work of the 1970s (13-19). While this previous work may not have been as dramatic or as fully realized as the later polyacetylene studies, many aspects and relationships attributed to the work recognized by the Nobel can be seen in these earlier contributions.

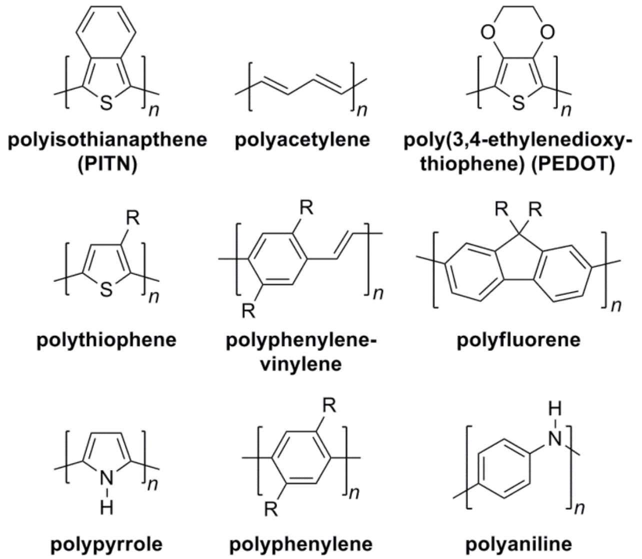


Figure 1. *Common parent conjugated polymers.*

The synthesis and study of conjugated organic polymers dates back to the early 19th century, but it was not until 1963 that the first organic polymer with significant conductivity (10^{-4}-10^{-1} S cm^{-1}) was reported by Donald Weiss and coworkers in Australia on conducting polypyrrole (20-22). This was then followed by the work of Rene Buvet and Marcel Jozefowicz in 1966 on conductive polyaniline powders (up to 30 S cm^{-1}) (14, 18). Two separate reports followed in 1968, which included the first report of doped conductive polyacetylene powders (10^{-4}–10^{-2} S cm^{-1}) by D. J. Berets and Dorian S. Smith, as well as the production of conductive polypyrrole films (7.54 S cm^{-1}) via electropolymerization by Vittorio Bocchi and coworkers (16-18). Shirakawa, MacDiarmid, and Heeger then reported their initial paper on halogen-doped polyacetylene (up to 38 S cm^{-1}) in the spring of 1977 (8). While the conductivity reported in this study was not considerably higher than some of the earlier reports, these authors reported more optimized results later that same year with conductivities up to 560 S cm^{-1} (9, 10). It is this second report that is more significant, as this was the first example of metallic conductivity in an organic polymer. In the following years, additional reports of doped conjugated polymers exhibiting metallic conductivity continued to appear in the literature.

As doped conjugated polymers can exhibit electrical conductivities in the metallic range ($>10^2$ S cm^{-1}) (23), such doped materials have been frequently referred to as *synthetic metals* (24-27). A primary example of this is Alan MacDiarmid's Nobel lecture entitled "'Synthetic Metals': A Novel Role for Organic Polymers" (26, 27). Common uses of the term can also be found as the title of the Elsevier journal dedicated to this class of materials (28) and in the name of the longstanding International Conference on the Science and Technology of Synthetic Metals (29). The descriptor "synthetic metals" has been in use long enough now that it has become somewhat commonplace and few question how or where this term originated. It was therefore thought worthwhile to review the history of this term as part of ongoing efforts to document a more complete history of conjugated organic materials. An initial communication presenting the origin of the term "synthetic metals" was recently published (19) and the current discussion will expand on this previous report with a more detailed history of the origin and evolution of the term.

In reviewing previous discussions of the origin of this term, it is found that credit is commonly given to Alfred R. Ubbelohde (1907-1988), who began using the term in reference to intercalated graphites as early as 1969 (30, 31). A clear example of this can be found in the biographical memoir of Ubbelohde written by F. J. Weinberg (32) which states:

> Ubbelohde coined the evocative expression "Synthetic Metals" to cover the creation of materials with metallic conduction but formed entirely of such non-metallic atoms as carbon, nitrogen, hydrogen, the halogens and oxygen. This expression was later adopted as the title of an international journal publishing papers on these materials from laboratories all over the world.

In reality, however, the term predates Ubbelohde's work and can be found as early as 1911 in the work of Herbert N. McCoy (1870-1945) (33). As a result, it is with McCoy that we will begin the current discussion before returning to the life and work of Ubbelohde.

Herbert N. McCoy

Herbert Newby McCoy (Figure 2) was born June 29, 1870, in Richmond, Indiana, to Sarah and James McCoy (34, 35). Losing his father at a young age, 13-year-old Herbert worked 10 hours a day to help support the family and held a wide variety of jobs by the time he finished his primary education. After graduating from Richmond High School in 1889, McCoy entered Purdue University to study chemistry under John Ulric Nef (1862-1915). Nef had just left Purdue, however, and McCoy thus began studying under Winthrop E. Stone (1862-1921) (34, 36). By taking special examinations, he was admitted as a sophomore, but had to take time off after a year due to lack of funds. Upon his return, additional examinations gave him credit for work done during his time away to raise money, and he was able to complete his bachelor's degree with only two years in residence (34, 36), finishing in the spring of 1892 (34-36). The following year he continued graduate studies under Stone, during which he was supported by a part-time teaching assistantship. He finished his M.S. in Chemistry in 1893 (34-36), with a thesis on the electrolytic oxidation of glycerin (34, 36, 37).

McCoy then worked as a chemist for Swift and Company in Chicago, but preferred academic work and left after a little more than a year to teach the Department of Science and Mathematics curriculum at Fargo College in North Dakota (34, 35, 38). Founded in 1887 and closed in 1922, Fargo College was a private non-sectarian Christian college (Figure 3) and should not be confused with its Fargo neighbor, North Dakota Agricultural College (founded in 1890 and now North Dakota State

University). McCoy stayed in Fargo for two years, during which he prepared for further graduate work (36). He was attracted to the University of Chicago, as John Nef had recently joined the faculty (34), and he started research work there during the summer of 1895. However, as Nef was not at campus that summer, McCoy began working on a problem in organic chemistry under Julius Stieglitz (1867-1937) (34, 35), before returning to Fargo College for the 1895-1896 academic year. The following summer, he was given a fellowship under Stieglitz and left Fargo to enter the University of Chicago as a full time student (36). He finished his Ph.D. in 1898 (34, 35), with a dissertation entitled "On the Hydrochlorides of Carbophenylimido Derivatives" (39). As jobs were scarce at the time, he remained at the University as a research assistant for Alexander Smith (34).

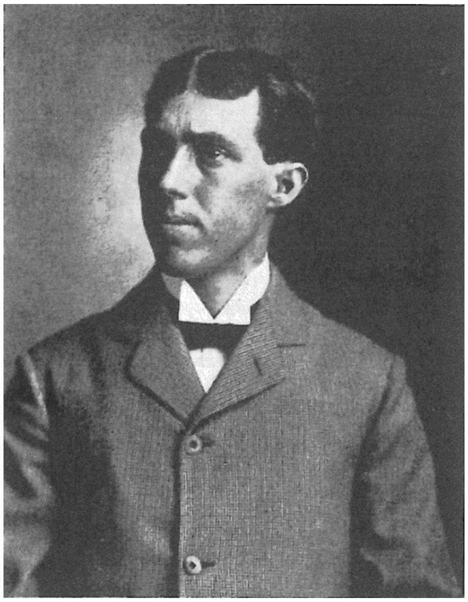


Figure 2. *Young Dr. McCoy (ca. 1900) [From Ref. 34].*

McCoy joined the University of Utah as assistant professor of chemistry in 1899. Because the head of department, Dr. J. T. Kingsbury, had just been appointed University President, McCoy also acted as the unofficial head (34, 36). He then returned to the University of Chicago as an instructor in 1901, replacing Dr. Felix Lengfeld in physical chemistry (34-36).

The University of Utah invited him to return as a full professor in 1903, but McCoy elected to stay at Chicago as an assistant professor (34). He was promoted to associate professor in 1908 and ultimately full professor in 1911 (34, 35). McCoy's research on radioactive chemical elements attracted significant attention from industry, and he ultimately left Chicago in 1917 to move to the Carnotite Reduction Company of Colorado, eventually becoming the company's president. He retired from Carnotite when it was sold in 1920, and became vice president of the Lindsay Light Company in Chicago (34-36). McCoy left Chicago in 1927 to move to Los Angeles, although he remained the vice president of Lindsay until his death (34, 35). In Los Angeles, McCoy became a guest in the research laboratory of University of Chicago alumnus Dr. B. A. Stagner, who was now a consulting chemist in Los Angeles. Here, McCoy continued to work on rare-earth problems beginning in 1930 (34). He then built a laboratory over the two-car garage of his Los Angeles home in 1934, where he continued his research on the rare earths, especially with europium and samarium, for the rest of his life (34, 36). His various accomplishments were recognized by receiving the Gibbs Medal in 1937 (36) and being awarded a D.Sc. by Purdue University in 1938 (34). He passed away on May 7, 1945 (34).

Figure 3. *Fargo College (ca. 1915) [Courtesy of the Institute for Regional Studies Archives, Fargo, ND (rs007656)].*

Although McCoy was known primarily for his work in rare earth chemistry, he has also been credited with the preparation of what was thought to be the first organic metal (34, 35). This work was reported in three papers over the span of 1911-1912, while he was still on the University of Chicago's faculty, and focused on efforts to produce a metallic species from the electrolysis of tetramethylammonium salts (33, 40, 41). Prior to these publications, the work was initially presented at American Chemical Society Meetings, first at Detroit in June 1909 (40) with a brief write-up in *Science* (42), and then at Minneapolis in December 1910 (33). These efforts were all based on earlier reports of ammonium amalgam, first prepared by Thomas J. Seebeck (1770-1831) in 1808 (43). As the ammonium cation is in many respects similar to alkali metal cations, it was thought that it could potentially be reduced to generate a neutral ammonium radical, which could theoretically give metallic properties similar to sodium or potassium metal. McCoy explained this hypothesis as follows (33):

> When we come next to consider the behavior upon electrolysis of a salt of a compound basic radical, it is difficult to see wherein its behavior should differ from that of a salt of a metallic element. In this case, as in the other, positive ions are attracted to the cathode, and upon striking the latter can gain electrons. If then the electron theory of the metallic state is as fundamental as it seems to be, the aggregate of such free "neutralized" radicals should be a body having metallic properties; in other words, a "synthetic metal."

In fact, when Seebeck first reduced ammonium carbonate with a mercury electrode (equation 1), a spongy mass was generated, which he believed to be an amalgam of ammonium and mercury (43). This amalgam was then shown to be similar to the mercury amalgams of sodium and potassium, first by Seebeck and later by Humphry Davy (1778-1829) (44). However, the true nature of this amalgam and whether or not it was metallic was heavily debated.

$$NH_4^+ \xrightarrow[Hg]{e^-} Hg/H_4N\bullet \qquad [1]$$

Roughly 100 years later, McCoy and William C. Moore extended these earlier efforts by investigating the electrolysis of organic quaternary amines, rather than just simple ammonium salts (33, 40, 41). Utilizing an electrolytic chamber comprised of silver-plated platinum gauze for the anode and a mercury electrode as the cathode, electrolysis of the salt resulted in the production of a crystalline solid of metallic luster. This solid product closely resembled sodium amalgam and was believed to be a mercury amalgam of ammonium radicals with the general formula $HgN(CH_3)_4$ (40). Although this organic amalgam was not very stable and reacted violently with water, it exhibited electrical conductivities comparable to that of a metal (ca. $7\text{-}9 \times 10^3$ S cm^{-1}) (33, 40, 41). Ultimately, McCoy concluded (33):

> The facts just reviewed, though few in number, seem to me to lend support to this hypothesis, and to lead to the conclusion that it is possible to prepare composite metallic substances, which may be termed synthetic metals, from constituent elements, some of which at least are nonmetallic.

Such ammonium and quaternary ammonium amalgams continued to be of interest up through the early 1970s (45). In 1986, however, the eminent electrochemist Allen J. Bard reported convincing evidence that such ammonium amalgams are more likely Zintl ion salts resulting from the reduction of mercury, rather than reduction of the ammonium cation (46). Thus, the more correct representation of this process would be that given in equation 2 below.

$$NH_4^+ + 4\,Hg \xrightarrow{e^-} NH_4^+(Hg_4^-) \qquad [2]$$

As such, the products generated by these electrolytic processes are not really organic metals, although they were believed to be at the time and do seem to be the origin of the term "synthetic metals." The term was then not used in the literature again until 1969, when Alfred René Ubbelohde of Imperial College described a new class of materials based on intercalated graphite as synthetic metals (28-31).

Alfred R. Ubbelohde

Alfred René Jean Paul Ubbelohde (Figure 4) was born December 14, 1907, in Antwerp, Belgium, the third son of the merchant Francis C. J. Ubbelohde (32). His family moved from Belgium to London when World War I broke out, initially residing in Richmond, Surrey. His education began at Richmond County School in 1918, followed by Colet Court (St. Paul's preparatory school) in 1920, and St. Paul's School. His interests fell equally to chemistry, mathematics, and literature, but he ultimately opted for chemistry and won a scholarship to Christ Church, Oxford, where he graduated with First Class Honors in 1930. He also supplemented his Oxford studies with a B.Sc. Special Chemistry from the University of London, which he passed with First Class Honors as an external student in 1928. Ubbelohde ultimately became a naturalized British citizen in his mid twenties (32).

Following his graduation, Ubbelohde remained at Oxford to spend another five years on postgraduate research, working mostly on hydrocarbon oxidation chemistry with Sir Alfred Egerton (1886-1959) (32, 47). During 1931-1932, he also spent a year at the Institut für Physikalische Chemie, Göttingen, with Arnold Eucken (1884-1950). Following additional research positions at the Royal Institution (1936-1940) and the Ministry of Supply (1940-1945), he became Professor of Chemistry and Head of the Department of Chemistry at Queen's University, Belfast, in 1945. Oxford University awarded him a D.Sc. in 1941 and he was elected a Fellow of the Royal Society in 1951 (32).

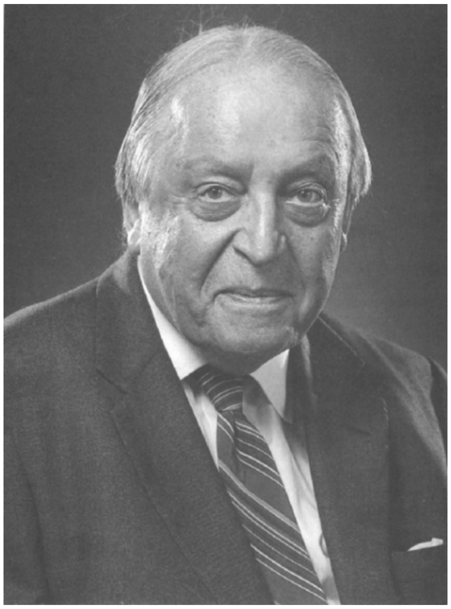


Figure 4. *Alfred R. J. P. Ubbelohde [From Ref. 32; Courtesy of JSTOR].*

In 1954, Ubbelohde moved to Imperial College to become Professor of Thermodynamics in the Department of Chemical Engineering and Chemical Technology. He then became Head of Department in the early 1960s, a post he held until his retirement in 1975. He remained as a Senior Research Fellow until his death on January 7, 1988 (32, 47). With an overall focus of thermodynamics, he spent his career working on a range of subjects including combustion, collision properties of hydrocarbon vapors, carbon, graphite and intercalation compounds, hydrogen in metals, phase transitions, and ionic melts (32). However, it is his work with graphite and its corresponding intercalation com-pounds (Figure 5) that is most critical to the current discussion (28, 29, 48-56).

The various graphite intercalation compounds reported by Ubbelohde during his career exhibited conductivities as high as 2.5 × 10^5 S cm^{-1} and thus provided the first practical and stable example of a carbon-based species that conducted in the metallic range (28, 29, 48-56). His first paper on these species, which reported graphite intercalated with either bromide or potassium to give metallic conductivities (up to 1.5 × 10^3 S cm^{-1}), was published in 1951 (48). While these materials would fit the definition of synthetic metals as discussed above, the first time that Ubbelohde uses the term is not until 18 years later when he published a paper on graphite nitrates and bisulphates in 1969, in which the effect of the intercalated ion concentration on conductivity was studied (28). He then followed this with another paper entitled "Electronic Properties of Some Synthetic Metals Derived from Graphite" later that same year (29). In comparison to his previous work, these papers reported significantly higher conductivities (10^4-10^5 S cm^{-1}) and were his first reports of such highly conductive intercalated graphites. It may have been the significantly higher conductivities that led to his use of the term "synthetic metal" to describe the species reported in these papers, or it may be the result of observations that intercalated graphites with high ion concentrations demonstrated greater three-dimensional metallic behavior. For whatever reason, the term then became a mainstay in his writings for the rest of his career (49-56), which thus resulted in the belief that the term was originated by Ubbelohde.

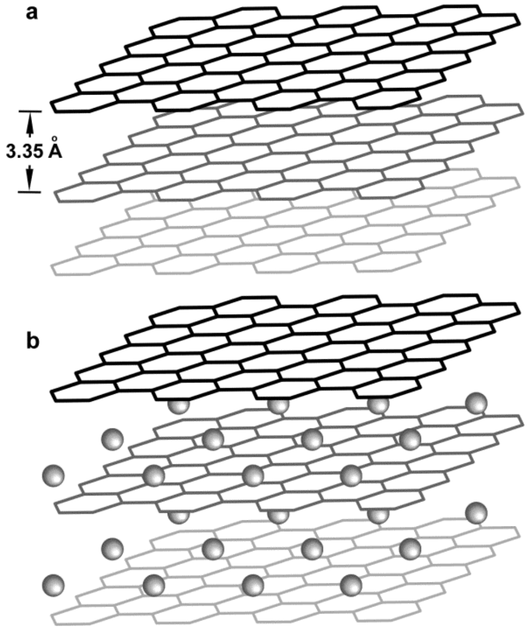


Figure 5. *Schematic representation of native graphite (a) and a simple intercalated compound (b).*

The remaining question at this point is whether Ubbelohde developed the term "synthetic metals" independently or if he learned of the term from McCoy's earlier paper and simply applied it to his own work. This is not possible to answer conclusively, although we can look to the language used by Ubbelohde for clues. It is important to note that Ubbelohde never claims the term as his own, nor does he even introduce or define the term in either of his two 1969 papers. In all cases, he always uses it as if it is a known term that does not require explanation. For example, the very first time we see the term used in his work is in the abstract of his first 1969 paper, where he states (28)

> Various electronic properties confirm a model for the acid salts in which layers of carbon hexagon networks act as macro-cations, separated by layers in which acid anions are linked to additional molecules of acid by hydrogen bonds. In conformity with this model, as the concentration rises, the resistance drops, at first steeply, finally asymptoting to a limiting value characteristic of a synthetic metal.

The term is then used again in the first sentence of the introduction, as follows (28):

> With the development of methods for producing near-ideal graphites by stress annealing pyrolytic graphite, and with improved methods for controlled progressive formation of intercalation compounds from specimens already mounted as electrical conductors, it becomes possible to study variations in charge carrier behaviour in these synthetic metals, in much greater detail than is usually feasible with natural metals.

As can be seen, no definition or explanation of the term is given. At the same time, he does not provide a source for the term and McCoy is never mentioned.

It should be noted, however, that before graphites became such a focus for Ubbelohde, he also studied the production of mercury-ammonium amalgam via the electrolytic reduction of ammonium cations, publishing two papers on the subject in 1951 (57, 58). Thus it seems quite plausible that he would be familiar with McCoy's earlier papers on the topic from 1911. This cannot be confirmed, however, as although Ubbelohde does reference work from the early 1900s in his ammonium amalgam papers, McCoy is again never mentioned and McCoy's paper using the term "synthetic metals" is not referenced. However, it should also be pointed out that even though Ubbelohde summarizes what is currently known on ammonium amalgam in one of his two papers and points to the fact that the topic dates back to the 19th century, none of the seminal ammonium amalgam papers are cited in his work, including no mention of either Seeback or Davy.

Overall, it is just not possible to make a definitive connection between McCoy and Ubbelhde. Still, due to their overlap in research on ammonium amalgams, combined with the fact that Ubbelohde never claims the term "synthetic metals" as his own, it is this author's belief that Ubbelohde learned of the term from the work of McCoy and did not develop it independently. Assuming that this is correct, the reason that Ubbelohde never mentioned, referenced, or acknowledged McCoy will continue to remain a puzzling mystery.

ICSM and New Examples of Synthetic Metals

Through the early 1970s, a variety of additional new materials were discovered that exhibited metallic conductivity, including organic charge-transfer salts, metal chain compounds, and the inorganic polymer poly(sulfurnitride), $(SN)_x$ (Figure 6). As this research spanned a range of scientific disciplines and geography, a specific venue that would bring these interdisciplinary researchers together was desired and thus a workshop was organized in the summer of 1976 in Siofok, Hungary (29). Discussion at this meeting spanned such subjects as charge density wave behavior in the Peierls-Frohlich state and the application of these concepts to charge-transfer salts such as tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), along with low-dimensional metal-containing materials such as the tetracyanoplatinates, and niobium triselenide ($NbSe_3$). Also considered was the possibility to chemically control the structural and electronic properties of these new materials, including the extent of charge-transfer, the degree and role of band filling, and the effects of extreme anisotropy, interchain interaction, and coulomb repulsion (29).

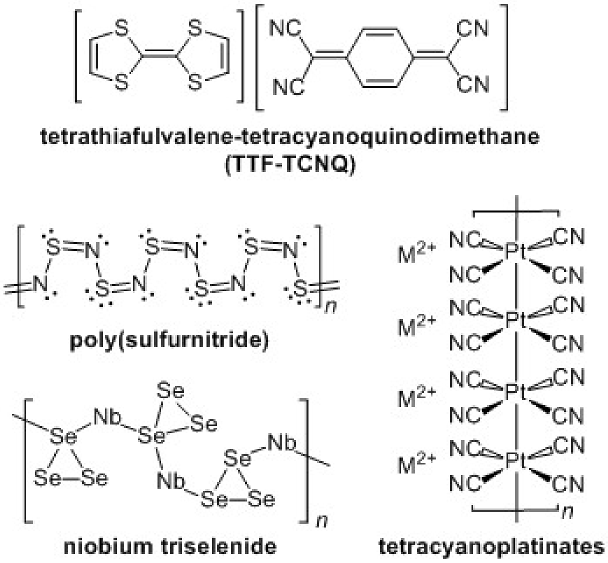


Figure 6. *New examples of synthetic metals.*

This workshop and the discussions that grew out of it resulted in the organization of a long-standing international conference on these materials and issues. This meeting was given the official title of the *International Conference on the Science and Technology of Synthetic Metals*, often referred to by those in the field as just ICSM. The conference was held annually from

1976-1982 and has been held biennially ever since (29). At the time of writing this manuscript, the most recent conference was held in Turku, Finland in 2014, while ICSM 2016 is scheduled to be held in Guangzhou, China.

Following the November 1976 (14, 16, 18) discovery by MacDiarmid, Heeger, and Shirakawa that free-standing films of polyacetylene could be oxidatively doped with bromine and iodine to give high conductivity materials, these results were first reported at the second ICSM conference in New York City (ICSM '77) (29). The production and study of these highly conducting doped polyacetylenes then appeared in the literature starting in the second half of 1977 (8-11), which resulted in the scope of carbon-based materials described by the term "synthetic metals" being expanded to include both intercalated graphites and doped polyacetylenes (59). As such, this broadened the field of synthetic metals and subsequent ICSM conferences included a broader range of polymer and materials scientists. Although Heeger, MacDiarmid, and Shirakawa never used the term in any of their initial polyacetylene papers of 1977-1978 (8-11), MacDiarmid published a review of synthetic metals in 1979 (60). The introduction of this review began with the statement:

> This report is directed toward the very new area of materials science which is concerned with the preparation and characterization of synthetic metals, many of which contain no atoms of any metallic element in their chemical constitution. The three main presently known classes and their potential technological significance will be described.

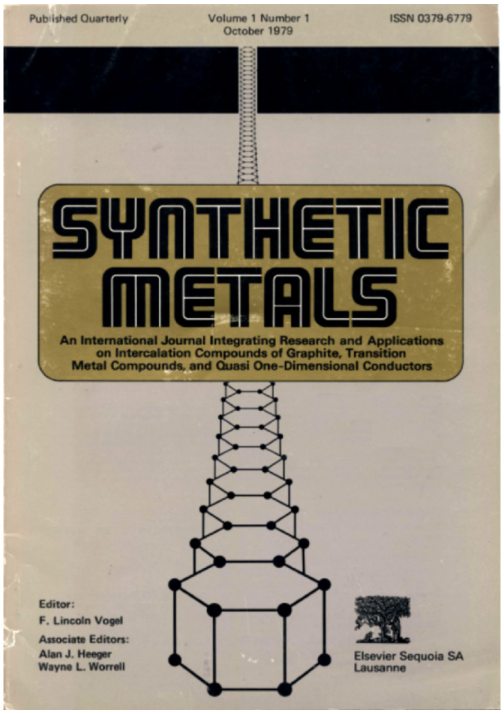
MacDiarmid then went on to state that these three classes were metallic compounds derived from poly(sulfurnitride), polyacetylene, and graphite (60). MacDiarmid had also previously used the term to describe poly(sulfurnitride) in a radio address in 1977 (61). By 1980, the term "synthetic metals" was starting to be used more and more often to describe doped polyacetylene, and as the field of conducting polymers continued to grow, the term was further expanded to include other doped conjugated polymers. By 1991, MacDiarmid and Arthur Epstein included doped polyparaphenylene, poly(phenylene vinylene), polypyrrole, polythiophene, and polyaniline (Figure 1) in a review of conducting polymers as synthetic metals (24).

A New Dedicated Journal

By October 1979, a new journal was launched by Elsevier dedicated to this growing class of materials, which was aptly titled *Synthetic Metals* (28). In the introduction (62) of the first issue (Figure 7), Editor F. Lincoln Vogel of the University of Pennsylvania (63, 64) described this publication as

> ... a new international journal for the publication of research and engineering papers on graphite intercalation compounds, transition metal compounds, and quasi one-dimensional conducting polymers.

The initial Associated Editors (63) included future Nobel laureate Alan J. Heeger and Wayne L. Worrell (1937-2012), best known for his work in solid electrolytes. Heeger would also go on to take over duties from Founding Editor Vogel to become Editor-in-Chief for the journal in 1984 (65). The initial Editorial Board also included Heeger's collaborator and future Nobel laureate Hideki Shirakawa, as well as Alfred Ubbelohde. The initial issue of the journal also contained Ubbelohde's final published paper on intercalated graphite (56). To date, this is still the only journal dedicated to organic conducting materials.



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SYNTHETIC
METALS

An International Journal Integrating Research and Applications on Intercalation Compounds of Graphite, Transition Metal Compounds, and Quasi One-Dimensional Conductors

Editor:
F. Lincoln Vogel
Associate Editors:
Alan J. Heeger
Wayne L. Worrell

Elsevier Sequoia SA
Lausanne

Figure 7. *The cover of the first issue of Synthetic Metals, published October 1979 [Synthetic Metals, Vol 1, Issue 1, Copyright Elsevier and used with permission].*

Conclusions

As hopefully illustrated by the above discussion, the history of synthetic metals can be traced much further back than commonly viewed by current researchers in the field. In addition, just as our concept of conducting materials has changed drastically over the last 50+ years, the specific materials represented by the term synthetic metals has also changed since its first use in the literature. However, in all cases, these materials have continued to fit the original use by McCoy in 1911 to represent "composite metallic substances ... from constituent elements, some of which at least are nonmetallic" (33).

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I would like to thank the Department of Chemistry and Biochemistry of North Dakota State University (NDSU) for continued support of my historical research, as well as the NDSU Interlibrary Loan Department, who went out of their way to track down many elusive and somewhat obscure sources. Additional thanks are given to the staff of the NDSU Archives and Institute for Regional Studies for allowing me access to the records of Fargo College and to Vijala Kiruvanayagam at Elsevier for helping me obtain the original cover for the first issue of Synthetic Metals.

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About the Author

Seth C. Rasmussen is Professor of Chemistry at North Dakota State University (NDSU) in Fargo. He received a B.S. in Chemistry from Washington State University in 1990 and a Ph.D. in Inorganic Chemistry from Clemson University in 1994, under the guidance of Prof. John D. Petersen. As a postdoctoral associate, he then studied conjugated organic polymers under Prof. James E. Hutchison at the University of Oregon. In 1997, he accepted a teaching position at the University of Oregon, before moving to join the faculty at NDSU in 1999. Active in the fields of materials chemistry and the history of chemistry, his research interests include the design and synthesis of conjugated materials, photovoltaics (solar cells), organic light emitting diodes, the history of materials, chemical technology in antiquity, and the application of history to chemical education. Prof. Rasmussen currently serves as the Program Chair for the ACS History of Chemistry division and as Series Editor for *Springer Briefs in Molecular Science: History of Chemistry*, as well as holding editorial positions for the journals *Cogent Chemistry*, *Fluorescent Materials* and *Topological and Supramolecular Polymer Science*.

11th International Conference on the History of Chemistry

In summer 2017, the fortieth anniversary of the creation of the Working Party (WP) on History of Chemistry of the European Association for Chemical and Molecular Sciences (EuCheMS) will be celebrated. The general aim of the conferences organized by the WP is to facilitate communication between historically interested chemists and historians of chemistry, and to gather the community on a regular basis. The most recent conferences organized by the WP were held in Rostock 2011 (Pathways of Knowledge), Uppsala 2013 (Chemistry in Material Culture), and Aveiro 2015 (Chemical Biography in the 21st Century).

The 11th International Conference on the History of Chemistry (11th ICHC) will take place from 29 August to 2 September 2017 in Trondheim, a city founded in 997 which served as Norway's capital during the Viking Age. The Norwegian University of Science and Technology (NTNU), which has been the country's centre for technology education since 1910, will host the conference. The conference is sponsored by NTNU, the Research Council of Norway, the Norwegian Chemical Society, the Chemical Heritage Foundation and Sintef Materials and Chemistry.

Keynote lectures will be given by Hasok Chang (University of Cambridge), Maria Rentetzi (National Technical University of Athens) and Anders Lundgren (Uppsala University).

For more information, see the website at http://www.ntnu.edu/web/11th-international-conference-on-the-history-of-chemistry-11ichc-/home

COMMENT AND RESPONSE
Rediscovering Pyrotartaric Acid

Volume 40, issue 1 contained a paper on the Volatile Salt of Tartar (G. Panzarasa, "Rediscovering Pyrotartaric Acid: A Chemical Interpretation of the Volatile Salt of Tartar," *Bull. Hist. Chem.,* 2015, *40*, 1-8). Prof. E. J. Behrman wrote to explain in greater detail some of the chemistry described in that paper, and to point out an error. Prof. Behrman's letter and Dr. Panzarasa's response are printed below.

—Editor

Comment by Prof. Behrman

Dear Editor,

Panzarasa's recent paper in this journal (1) discussed the early history of pyrotartaric acid (2-methylsuccinic acid). The final section of this paper is titled "Modern Organic Chemistry and the Solution to the Enigma". His Figure 4 shows the transformation of tartaric acid (4 carbons) to pyrotartaric acid (5 carbons) by loss of water. The chemistry is clearly more complex. There has not been a great deal of work on this chemistry but Erlenmeyer made a plausible suggestion in 1885 (2) which was substantiated by Wolff and by de Jong with experimental work in 1901 (3, 4). Brown's work in the middle of the twentieth century (5) is also relevant. The process is initiated by condensation of two molecules of pyruvic acid (another decomposition product of tartaric acid) followed by lactonization and then decarboxylation. Panzarasa also states in footnote 25 that pyrotartaric acid plays a large part in the Krebs cycle. This is not so.

E. J. Behrman, Department of Chemistry & Biochemistry, The Ohio State University, Columbus, OH, Behrman.1@osu.edu

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Response by Dr. Panzarasa

Dear Editor,

I would like to express my gratitude to Prof. E. J. Behrman for suggesting such interesting references. Many thanks are due to Dr. A. Osypova for kindly providing access to original papers.

About the statement in footnote 25: it is pyruvic acid, which plays a protagonist role in the Krebs cycle. I apologize for this inaccuracy.

G. Panzarasa, Empa Materials Science and Technology, St. Gallen, Switzerland, gp4779@gmail.com

BOOK REVIEWS

A Chemical Life, Joseph B. Lambert, De Rigueur Press, North Manchester, IN, 2014, 388 pp, ISBN 978-0-9916503-0-9, $15.00.

The realm of non-fiction is inundated nowadays with memoirs. These are typically written by actors, politicians, musicians, has-beens, never was's, celebrities, and some few people of genuine merit. Those of us who would like to see what our fellow chemists would say in a memoir have precious few examples. Jeffrey Seeman tried to fill the void with his "Profiles, Pathways, and Dreams" series of memoirs by prominent organic chemists published by ACS in the 1990s. Now we are blessed with a new memoir by prominent physical organic chemist Joseph B. Lambert, who also has strong credentials in history of chemistry. He was Chair of HIST in 1996 and a winner of HIST's Edelstein Award in 2004. Lambert has pioneered in the use of spectroscopy in archaeological chemistry, and he has continually applied nuclear magnetic resonance (NMR) toward significant problems in physical organic chemistry. Furthermore, he was the founding editor of the *Journal of Physical Organic Chemistry*, holding the post of Editor-in-Chief from 1986-2010.

Along with the excellence of the book's content, I was knocked out by how fine the book's production values were for such a low price. True, it is a paperback, but it is a paperback that is of equal quality to trade paperbacks that market for $50-60. The binding is firmly set with high quality color illustrations on the cover, internal illustrations are ample and of high resolution, and the copious numbers of formulae and equations make it easy to follow the trail of Lambert's chemistry. When one learns that De Rigueur Press is owned by long-time HIST secretary-treasurer Vera V. Mainz, then the combination of high quality and reasonable price becomes more understandable. The book can be ordered online for the price listed above plus $3.99 postage and handling.

The book's eleven chapters cover 309 pages followed by ten appendices totaling around 80 pages. The short Chapter 1 titled "Science before Research" deals with Lambert's early years as a budding physics major, who switched to chemistry as an undergraduate at Yale. Chapter 2 on "Thermal Rearrangements" covers Lambert's undergraduate research with Bill Doering. Chapter 3 dealing with "Alicyclic Conformational Analysis" describes his graduate research at Cal Tech with John Roberts and his initial independent research as a faculty member at Northwestern. Lambert was one of those few people who were able to skip a post-doctoral appointment to go directly to a faculty position. Cal Tech required that budding Ph.D. students develop five proposals for research. Three of those proposals developed by Lambert were the basis for his initial research program at Northwestern.

Chapter 3 plus succeeding Chapters 4, 5, and 6, respectively, on "Heterocyclic Conformational Analysis," "Atomic Inversion and Bond Rotation," and "Nuclear Magnetic Resonance Spectroscopy" deal with applications of spectroscopy to physical organic chemistry. The title of Chapter 6 is a little misleading, as Chapters 3-5 also involve much NMR.

In the 1960s, solvolysis was a hot topic, with compelling research carried out by such illustrious organic chemists as Winstein, Cram, Roberts, and Brown. Chapters 7 and 8 describe Lambert's work on reaction mechanisms, with Chapter 7 covering solvolysis and

Chapter 8 other mechanisms. Chapter 10 deals with "Organosilicon Chemistry," although work with germanium and tin compounds is also described therein. Lambert's silicon work provoked a feud with George Olah described in detail in Chapter 10, but Lambert's work in this area was recognized with the ACS Kipping Award in Silicon Chemistry in 1998.

In some ways Chapter 9 on "Archaeological Chemistry" and Chapter 11 on "Amber and Exudates" are the most interesting, as Lambert breaks out of the trap of doing the same sort of thing over and over by becoming a Guggenheim Fellow at the British Museum in 1973. When he returned from London, he continued his physical organic work, but he also set up an archaeological chemistry laboratory. When you go into archaeological chemistry, you can kiss those NSF, NIH, and DOE grants goodbye. However, Lambert was able to find a few graduate students who wanted to work in that area. He mounted a significant program and won several awards. His Edelstein lecture and paper was on "The Deep History of Chemistry" to distinguish archaeological chemistry from the history of chemistry. After Lambert's 2010 retirement from Northwestern, he returned to his hometown of San Antonio to the position of Research Professor of Chemistry at Trinity University, where he continues archeological chemistry research.

Although they seldom admit it, academic research directors are only as good as their students and post-docs. Lambert is zealous about admitting his debt to his coworkers. Every mention of a student or post-doc is accompanied by a capsule description of what he or she did and where she or he is now. The book ends with color photographs of the Lambert group from 1972 till 1998. All of his coworkers are listed in Appendices 5-7.

It would be a pity to leave the impression that this book is just a series of *Accounts of Chemical Research* and *Chemical Reviews* articles cobbled together. It IS a scientific memoir but with aspects of a personal memoir mixed in. We learn the reasoning behind his choices of research areas and experimental procedures, but we also learn about his feuds with George Olah and Philip Skell, his girl friends before he met his wife, his enjoyment of the "Batman" TV program, his teaching evaluations (Lambert won the Norris Award for teaching in 1987), and his bout with colon cancer. Lambert also gives succinct, accurate definitions of new terms as he goes along, and the text is leavened by his wit. This book serves as a fine overview of the main currents of physical organic chemistry during the 1960-2010 time period.

Do I have any reservations about this book? Only one, but it is a significant reservation. The book has no index. No doubt omission of an index helped keep the price down, but an index is always an asset. This problem is mitigated somewhat in the appendices of student names, where the student name is accompanied by the page number where the student's work is discussed. However, even without an index, for this low price I think any student of organic chemistry history would find "A Chemical Life" an outstanding value. I recommend this book highly.

E. Thomas Strom, Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX; tomstrom@juno.com

The Matter Factory: A History of the Chemical Laboratory, Peter J. T. Morris, Reaktion Books, London, 2015, 416 pp, ISBN 978-1-78023-442-7, $45.00 (distributed in the Americas by University of Chicago Press).

Even more than most historical narratives, *The Matter Factory* is rooted in the concrete—in particular places and particular objects. Of course histories of all kinds abound in particularities, in contingencies, and in events that could easily have happened differently if circumstances had been different—and history of chemistry is no exception. But such concrete considerations as locality and apparatus are rarely the organizing principle of such narratives, especially by comparison to more conventional foci such as biography, institution, or development of a particular theory or subfield.

To chemists across the discipline, lab fixtures and glassware are as iconic as the periodic table: even theoretical and computational chemists spend hours in laboratories during their training! The concentration of *The Matter Factory* on the chemistry lab and its equipment makes it a history that has the potential to appeal to chemists and chemistry students of any subdiscipline and at any stage of career. That potential appeal is realized in a highly engaging volume full of interesting facts, photos, insights, and connections to the broader history of chemistry.

Chemists were certainly part of the audience Peter Morris, longtime curator at London's Science Museum, had in mind when he wrote the book. To be sure, as an accomplished historian of chemistry (recipient of the 2006 Sidney M. Edelstein Award in History of Chemistry), Morris had his fellow scholars in that field in mind as well. He set out to describe how laboratories and the buildings that they occupy developed, alongside the practices and theories of chemistry, over four centuries. By focusing on selected manifestations of the infrastructure of the chemical enterprise, Morris also sheds light on the societies and economies in which chemistry was and is practiced.

Each of the book's twelve chapters, which are arranged in roughly chronological order, features one laboratory—although several are replete with many supporting examples. In each chapter, Morris intertwines a biographical sketch of a prominent chemist closely associated with the featured laboratory and a description of the development of an important chemical technique with the story of the chapter's featured laboratory. Each chapter is largely self-contained, so that the book as a whole constitutes a series of connected vignettes rather than a comprehensive or continuous narrative. This structure thus would repay both systematic readers and browsers. The wealth of illustration also rewards browsers and casual: there are 139 numbered images, mainly of buildings, labs, or equipment.

Alchemical and metallurgical practices are front and center in the first chapter, in which Morris looks for the origins of specialized chemical workspaces. Several striking depictions of alchemists at work, including paintings by Pieter Breugel the Elder and David Teniers the Younger are viewed with a healthy dose of historical skepticism. The central laboratory of the first chapter is the chemical workshop of Wolfgang von Hohenlohe at Schloss Weikersheim shortly before the turn of the 17th century. It was not depicted by a recognized artist, though, but through a sketch that depicts a scholarly reconstruction by Jost Weyer of that workshop. Furnaces of various sorts are the chapter's featured apparatus.

The second chapter jumps ahead nearly two centuries to the late 18th century. Antoine Lavoisier is the featured chemist and his laboratory at the Paris Arsenal the focal laboratory. Several of the images included in this chapter were prepared by Marie-Anne Lavoisier (née Paulze) in order to illustrate her husband's work. Pneumatic chemistry was the hot research area of the time, and the chapter depicts and discusses apparatus that facilitated experiments on gases. But the humble work table also receives attention as the substrate required for table-top equipment like pneumatic troughs.

Chapter three is the first of eight chapters on 19th-century chemical laboratories and the first of six that have a considerable pedagogical or educational aspect. Its protagonists are Michael Faraday and the Royal Institution of Great Britain. At the Royal Institution, chemical researchers at the pinnacle of their fields—Faraday and Humphry Davy before him—engaged in public outreach to crowds of fashionable and curious spectators in a large lecture theater. The lecture hall included space for demonstrations, connected to and supplied by laboratories where the demonstrations were prepared. The design feature of prep room connected to lecture hall became common in university laboratory buildings erected in the 19th century.

University education moves to the forefront in chapter four, which features Justus Liebig's laboratory at the University of Giessen. Morris summarizes Liebig's major research accomplishments before alluding to Liebig's justly famous innovative methods for training chemists. He points readers to other works that describe and analyze those methods in detail. Morris's focus, though, is on descriptions and illustrations of the laboratory where this training occurred, concentrating on its state in the 1840s after a major expansion. An 1842 illustration of the Giessen laboratory depicts fume cupboards (better known to American chemists as fume hoods). This piece of safety equipment spread in new or renovated university laboratories in the second half of the 19th century, appearing most often on the inside of the lab's exterior walls, especially on the interior of the building's exterior walls. The 1842 illustration of the Giessen lab also shows cabinets for equipment storage built under the work surface; it shows patterns of drawers and doors that would still be recognizable today as belonging to a chemistry laboratory.

Robert Bunsen and his new laboratory at the University of Heidelberg, opened in 1855, are the stars of chapter five. That lab serves as the focal point of a treatment of utilities that 20th- and 21st-century chemists take for granted: gas, water, and electricity were "modern conveniences" in the mid 19th century. The laboratory building had water and gas supplied from municipal services, and that could only happen in localities which made such services available. Every chemist—indeed, every student of introductory chemistry—knows the name Bunsen from the eponymous burner that produces a hot and stable flame of low luminosity. So Bunsen's lab is an obvious touchstone to discuss the innovation of gas utilities in chemical labs. It is also appropriate for water utilities, for Bunsen also invented the water aspirator widely used in vacuum filtration. That apparatus is hardly less widespread than the Bunsen burner, but its connection to Bunsen is much less well known.

Chapter six focuses on chemical palaces, monumental buildings that housed large lecture halls, laboratories and specialized accessory rooms (for balances or polarimeters, for example), museum-like displays, and often residential quarters for the professor and his family. Wilhelm Hofmann is the chief figure of the chapter, and the new chemistry building he designed as part of his move to accept the chair of chemistry at the University of Berlin in the 1860s is the chief edifice. Chemical palaces such as this reflected the wealth and prestige of chemistry as a discipline, of the chemists who directed them, and of the states that constructed them. Indeed, the promise of a new chemistry building was often an incentive for attracting a prominent chemist to accept move to a chair at a different university. By the last third of the 19th century, the laboratory spaces inside a university chemistry laboratory building would be recognizable as such by any early 21st-century chemist. Benches, aisles, and bottle racks were by then common.

The diffusion of the "German model" academic laboratory building throughout Europe and North America in the late 19th century is the subject of chapter seven. Henry Enfield Roscoe and his laboratory at Owens College, Manchester, England, are the featured chemist and institution, but this chapter intentionally casts a wide net to examine the spread of buildings like Hofmann's Berlin and Bonn palaces. Indeed, Hofmann continues as an important figure in this chapter because of his openness in publishing relevant details of those palaces.

Chapter eight closes this run of chapters on academic chemistry laboratories by scrutinizing a feature of such buildings that arose in Germany and proved particularly popular in the United States: the chemical museum. Chemical museums were collections of artifacts used in teaching—objects such as products of chemical industry, minerals, chemical specimens, and the like. Chemical museums flourished around the turn of the 20th century, and they disappeared over the course of that century and were largely forgotten. For the most part, historians of chemistry have not written about this type of chemical museum, with the exception of the one featured in this chapter, Charles Frederick Chandler's chemical museum at Columbia University in New York. This chapter, like the previous one, ranges over much of Europe and North America to show many examples of this peculiar kind of chemical space.

Chapter nine leaves the palaces of academe for laboratories in chemical industry. Late 19th-century research labs in industry were often similar in appearance to the German-style academic laboratory, though usually less opulent. Here the exemplar was the pharmaceutical lab at Bayer's facility in Elberfeld, Germany, and the featured chemist is Bayer's Carl Duisberg. Morris reminds readers that chemical industries needed labs for more than research and development. Analytical labs devoted to quality assurance and process control were typically much more basic than their academic counterparts.

Morris treats government laboratories in chapter ten. Their principal task in the late 19th century was analytical work in support of enforcing regulations for revenue and safety. The Government Chemist's Laboratory in London, and its first principal chemist, Thomas Edward Thorpe, are the chief examples of this chapter.

Morris returns to academic laboratories in the book's final two chapters, bringing the subject into the present century after a stop in the 1960s. Chapter 11 concentrates on the Stauffer Chemistry Building at Stanford and the department chair who presided over it, William Summer Johnson. The Stauffer building was one of the first designed for the "instrumental revolution" in chemistry research (NMR in particular). It segregated many of the electronic instruments that supported chemical research, along with their specialized operators, from the laboratory spaces where wet chemistry was done. Both the architectural features of the exterior and the interior arrangement of instrument rooms were departures from the monumental style of the chemical palace and its laboratories of aisles and benches.

Oxford University's Chemistry Research Laboratory (CRL), opened in 2004, is the focus of Chapter 12. In several ways, this building extends trends first mentioned in the previous chapter: instrumentation and specialization are taken still further in the CRL. Even the less specialized workspaces there have "clean" and "dirty" areas physically separated but visually connected by glass partitions. Even more prominent than form and function in Morris's account of the CRL is its financing, which relied heavily on commercial companies spun off from Oxford. This too is a continuation of a trend noted in the previous chapter. Graham Richards was chair of Oxford's recently unified chemistry department when the new building was planned and constructed; Richards had previously served as chairman of the University and Industry Committee at Oxford and was an important figure in setting up some of the university's commercial spin-offs.

Morris is an expert and congenial guide in this tour of twelve sites of chemistry highlighted in the book (and of countless additional ones) over four centuries. Many of the sights are familiar to chemists, especially the humble equipment practicing chemists see nearly every day and take for granted. Morris provides insights of context and origin into those material artifacts. Chemists may look a little differently at their water aspirator, fume hood, or instrument room after reading *The Matter Factory*.

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