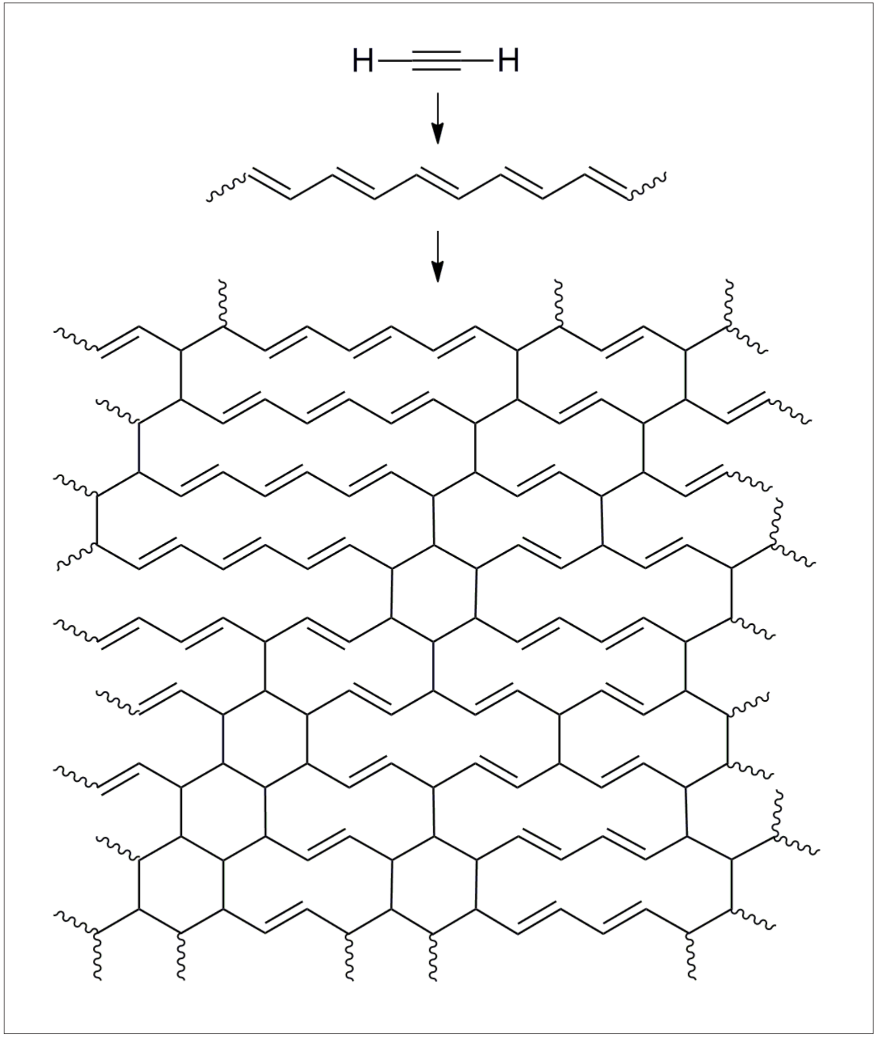
BULLETIN FOR THE HISTORY OF CHEMISTRY

Division of the History of Chemistry of the American Chemical Society

VOLUME 42 Number 1 2017



How does acetylene react with itself?

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The Cover … Reaction scheme for the polymerization of acetylene to cuprene. See p 63.

CHEMISTS FOR THE COMMON GOOD (1)

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Introduction

Martin Heinrich Klaporth (1743-1817) was the most famous German chemist in the last third of the eighteenth century. He was well known in Europe as an excellent analytical chemist, discoverer and inventor. In 1789 he discovered uranium (in the form of oxide) and what was called "earth of zirconium," that is, zirconium dioxide. In the years to follow he discovered or rediscovered six additional substances: strontia (1793), earth of titanium (titanium dioxide, 1795-97), tellurium (1798), chromium (1798), beryllia (1801), and ceria (1804) (2). Throughout his chemical career Klaproth analyzed, qualitatively and quantitatively, more than 200 substances, most of mineral origin. In each single case "analysis" meant a true research program consisting of numerous experiments (3).

Klaproth carried out most of his experiments in his pharmaceutical laboratory. He was not just a chemist but also an apothecary, who ran his shop until 1800 when, aged 57, he became the director of the laboratory of the Royal Prussian Academy of Sciences. Klaproth came from humble origins. The son of a tailor, he completed a pharmaceutical apprenticeship training (from 1759 until 1764), followed by seven years of service as a journeyman. The famous chemist had neither visited a university nor received any other formal academic education. In 1780, through his marriage to a niece of the Berlin apothecary-chemist Andreas Sigismund Marggraf (1709-1782), he came into sufficient funds to buy his own apothecary's shop in the city of Berlin. In the two decades that followed, his shop prospered both economically and scientifically. Klaproth produced and sold all kinds of remedies as well as luxury goods and chemicals. The eighteenth-century pharmaceutical laboratories belonged to the precursors of the nineteenth-century chemical industry. But Klaproth's reputation as a chemist also grew apace. His private lectures on chemistry became the latest fashion among Berlin's intellectual elite. In 1782, he received a teaching position at the Medical-Surgical College of Berlin (*Collegium medico-chirurgicum*), followed (in 1784) by a salaried teaching position at the Mining Academy of Berlin and another teaching position (in 1787) at the Artillery School of General G. F. v. Tempelhoff (renamed Royal Artillery Academy in 1791), which earned him the title of professor (4). In 1788, he was elected to the Royal Prussian Academy of Sciences, and in 1810, he was appointed the first professor of chemistry at the newly founded University of Berlin.

Parallel to his increasing fame as a chemist, Klaproth also became involved in public service, first as a member of Prussia's highest medical board (in 1782), and then as a consultant to Prussian Minister Friedrich Anton von Heinitz (1725-1802). Beginning in 1786, Minster von Heinitz, who also headed the Department of Mining and Smelting Works in the Prussian government (*Generaldirectorium*), frequently sought Klaproth's chemical and technical counsel concerning industrial inspections and useful practical projects such as Achard's project to extract sugar from beets. Thus the year 1786 seems to have been "the crucial year" in the chemical career of the German Lavoisier. For it was at precisely this time that his research interests turned to mineral analysis and chemical mineralogy. He then designated himself a chemical mineralogist. By contrast, before this time he had studied a broad variety of different subjects, including pharmaceutical preparations (5).

Klaproth understood chemistry as a scientific endeavor that contributed to our understanding of nature, and at the same time as an enterprise that contributed to technological improvement and innovation. Like many scientists of his time, he participated in a social movement that defined technical innovation as a crucial factor for promoting "the common good" (*Gemeinwohl, gemeiner Nutzen*) and social progress. In the last third of the eighteenth century, Prussian chemists and other scientists frequently talked about "useful knowledge," "useful science," "technical progress," and "the common good" (6). They viewed chemistry and chemical mineralogy to be particularly useful knowledge for the Department of Mining and Smelting Works, which directed the Prussian mines and foundries as well as factories linked to mining, such as the Royal Prussian Porcelain Manufactory. Was their talk about useful chemical knowledge mere rhetoric? Or did it have consequences for doing chemistry? My answer to the latter question is a clear Yes, and I want to show this in the next part by discussing briefly Klaproth's discovery of uranium.

Klaproth's Discovery of "Uranium" and the Invention of "Uranium Yellow

Klaproth discovery of "uranium" relied on long series of experiments in which he analyzed the ore pitchblende, first in the dry way and then in the wet way, using a broad variety of different reagents and analytical techniques (7). When the result of an experiment was ambiguous, he repeated it and performed additional experiments using alternative reagents. After dozens of experiments he was convinced that he had isolated from pitchblende a novel "metal calx" (later: metal oxide). He then tried to reduce the metal calx to a metal. In this final part of his investigation he encountered obstacles. Thus, in his publications, Klaproth openly admitted that his final experiments did not yield absolutely clear results, but ultimately he concluded that he had discovered a novel metal, which he named "uranium" after the planet Uranus discovered by Herschel in 1781 (8). Today we know that Klaproth's uranium was actually uranium dioxide, and that it was Eugène Melchior Peligot (1811-1890) who actually prepared metallic uranium in 1841.

In the very same two publications from 1789 in which Klaproth announced his discovery of uranium to the Republic of Letters, he also announced a new invention—or the incipient work on an invention: the use of "uranium calx" (later: uranium oxide) for coloring glass and porcelain. It was not just a lucky guess by Klaproth that uranium calx might be used as a new color to decorate glass and porcelain. Nor was it just his outstanding experimental skill that enabled him to separate uranium calx from pitchblende. For both his discovery and his invention, the social milieu in which he worked played a crucial role. Pitchblende was an extremely rare mineral, found only in certain mines in Saxony, Bohemia and Sweden. Klaproth experimented with two specimens of pitchblende, which came from a mine (named *Georgwagsfort*) located in the town of Johanngeorgenstadt in Saxony, and from two mines (named *Sächischer Edelleutstollen* and *Hohe Tanne*) located near Joachimsthal in Bohemia. He had access to these materials through his connections to Minister von Heinitz. Since 1786 he had become a member of the inner circle of this influential minister, who directed the Department of Mining and Smelting Works. Just a year before his discovery, in summer 1788, he had traveled to the Saxon towns of Dresden and Freiberg, visiting mines and the famous Mining Academy of Freiberg, where the mineralogist Abraham Gottlob Werner (1749-1817) was teaching. Werner had analyzed pitchblende before Klaproth, and it is very likely that Klaproth received the specimen of pitchblende from him. Clearly, Minister von Heinitz, who had been a leading Saxon mining official from 1763 until 1774, had paved the way for this important visit.

Likewise, Klaproth's role as a consultant to Minister von Heinitz also conditioned his investigation of the practical use of uranium calx. Since 1787 Klaproth had been a member of a committee that inspected the laboratory of the Royal Prussian Porcelain Manufactory, where the pigments for decorating porcelain were prepared (9). Almost all of these pigments were metal calces or metal oxides in our terminology. As uranium calx had a nice yellow color, it was not too far-fetched to assume that one might use it as a new color for porcelain as well as glass, which has properties similar to porcelain. In his publications of 1789, Klaproth described six experiments that "examined the coloring properties" of uranium calx. Three years later, a laboratory worker of the Porcelain Manufactory named Friedrich Bergling, who was a pupil of Klaproth and his experimental collaborator at the manufactory (in the context of the inspection committee), reported on the results of further experiments (10). He had succeeded in preparing a new pigment yielding "a nice yellow color" on porcelain (11). Well into the nineteenth century, the Royal Prussian Porcelain Manufactory used the radioactive "Urangelb" to decorate its products.

Franz Carl Achard's Projects

When Klaproth entered the laboratory of the Royal Prussian Academy of Sciences as its new director in April 1801, he was shocked. The floor, the walls and the ceiling of the lab were covered with an ugly brownish substance. Literally everything in the room was filthy. He immediately sent a letter to the directors of the Academy requesting the "quick re-organization of the academic building" as "benefits the honor of the Academy" (12). It was one of the few occasions on which he was truly outraged, but he was partly responsible for the situation. In the year before, he had performed experiments with his friend Franz Carl Achard (1753-1821) on the production of sugar from the syrup of sugar beets. These experiments were carried out on a large technological scale. For this purpose, the Academy's laboratory was rebuilt and equipped with new instruments and officially renamed "sugar beet factory." The experiments in the academic sugar beet factory were crowned with success, yielding several hundred "centner" of sugar (a "centner" is 50 kilograms). Less welcome, however, were the proliferating traces of the large-scale experiments, which had affected not only the laboratory room, but also the apartments of the Academy's chemist and astronomer located in the second floor of the building. While the apartments could be renovated, the state of the laboratory was so desperate that the Academy decided to built a new one.

In spring 1801 Achard, who had been the director of the academic laboratory before Klaproth, was establishing a real sugar beet factory in Silesia. His invention of beet sugar is well known today, but it is by no means his exclusive invention. Achard was perhaps the most energetic academic inventor and researcher in late eighteenth-century Prussia (13). He came from a wealthy family of Huguenots, and, like Klaproth, he had never visited a university. In 1776, at the age of 23, he became Andreas Sigismund Marggraf's laboratory assistant and a member of the Royal Prussian Academy of Sciences. From Marggraf he learned careful chemical experimentation and further received important incentives for his invention of beet sugar. In 1747, Marggraf had discovered that certain kinds of native plants (such as *beta vulgaris*) contained sugar that was identical with the expensive, imported cane sugar. The discovery was made in the context of systematic series of experiments, whose goal to isolate and identify those "proximate components" of plants that caused their sweet taste. These types of experiments were typical for the new field of "plant and animal chemistry," the predecessor of modern organic chemistry (14). Like Klaproth's discovery of uranium, Marggraf's discovery was made in a pharmaceutical laboratory, as Marggraf was also an apothecary (15).

After Marggraf's death, in August 1782, Achard became director of the Academy's laboratory and of its physical class. Yet Achard did not restrict himself to a purely academic life. The Academy of Sciences strongly supported all kinds of combinations of natural research and technological investigation. It encouraged its members to carry out work of invention and participate in practical projects for the state. Most of the members of the physical and mathematical classes of the Academy were not just scientists, but also technical experts and inventors, many of whom were also civil servants in the newly created state departments that directed manufacture, mining, civil architecture, and forestry. Thus, from the beginning of his membership in the Academy, Achard undertook various kinds of useful technological projects. To these belonged the installation of lightning conductors, the examination of building materials, the preparation of new kinds of alloys, the cultivation of exotic tobacco, and the invention of new colors for the Royal Prussian Porcelain Manufactory (15). One of his inventions was *bleu mourant*, a light blue color that had previously been used exclusively at the Royal Porcelain Manufactory of Sèvres. Achard's private life was no less turbulent. He financed many of his technical projects privately, and he went deeply into debt for this purpose. And there were other kinds of temptation. In 1776, the same year he became a member of the Academy of Sciences, he apparently married the wrong woman: she came from a craftsman family, was divorced, and nine years older than himself. In 1784, their marriage ended in divorce. The reasons for this became clear only three years later, when the wife's daughter from her first marriage, then aged seventeen, gave birth to a child by Achard. He and the young lady lived together for many years without getting married, but this second relationship eventually ended in similar circumstances as the first. Achard was attracted to a pretty maid working in the shared household and entered into a new relationship, again without marriage. Needless to say, the directors of the Academy were not terribly pleased by this conduct, but they always helped their members get out of trouble. As a member of an old and influential family of Huguenots, Achard also received support directly from Friedrich II. It was the king himself who had encouraged him to reinvent *bleu mourant* for his Royal Porcelain Manufactory and to cultivate American and Asian tobaccos.

In 1782 Achard bought an estate in the village of Kaulsdorf, east of Berlin, where he began cultivating "sugar beets" with a higher concentration of sugar than the available species of beets. This was the first, agricultural part of his work to invent beet sugar, which took more than ten years. From 1790, he continued the cultivation of sugar beets in a new estate in *Französisch Buchholz*, a Huguenot settlement near Berlin. In 1798, when he published the results of his trials, he wrote to the king that he hoped to have "been useful to the economy of his fatherland." In another letter he wrote that it was his "most ardent wish" that his "work was *gemeinnützig*," that is, promoting the common good (16). One year later, he started the second part of his project: the extraction of sugar from the syrup of sugar beets on a large technological scale, which eventually led to the transformation of the Academy's lab into a "sugar beet factory" and its unwanted consequences.

As I mentioned before, after Achard had begun to establish a sugar beet factory in Silesia, Klaproth became his successor as the director of the Academy's laboratory. A decade later, Klaproth's scientific career culminated in his nomination as the first professor of chemistry at the newly founded University of Berlin. In 1814, at the age of 71, Klaproth suffered a severe stroke, but he continued his lectures at the Berlin University until his illness forced him to retire in 1816. In the time remaining until his death on 1 January 1817, he tried to sell his collection of chemical instruments and preparations to the Prussian state. As a man who had always tried to serve the common good and his "Vaterland," he had privately financed a large part of his research and teaching equipment. In December 1816 he wrote in a letter to the king that his life would soon end and that he hoped that after his death his chemical collection would not be divided into parts and spread outside of the country. It was his "greatest wish," he stated, to submit it as a whole to his "Vaterland." "If I had no children," he continued, "I would sacrifice this beautiful collection to my fatherland" (17). In the next section I will shed light on the social movement in which terms like fatherland and the common good figured prominently.

The Social Movement

After the so-called Wars of Liberation (1813-1815) against Napoleon, the word "Vaterland" cropped up more frequently. For the majority of aristocratic landowners it referred to Prussia, while for the liberals it meant Germany, which was not yet a unified state but divided into dozens of small German-speaking states. In any case, in the decades around 1800 talk about "Vaterland" did not yet serve to legitimize political hegemony and imperialism. It was only after the unification of Germany in 1871 that "Vaterland" acquired a chauvinist connotation. The discourse about the "the common good" was significantly older than that on "Vaterland." It went back to seventeenth-century cameralism and the Enlightenment, but also acquired new facets in the context of nation-state building, the expansion of state bureaucracy, and the establishment of technological schools around 1800. For the liberals participating in the latter discourse, terms like "the common good" and fatherland pointed to more or less the same goals of social and educational reform (18).

Achard and Klaproth were very different individuals, but their social role, and the goals, interests and ideals connected to it, were largely identical. The two men participated in a social and cultural movement that held knowledge and the improvement of technology to be the most promising ways to promote the fatherland and the common good. They struggled to realize an ideal shared by most members of the Royal Prussian Academy of Sciences: the public man serving the common good (*Ideal des gemeinnützigen Mannes*). Acquisition of "useful knowledge" was an important element of the strategy to improve technology for the good of society. The Academy's chemists, in particular, were engaged in numerous useful projects and civil service. Friedrich Hoffmann (1660-1742), Caspar Neumann (1683-1737), Johann Heinrich Pott (1692-1777), Andreas Sigismund Marggraf, Franz Carl Achard, Martin Heinrich Klaproth, Carl-Abraham Gerhard (1738-1821) and Sigismund Friedrich Hermbstaedt (1760-1833) were not just chemists but also inventors, technical experts and consultants to the state. These men asked for neither privileges (or patents) for their inventions nor any financial gratification. On the contrary, they often invested private money in their projects. In correspondence with their technological endeavors, their scientific interests focused on experiments, empirical knowledge about substances, generalized concepts and empirical rules about types of reactions, chemical affinities, and chemical analysis, including quantitative analysis. In the last third of the eighteenth century these chemists were also engaged in the institutionalization of technological research and teaching. In so doing, they contributed to the newly emerging chemical subdisciplines of "metallurgical chemistry" and "technical chemistry" as well as to the so-called "useful sciences" like mining and agriculture (19).

In the discourse about useful knowledge and the common good, neither "useful knowledge" nor "the common good" were sharply defined terms. But in the eighteenth century the meaning of these two terms was more or less evident to everybody. "Useful knowledge" was directed towards mundane practices and improvements to technology (20). Thus it was clearly demarcated from high theory, natural theology and abstract philosophy of nature. It was further distinguished from everyday beliefs and from those parts of artisanal knowledge that were clearly restricted to local observation and narrowly defined local interests. However, "useful knowledge" by no means excluded artisanal knowledge *per se*. On the contrary, it included all kinds of articulated and more generalized experiential knowledge, originating in academic and artisanal or in industrial contexts.

Likewise, talk of "the common good" and "civil service" promoting the common good conveyed a clear message, although these terms were not clearly defined. The message was political, and it was paralleled by the emergence of the modern nation-state and state departments promoting industry, the military, and civil service. In continental Europe these deep historical changes began while absolutism was still flourishing. Thus talk of "the common good" and civil service meant a reorientation away from the absolutist king and towards civil society. In Prussia, unlike France, this discourse did not feed into a political revolution, but it helped to achieve more modest political and social reforms in the early nineteenth century.

Conclusion

Like their European colleagues, late eighteenth-century Prussian chemists performed technological experiments and work of invention. Franz Carl Achard transformed the laboratory of the Royal Prussian Academy of Sciences into a "beet factory" in order to test the production of beet sugar on a large technological scale. Martin Heinrich Klaproth, who had discovered uranium in 1789, performed experiments with a laboratory worker (*Laborant*) of the Royal Prussian Porcelain Manufactory in order to prepare "uranium yellow" to be used for decorating porcelain. All Prussian chemists argued for the usefulness of chemistry, and they further highlighted distinct parts of chemistry—"metallurgical chemistry," "technical chemistry," "applied chemistry" and analytical methods—that matched with practical fields. In the eyes of these chemists, chemical knowledge was an indispensable part of useful knowledge, technological innovation and progress, which would promote the economy of their fatherland and the common good. Around 1800, "fatherland" and "the common good" were key words in the discourse about the usefulness of knowledge and the promotion of the common good. A century later, these words still played an important role, but their meaning had been transformed. When Fritz Haber performed research on chemical weapons for the sake of his fatherland and the common good, nationalism and imperialism had radically changed the originally liberal meaning of these two terms.

References and Notes

1. HIST Award Address, presented at the 252nd National Meeting of the American Chemical Society, Philadelphia, PA, August 23, 2016, HIST 34.
2. See also J. R. Partington, *A History of Chemistry*, 4 vols., Macmillan, London, 1961-1970, vol. 3, 656f.
3. This paper is based on U. Klein, "Klaproth's Discovery of Uranium," in U. Klein and C. Reinhardt Eds., *Objects of Chemical Inquiry*, Science History Publications, Sagamore Beach, MA, 2014, 21-46; U. Klein, *Humboldts Preußen, Wissenschaft und Technik im Aufbruch*, Wissenschaftliche Buchgesellschaft, Darmstadt, Germany, 2015, and U. Klein, *Nützliches Wissen, die Erfindung der Technikwissenschaften, Wallstein*, Wallstein, Göttingen, 2016. For a biography on Klaproth see also G. E. Dann, *Martin Heinrich Klaproth (1743-1817): Ein deutscher Apotheker und Chemiker, sein Weg und seine Leistung*, Akademie-Verlag, Berlin, 1958.
4. The Berlin "Mining Academy," founded in 1770, was not a true academy or school but rather a series of lectures organized and funded by the Mining and Smelting Department; see U. Klein, "Ein Bergrat, zwei Minister und sechs Lehrende: Versuche der Gründung einer Bergakademie in Berlin um 1770," *NTM Zeitschrift für Geschichte der Wissenschaften, Technik und Medizin,* **2010**, *18*, 437-468. See Ref. 3, (2015) and (2016).
5. Klaproth collected his most important experimental essays in book form, entitled *Beiträge zur chemischen Kenntniss der Mineralkörper* (1795-1810). By 1810 the six volumes of this book comprised a total of 207 experimental essays, which dealt with nearly the same number of different mineralogical species along with their chemical analysis.
6. See Ref. 3 (2016).
7. These experiments are described in detail in Ref. 3 (2014).
8. See M. H. Klaproth, "Chemische Untersuchung des Uranits, einer neuentdeckten metallischen Substanz," *Ann. Chem.,* **1789**, part 2, 387-403; M. H. Klaproth, "Mémoire chimique et minéralogique sur l'Urane," Mémoires de L'Académie Royale des Sciences et Belles Lettres **1786/87**, 160-174; the latter paper appeared in 1789 as

well.

9. One of the goals of this committee was to foster improvements of pigments used for overglaze painting on porcelain. This included the organization of written, reliable recipes for the preparation of long-used pigments as well as the invention of new pigments that extended the spectrum and shades of colors. See U. Klein, "Chemical Experts at the Royal Prussian Porcelain Manufactory," *Ambix,* **2013**, *60*, 99-121; U. Klein, "Depersonalizing the Arcanum," *Technology and Culture,* **2014**, *55(3)*, 591-621; U. Klein, "Chemical Expertise: Chemistry at the Royal Prussian Porcelain Manufactory," *Osiris*, **2014**, *29*, 262-282.
10. Königliche Porzellan-Manufaktur archive, XVII.12, folios 51-59.
11. Ref. 10, folio 58. Uranium yellow (*Urangelb*) is mentioned in a table of porcelain colors from 1838 by the manufactory's director Georg Friedrich C. Frick; see E. Köllmann and M. Jarchow, *Berliner Porzellan*, *Textband*, Klinkhardt & Biermann, Munich, 1987, p 323 (color number 28 of the table).
12. Archive of the Berlin-Brandenburg Academy of Sciences I-XIII-26, folio 11.
13. On Achard, see also H.-H. Müller, *Franz Carl Achard (1753-1821), Biographie*, A. Bartens, Berlin, 2002.
14. F. L. Holmes, *Eighteenth-Century Chemistry as an Investigative Enterprise,* University of California Press, Berkeley, 1989. U. Klein, "Shifting Ontologies, Changing Classifications: Plant Materials from 1700 to 1830," *Stud. Hist. Phil. Sci.*, **2005**, *36A*, 261-329. U. Klein and W. Lefèvre, *Materials in Eighteenth-Century Science: A Historical Ontology,* MIT Press, Cambridge, MA, 2007.
15. See Ref. 3 (2015).
16. Quoted in Müller, Ref. 13, p 165.
17. Geheimes Staatsarchiv Preußischer Kulturbesitz, I. HA, Rep. 76 Kultusministerium, Abt. Va, Sekt. 2, Tit. X, Nr. 17, folio 12.
18. For more details, see Ref. 3 (2015).
19. See P. M. Jones, *Agricultural Enlightenment: Knowledge, Technology, and Nature, 1750-1840*, Oxford University Press, Oxford, 2016. Ref. 3 (2016).
20. For more details, see U. Klein, "'Useful Knowledge'—'Useful Science'," in T. Morel, G. Parolini, and C. Pastorino, Eds., *The Making of Useful Knowledge*, Preprint 481 of the Max Planck Institute for the History of Science, Berlin, 2016, pp 39-48. Ref. 3 (2016).

About the Author

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National Historic Chemical Landmarks

The National Historic Chemical Landmarks program is celebrating its 25th anniversary this year. A half-day symposium in its honor is scheduled for the HIST program at the 254th American Chemical Society meeting in Washington. The symposium is scheduled for Monday morning, August 21. The landmarks program began in 1992 as an effort of HIST and the ACS Office of Public Outreach, and it is currently under the ACS Committee on Public Affairs and Public Relations. The first Landmark dedicated by the program was on Leo Hendrick Baekeland and the Invention of Bakelite, at the National Museum of American History in Washington, DC, in 1993. The most recently dedicated Landmarks were on Chlorofluorocarbons and Ozone Depletion (at the University of California, Irvine) and the Mars Mariner Infrared Spectrometer (at the University of California, Berkeley) both in 2017. More information on the Landmarks program can be found at https://www.acs.org/content/acs/en/education/whatischemistry/landmarks.html

THE CHANGING CONTENT OF *CONVERSATIONS ON CHEMISTRY* AS A SNAPSHOT OF THE DEVELOPMENT OF CHEMICAL SCIENCE

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Mrs. Marcet's two-volume *Conversations on Chemistry* was initially published anonymously in 1806 (1). The name of the author, Jane Marcet, first appeared on the thirteenth edition of 1837 (2), though her name and reputation were widely known long before then. A biography of Jane Marcet has been published (3), and there are numerous short articles about her, principally concerning *Conversations on Chemistry* and another popular book *Conversations on Political Economy*. *Conversations on Chemistry* was one of the most influential chemistry books of the nineteenth century. The way in which it came to be written has recently been described in detail (4, 5) though other writers have provided some of the background material (6). The appearance of the title page and the kind of content, a series of dialogues between two students and a teacher, were not novel for the period, and even already a little dated in 1805. That the anonymous writer and the teacher in the book, Mrs. B, were both women certainly was novel. Even more noteworthy is that the preface states that the book was directed at women. It also described experiments that could be performed at home, perhaps in the kitchen, though most were originally performed by Mrs. Marcet in the laboratory set up by her husband in her father's house in St. Mary Axe, in London. It is remarkable that a popular chemistry book first published in 1806 should still excite interest today, but it has concerned historians not only because the author was a pioneer in writing about chemistry but also because she was a rarity as woman writer in a field of science. *Conversations in Chemistry* was also an unusual chemistry book in that it was continuously revised by its

Table 1. The publication dates and print runs of the various editions of *Conversations on Chemistry*, data abstracted directly from the Longmans Archive at the University of Reading, UK.

Year	Edition or Impression	Print Run
1806	First edition	1000
1807	Second edition	1000
1809	Third edition	1500
Not recorded	Fourth edition	Not recorded
1813	Fifth edition	1500
1817	Sixth edition	1500
1819	Seventh edition	1500
1822	Eighth edition	1500
1824	Ninth edition	1000
1825	Tenth edition	2000
1828	Eleventh edition	2000
1832	Twelfth edition	1500
1837	Thirteenth edition	1000
1841	Fourteenth edition	1000
1846	Fifteenth edition	1000
1852	Sixteenth edition	1000

author throughout its sixteen editions, which are listed in Table 1, and the author took every opportunity in her text to echo the latest scientific developments. She personally knew luminaries such as Wollaston, Davy, Berzelius, Smithson Tennant, and Faraday, and she certainly relied upon them for the latest scientific information (6).

When Jane Marcet died in 1858, she was widely recognized as an expert in education, science and economics, despite never having attended a formal education establishment at any time in her life. After the French revolution of 1789, there was a widespread antagonism in parts of British society towards French ideas, but nevertheless after 1790 the "French chemistry" propounded by Lavoisier and his colleagues gradually established itself in both Scotland and England. This process took perhaps twenty years, and one of the major influences in its general adoption was *Conversations in Chemistry,* written by an author who was at the time of the original publication essentially unrecognized outside her family.

How this came about raises the questions of what kind of person the author, Jane Marcet, was. Her preoccupations were often not dissimilar to those of many contemporaneous researchers, as illustrated by Jenny Uglow's masterly accounts (7, 8) of the people who provided a significant impulse to the British Industrial Revolution in the 1780s.

Jane was the daughter of a wealthy Swiss banker and businessman, Antoine Haldimand, who settled in London after working for some time in Italy. He became a British subject and married the daughter of a British business acquaintance. Jane was born in 1769. He and later Jane maintained the connection with their Swiss relations. In 1794 Alexandre (later Alexander) Marcet was born in Geneva in 1770, and was banished from his home city as a consequence of his life and activities when the French Revolution finally reached there. He went to study medicine at what was then the foremost school of medicine in Europe, the University of Edinburgh, and there he came under the influence of Joseph Black and became interested in chemistry. He graduated in 1797 and moved to London where he practiced as a fever surgeon and physician. He married Jane in 1799 and remained interested in chemistry until he died in 1822. Whether he still pronounced his surname in the French style ("Marsay") or adopted an English variation ("Marset") is impossible now to determine.

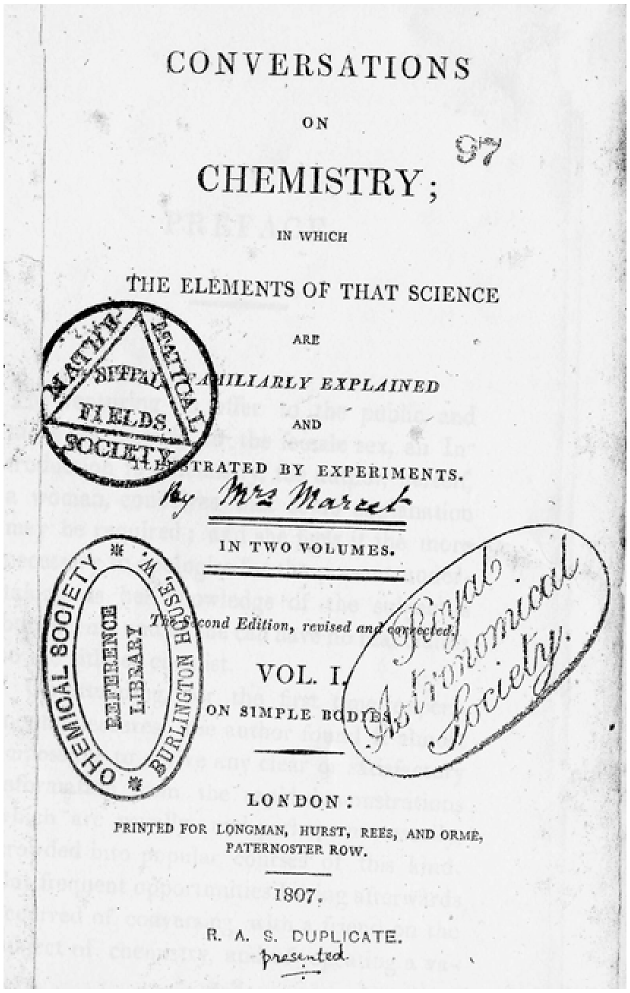
The Chemistry Content of *Conversations on Chemistry*

Chemistry books of the early nineteenth century, like *Conversations on Chemistry* itself, were generally directed to a voluntary audience (9, 10). Discussion of *Conversations on Chemistry* in the past has tended to be based upon selected editions, often the first of 1806, of which an account has recently been published (11). Though that account is titled *Chemistry in the Schoolroom: 1806*, there were precious few schoolrooms in which chemistry was taught at that time.

People who read such books usually studied alone and voluntarily rather than enrolling as students in classrooms. Jane Marcet revised her text throughout its publication life of about fifty years, so that a comparison of an early edition and a late edition provides an informative picture of how chemical science was changing. The reactions of the three participants in the *Conversations*, a tutor Mrs. B and two students, Emily and Caroline, also convey a picture of the political and social atmosphere of that period. *Conversations* is not a dry text. The participants emerge from the two volumes as real individuals. Here we compare the twenty-five *Conversations* of the second edition (12, Figure 1) with the corresponding *Conversations* in thirteenth edition (Figure 2), the first to bear the author's name, and described by her as enlarged and corrected (2), but it is not intended to imply that the changes noted in the thirteenth edition compared to the second edition were made only in 1837. Changes were made gradually in successive editions, but the thirteenth edition provides a useful place to summarize the changes up to that edition. In both editions, Volume 1 carries the subtitle On Simple Bodies, and Volume II the subtitle On Compound Bodies. We consider first Volume 1.

Conversation 1, On the General Principles of Chemistry

Mrs. B makes clear that Emily and Caroline should already be familiar with "elementary notions of NATURAL PHILOSOPHY" but Caroline is not so keen on learning more: "To confess the truth, Mrs. B I am not disposed to form a very favourable idea of chemistry, nor do I expect to derive much entertainment from it." This provokes a little lecture from Mrs. B: "I rather imagine, my dear Caroline, that your want of taste for chemistry proceeds from the very limited idea you entertain of its object ... Nature also has her laboratory, which is the universe, and there she is incessantly employed in



CONVERSATIONS

ON

CHEMISTRY;

IN WHICH

THE ELEMENTS OF THAT SCIENCE

ARE

FAMILIARLY EXPLAINED

AND

ILLUSTRATED BY EXPERIMENTS.

By Mrs Marcet

IN TWO VOLUMES.

The Second Edition, revised and corrected.

VOL. I.

ON SIMPLE BODIES.

LONDON:

PRINTED FOR LONGMAN, HURST, REES, AND ORME,
PATERNOSTER ROW.

1807.

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Royal Astronomical Society
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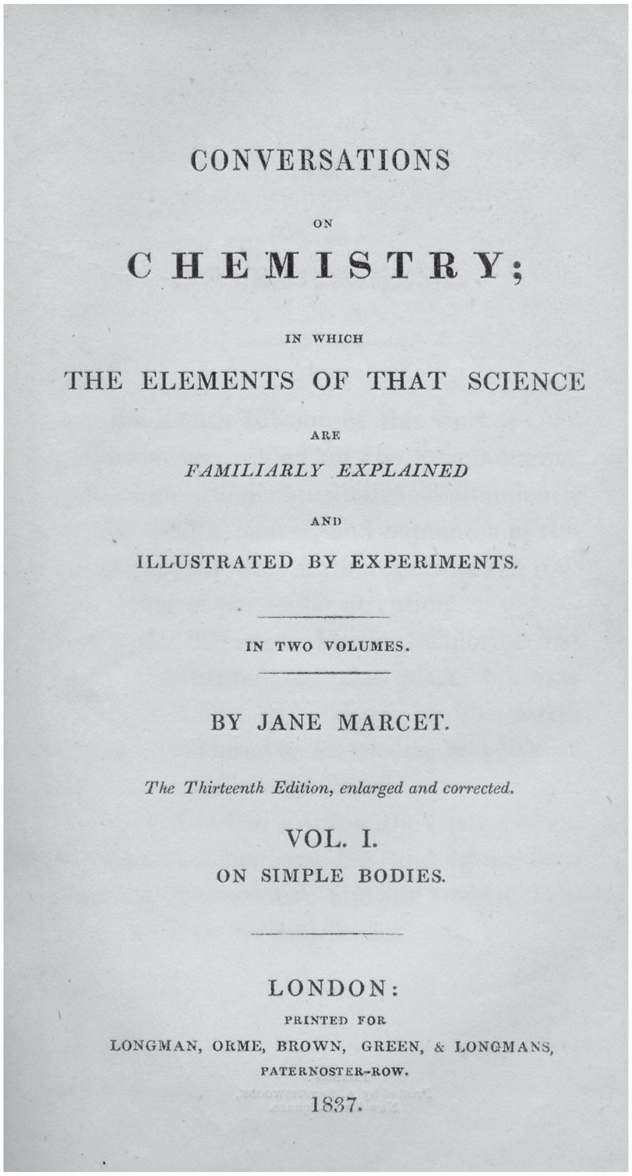
Figure 1*. The title page of Volume 1 of the second edition of* Conversations on Chemistry *published in 1807. A facsimile of the first edition has recently been published by Cambridge University Press. The volume illustrated seems to have passed through the libraries of several learned societies in London, and is now in the library of the Royal Society of Chemistry. The hand-written words "By Mrs. Marcet" must have been added some years after publication, perhaps by a librarian.*



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IN TWO VOLUMES.

BY JANE MARCET.

The Thirteenth Edition, enlarged and corrected.

VOL. I.

ON SIMPLE BODIES.

LONDON:

PRINTED FOR
LONGMAN, ORME, BROWN, GREEN, & LONGMANS,
PATERNOSTER-ROW.

1837.

Figure 2*. Title page of Volume 1 of the thirteenth edition of* Conversations on Chemistry *of 1837, the first that bore the author's name.*

chemical operations." Caroline is still not entirely convinced until Mrs. B tells her that "Without entering into the minute details of practical chemistry, or penetrating into the profound depths of the science, a woman may obtain such a knowledge of chemistry as will not only throw an interest on the common occurrences of life, but will enlarge the sphere of her ideas, and render the contemplation of nature a source of delightful instruction." What is surfacing here is a common attitude of the period to what might be expected of a cultivated but leisured woman, and also a semi-religious justification of learning for its own sake.

Emily then asks about chemists and the philosophers' stone. Mrs. B dismisses alchemists with the observation that "chemistry ... has now become a regular and beautiful science" and she justifies it in terms of the useful products that have developed from it. Emily again interjects "But I do not understand by what means chemistry can facilitate labour: is that not rather the province of mechanics?" Mrs. B puts her right, citing, amongst other developments, the Steam-Engine, not today generally regarded as a chemistry subject, but chemists of the period were concerned about the mysteries of the amounts of heat involved in chemical reactions and topics such as the latent heats of melting and vaporization. In that context the steam engine was indeed applied chemistry. Mrs. B now gets down to work. She describes elementary bodies: "chemists now reckon no less than fifty-eight elementary substances." The second edition had mentioned only forty, plus possibly heat or caloric, light and electricity, so at least eighteen new elements had been identified in about thirty years since the beginning of the nineteenth century. It is difficult to assess precisely which were those elements regarded as new by 1837, but what is notable is that most of the elements "discovered" between 1803 and 1835 and which Jane Marcet would have considered to be new were actually discovered by people she knew well, Wollaston, Davy, Tennant and Berzelius. There are several accounts of the discovery of the elements, and a version available online is cited here (13). The new elements listed in the text are: palladium (discovered in 1803 by Wollaston), chromium (1803, Tennant), sodium (1807), potassium (1807), barium (1808), calcium (1808), strontium (1808), magnesium (1808), boron (1808) (all by Davy, though others contributed to the discovery of the last two), iodine (1811), lithium (1817), cadmium (1817), selenium (1817), silicon (1824), zirconium (1824) (the last three principally by Berzelius), aluminum (1827), bromine (1826), and thorium (1828, Berzelius). Though in 1837 she did not list rhodium (discovered by Wollaston in 1803) and indium (discovered by Tennant also in 1803) as new, she still listed ammonium as a metallic element giving rise to ammonia (p 15), though in Volume II she notes that ammonia was shown by M. Berthollet to be a compound of nitrogen and hydrogen (p 37), a result originally published in 1785, so this is one of Mrs. Marcet's few inconsistencies.

In 1805 the importance of oxygen in combustion had been recognized only recently. In 1837 Mrs. Marcet lists the agents capable of uniting with inflammable bodies as oxygen, plus chlorine, iodine, brome, and fluorine. Davy's battle with fellow chemists over the nature of materials such as chlorine, which had been posited to contain oxygen which allows it to support combustion, was well and truly won by 1837. This complexity overwhelms Caroline: "… instead of one single elementary earth, according to the simple science of the good old times, we have nearly a dozen, and all of them compounds. You must acknowledge, Mrs. B, that the philosophy of our ancestors had the advantage of simplicity." Identification of the new elements allowed the identification of many of their oxides as earths (in 1813 in *Elements of Agricultural Chemistry* Davy described siliceous, magnesian, calcareous and aluminous earths as four constituents of soils) so that the ancient concept of earth as one of four elements was truly dead, despite Caroline's desires (14). Mrs. B scolds her. "Simplicity has charms only in so far as it accords with the truth." The second edition did not mention the classes which so overwhelm Caroline but it included a magnetic fluid, which is not cited in this later version. An experimental demonstration is then described, involving observing the reaction of metallic copper with nitric acid, though a footnote explains that a mixture of nitric and sulfuric acid is an even better reagent for ultimately producing blue crystals, which move Caroline deeply. "How very beautiful they are, in colour, form and transparency! Nothing can be more striking, than this example of chemical attraction." Chemical attraction was still a mystery in 1837, and this *Conversation* ends with a statement that reflects Mrs. Marcet's religious views rather more than current chemical knowledge. "Chemical attraction is, probably, like that of cohesion or gravitation, one of the powers inherent in matter, in which our present state of knowledge admits of no other satisfactory explanation than an immediate reference to a Divine cause."

A close comparison of the two editions reveals many minor changes. All words ending in -ize, such as "characterize" in 1806, became uniformly "characterise" by 1837. The former spellings are still largely used in the United States but not in Britain where z has been replaced almost everywhere in such words by s. *Conversations on Natural Philosophy*, another of Jane's books, was cited in the thirteenth edition of 1837. It could not have been cited in 1807 as it was yet to be published. Pharmacy was important enough to be mentioned by 1837, but not in 1806. Very often there minor cosmetic changes. On page 6 the word "unfair" in 1806 becomes "injudicious" by 1837. During the period between 1807 and 1837, carbone lost its final e, and sulphat, phosphat, and nitrat received theirs. Some comments exchanged between Emily and Caroline in 1807 are combined and ascribed to Caroline alone in the later version. The phrase "on crumbling to atoms" on page 8 was excised by 1837, presumably because after Dalton developed his atomic theory after 1803 and finally published it in full in 1808 (15), by 1837 atoms were still not universally accepted to be the basic elemental units. The atomic theory, whether valid or not, does not seem to have affected daily chemical practice, and was to remain a theory until much later. Chemical industry, as it then was, used traditional methods, and was not professionalized and researched as it is today. Theory was the province of philosophers, though the adoption of quantitative methods in research, by pioneers such as Lavoisier, Wollaston, Berzelius and

Avogadro, clearly lent support to an atomic theory. The laws of constant proportions and multiple proportions were clearly consistent with atomic theory. However, chemists could never "prove" its truth, only demonstrate that many chemical fact were consistent with it. The final proof required the application of physics much later in the nineteenth century.

From the beginning Mrs. Marcet had used the element classification that is essentially that of Lavoisier, even though many British chemists did not at first readily adopt it, but the subsequent editions of *Conversations* go through this classification systematically.

Conversation 2, On Light, and Heat or Caloric

The nature of light was still a mystery in 1807, but by 1837 Mrs. Marcet used Herschel's experiment of 1800 to demonstrate what we now regard as infrared radiation (16).

Herschel had noticed that sunlight split into a visible spectrum by a prism also seemed to contain an invisible radiation which could be detected by a thermometer placed just beyond the red end of the spectrum. Mrs. B also mentions M. Pictet's related but similar observations published in Geneva in 1790, which have generally been ignored by historians of science (17). That the Pictet family were well acquainted with the Marcet family in Geneva could not have been a coincidence. The then current conclusion to such findings was that both caloric and visible light obey the laws of optics. In 1837 she also mentioned Wollaston's analogous demonstration of ultraviolet radiation. This was done in 1802 when he noted that invisible rays beyond the blue end of the normal visible spectrum could induce silver chloride to turn black, just as visible light does. The students were intrigued by the fact that white light can be split into colors and can also bleach colors. Mrs. B patiently explained it all in terms of the fluid caloric, either free or combined, as well as latent heat and chemical heat. She defends the description of the latter as forms of heat rather than forms of caloric because the terms were coined by Dr. Black before the French chemists introduced the word caloric, and "... we must not presume to change it, as it is still used by much better chemists than ourselves." She also demonstrates the expansions of a metal bar when heated by flame, and of water and colored alcohol in bulbs with attached tubes. These no-doubt expensive experiments are illustrated by the author's own drawings, professionally engraved. For the later editions these plates were sometimes amended, both in content and in the numbering of the Figures.

Mrs. B then used a pair of concave mirrors to show that the caloric given out by a heated bullet at the focus of one mirror can travel to a thermometer bulb suitably placed at the focus of another. Replacing the bullet by ice cools the further thermometer bulb. Finally, the two girls were shown Leslie's cube, which has four faces of different materials, all at the same temperature, but which radiate with different efficiencies to a thermometer. Mrs. B admitted that no clear explanation for these observations had yet been found. Sir John Leslie's book, replete with many experiments on radiation and heat transfer and titled *An Experimental Inquiry into the Nature and Propagation of Heat*, had been published in 1804. He published a further book, *A Short Account of Experiments and Instruments, Depending on the Relations of Air to Heat and Moisture,* in 1813 (18). I have found no correspondence to indicate that the Marcets knew Leslie personally, but he could have been an acquaintance of Alexander during his time in Edinburgh between 1794 and 1797.

Conversation 3, Continuation

The students discover by experiment that some bodies conduct caloric better than others. Sometimes the explanations become a little tortuous. Emily says: "Heat, whether external or internal cannot easily penetrate flannel; therefore in cold weather it keeps us warm; and if the weather were hotter than our bodies, it would keep us cool." This is accepted by Mrs. B without comment. Later Caroline states: "It is a very fortunate circumstance that air should be a bad conductor, as it tends to preserve the heat of the body when exposed to cold weather." Mrs. B replies that this "is one of the many benevolent dispensations of Providence, in order to soften the inclemency of the seasons and to render almost all climates habitable." A treatment of the atmosphere, wind, dew, water vapor, and steam are all additions to the earlier version.

Mrs. B later described Count Rumford's experiments on conduction in liquids, which dealt with convection, and which she illustrates with colored liquids. She knew both Rumford and his one-time wife, the widow of Lavoisier. She had been born Marie-Anne Paulze, she fought bravely to retain the family property after her husband, Antoine Lavoisier, was executed in 1794, and she married Rumford subsequently in 1804. Rumford believed that heat conduction in liquids occurred primarily by movement of particles, and Mrs. B shows, in an addition to the second edition version, this not to be entirely correct. She even comments on the radiation of heat by the earth, and when Caroline remarks on this waste of heat, Mrs. B sternly chides her: "Before you are tempted to object to any law of nature, reflect on whether it may not prove to be one of the numberless dispensations of Providence for our good." She concludes that this loss of heat makes the earth comfortable for humans, an interesting gloss on current fears of the greenhouse effect and global warming. Without elaborating greatly, Emily introduces the idea of specific levity of gases, and this leads to a discussion of ebullition, evaporation and condensation, and the dissolution of solids by liquids. Dew is supposed to deposit more effectively on vegetables than on rocks, another wise and bountiful dispensation of Providence.

Mrs. B next uses a pneumatic pump to show the rapid evaporation and cooling of ether, upon which Mrs. Marcet's husband, Alexander, had worked (19). This leads to the concept of latent heat and enables her to introduce the work on melting substances under pressure carried out by Sir James Hall, who, as it happens, was also well known both to Mrs. Marcet and to Alexander. Hall was a student of Black in Edinburgh during Alexander's period there and was a chemist and perhaps the first experimental geologist (20, 21). He studied the melting and crystallizing of rocks and lava. Detailed personal correspondence in the archive at the Bibliothèque de Genève shows that the Marcets tried to help the Hall family who had a son who was evidently mentally disturbed. His family preferred to send him to London so that their immediate neighbors in Scotland might not learn of this family disgrace.

Conversation 4, On Combined Caloric, Comprehending Specific and Latent Heat

All the physical rationalizations cited by Mrs. B are based on the caloric theory and in this *Conversation* she continues to develop ideas about caloric to explain the phenomena of latent heat, specific heat, and the differing heat capacities of various bodies. The thirteenth edition account is much expanded compared to the second edition, with more experiments and even a new diagram. It is the experiments that impress the reader, as they did Emily and Caroline. For the discussion of latent heat, described as a form of combined caloric, Mrs. B invokes the work of her Swiss family friend Mr. Pictet, and Caroline sagely remarks that latent heat should really be called latent caloric. Mrs. B explains that the name latent heat is due to Dr. Black, and was coined before French chemists invented the notion of caloric (21). Dr. Black was the teacher from whom Alexander Marcet first learned of the new "French chemistry" while he was studying medicine in Edinburgh.

Caroline is continually amazed by the observations. That water boils at a constant temperature as heat is supplied is "wonderfully curious." Mrs. B introduces Rumford's steam kitchen, an early kitchen range, which was designed to use both the heat content and latent heat of steam both for large-scale cooking and for house heating. It used the volatilization of water and its subsequent condensation essentially as a heat transfer agent. Emily sagely remarks that that: "When the advantages of such contrivances are so clear and plain, I cannot understand why they are not universally used," Mrs. B counters: "A long time is always required before innovations, however useful, can be reconciled with the prejudices of the vulgar … yet sometimes, it must be admitted, [they] prevent the propagation of error." Rumford was an enthusiast for using science to improve the human condition, but in this particular case, the fact that there were reports of models of Count Rumford's steam kitchen exploding, causing considerable injuries, might have discouraged its widespread adoption. Jane certainly attended chemistry lectures at the Royal Institution, of which Rumford (Benjamin Thompson) was a co-founder, and probably knew him personally, though no correspondence between them has been identified.

Mrs. B shows the girls an experiment in which the addition of sulfuric acid to a solution of calcium chloride causes the mixture to solidify, and to produce a "white vapour." She warns Caroline: "You are not yet enough of a chemist to understand that. —But take care … for it has a pungent smell." In the second edition this phrase was: "for it smells extremely strong." The discussion next turns to cooling, and Leslie's Cryophorus and a variant on Leslie's experiment, with the following footnote: "This mode of making the Experiment was proposed, and the particulars detailed, by Dr. Marcet, in the 34th vol. of Nicholson's Journal, p. 119." Of course, Dr. Marcet was Jane's husband, and he certainly demonstrated this apparatus to his friends, as some later personal correspondence shows (see also Ref. 19). The term "cryophorus" (bearer of frost) was actually coined by Wollaston who was certainly aware of Leslie's work and who must also have discussed the problems of heat and cold with Alexander. In the text Mrs. B finally leaves open the question whether heat is a form of motion or is a distinct substance.

Conversation 5, On the Steam-Engine

This *Conversation* is not found in the second edition. In 1807 steam engines were not of general interest to chemists, but the subject was first introduced in the tenth edition of 1825. The 1837 edition presents an extensive discussion of the beam steam engine, with very detailed drawings (apparently not due to the author). Although Thomas Newcomen invented the steam beam engine in 1704, its efficiency was much improved by various engineers, especially Mr. Watt, whom Mrs. B particularly selects for praise. Such engines were widely used in mines throughout the nineteenth century and later and were partly a result of philosophers' interest in caloric. Caroline continues to effuse, Emily to pose questions, and Mrs. B to put everything into context. "But one would suppose the valve to be endowed with intelligence …" "Pray how are high-pressure engines constructed ...?" "It is our improved steam-engine that has fought the battles of Europe, and exalted and sustained, through the late tremendous contest [the Napoleonic Wars], the political greatness of our land … [and] that now enables us to pay the interest on our debts, and to maintain the arduous struggle in which we are still engaged, against the skill and capital of all other countries." Mrs. Marcet's interest in the embryonic science of economics makes itself evident here. She had published *Conversations on Political Economy*, using the same conversationalists, in 1816. This went through some six editions, continuously improved and enlarged (22).

Conversation 6, On the Chemical Agencies of Electricity

Again, this is an addition compared to the second edition. Mrs. B includes electricity here, though she cannot really define it, which upsets Caroline: "Well, I must confess, I do not feel nearly so interested in a science where so much uncertainty prevails …" This *Conversation* is a quick run through static electricity, Galvani (and muscular irritability of a frog's leg), Galvanism, Volta and the Voltaic pile, and an electrical machine based upon friction. Sir H. Davy receives his first mention (p 181), and as do Mr. Oersted and magnetism (p 184). Although Alexander Marcet had carried on an extensive correspondence with Berzelius, some of which concerned the latter's researches on electricity and magnetism, no mention of such work is made here. Caroline: "Well now that we understand the nature of the action of the Voltaic battery, I long to hear an account of the chemical discoveries to which it has given rise." "You must restrain your impatience, my dear … till we come to them in the regular course of our studies." So, after about one third of the text, and a quarter of the *Conversations*, we are about to embark for the first time upon what would be today considered as real chemistry.

Conversation 7, On Oxygen and Nitrogen

This starts with the definition of a gas, which excludes water vapor, since water is a liquid at normal ambient temperatures. Mr. Faraday's and Mr. Perkins's experiments on condensing gases by high pressure are mentioned here, though not in the 1807 version. The separation of oxygen and nitrogen by removing the former by burning wood in air is described. This is actually a form of the old candle experiment going back perhaps two thousand years (23). In this edition the chemistry of combustion is introduced. Heat given out in such combustions arises from the caloric contained in the oxygen gas as well as that in the combusted material. The girls are entranced. Caroline: "You astonish me." And "Since I have learned this wonderful theory of combustion, I cannot help gazing at the fire." Emily: "I have not yet met with any thing in chemistry that has surprised and delighted me so much as this explanation of combustion."

In the second edition, vapors and gases were considered to be different, and the word "gases" was spelled "gasses" and the word oxide was spelled "oxyd." The process of combining with oxygen is properly called oxygenation or oxidation in the later edition, and the products are oxides, and it is noted that metals increase in weight upon oxidation, which was one of the key observations that helped discredit the phlogiston theory. Nevertheless, one of the key researchers whose work helped establish the role of oxygen in combustion, Joseph Priestley, who died in Pennsylvania in 1804, apparently never lost his belief in the validity of the phlogiston theory (24).

Mrs. B demonstrates how heating manganese oxide in a retort can release pure oxygen, which is collected over water (p 202). This is a laboratory experiment clearly illustrated in Plate X (Figure 3), that would not be a feasible undertaking in domestic kitchens or drawing rooms. Jane had access to her husband's own private laboratory where she could certainly have carried out such an experiment rather than in her kitchen. However, that detail is not mentioned. The fact that oxygen combines with mercury and that the same amounts of oxygen and mercury can then be recovered was revealed by Lavoisier at least by 1789, and he was already very skeptical about phlogiston by 1785 (25). This must have been well known to Mrs. Marcet, but Mrs. B also implies in her discourse that no weight is overall gained or lost in experiments such as these; in other words, she refers to the law of the conservation of mass, also due to Lavoisier, though this is not mentioned. At no time does Mrs. B imply that oxygen and nitrogen in the air are combined together in some fashion ("… in the atmosphere these two substances are separately combined with caloric, forming two distinct gases"), though this idea had at least been ventured in some quarters (26). Even in 1837, Mrs. B follows Sir H. Davy in believing that atmospheric nitrogen may be a "compound body," presumably meaning not an elementary substance (p 213).

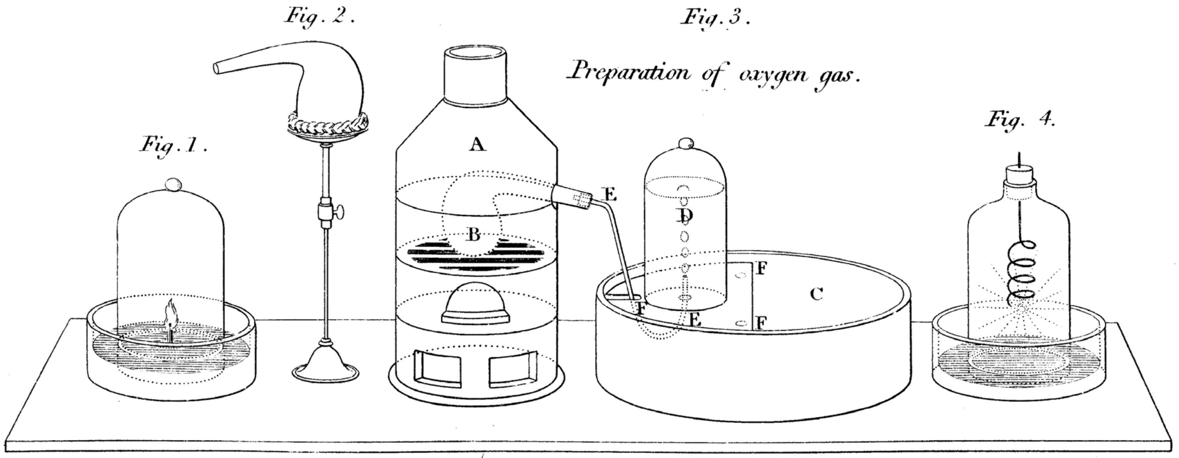

Fig. 1. Combustion of a taper under a receiver. — Fig. 2. A Retort on a stand. — Fig. 3. A *Furnace.* B *Earthen Retort in the furnace.* C *Water bath.* D *Receiver.* E.E *Tube conveying the gas from the Retort through the water into the Receiver.* F.F.F *Shelf perforated on which the Receiver stands. Fig. 4. Combustion of iron wire in oxygen gas.*

Drawn by the Author. *Engraved by Lowry.*

Published by Longman & C^o. Paternoster Row.

***Figure 3**. The preparation of oxygen, from an illustration between pages 204 and 205 of Volume I. In the text it is designated Plate X, and is from a drawing originally made by the author.*

Conversation 8, On Hydrogen

Although Mrs. B mentions here all the halogens (which halogens had not been discovered in 1807 when the second edition appeared) along with oxygen as bodies capable of effecting combustion, she skips them to move to hydrogen (p 214), which apparently cannot be considered a simple substance because, as a gas, it is combined with heat. Caroline is overwhelmed to learn that water is a compound of hydrogen and oxygen. "Really! Is it possible that water should be a combination of two gases, and that one of these should be inflammable air?" This allows Mrs. B to explain the difference between compounds and mixtures, but the idea of fire (in the burning of hydrogen) producing water entrances Caroline. "You love to deal in paradoxes to-day, Mrs. B —Fire, then, produces water?" A discussion of the decomposition of water allows Mrs. B to introduce electrolysis of water using a Voltaic battery, which Caroline finds "wonderfully curious." No mention of the Voltaic battery was made in the second edition.

Next Mrs. B generates hydrogen from metallic iron and sulfuric acid (p 223), though this is explained by the greater affinity of iron for oxygen than for hydrogen. The hydrogen is collected over water and the experiment is described in considerable detail. The hydrogen is ignited with a candle flame, producing "a detonation" ("as chemists commonly call it"), regenerating water (p 227). The girls take some convincing that all this is true, but Mrs. B uses experiment to convince them. Caroline: "How glad I am to that we can see that water is produced by this combustion." Emily: "It is exactly what I was anxious to see; for I confess I was a little incredulous." At this stage Mrs. B invokes both Mr. Cavendish and "the celebrated French chemist Lavoisier" who recognized the composition of water, but she omits to mention that the latter had been executed some 40 years earlier during the French Revolution.

The sound produced by a gentle hydrogen flame burning at the end of a long glass tube is next demonstrated, and the mechanism of sound generation rationalized by a combination of glass vibration, gas condensation, gas formation and influx of air. Why this is introduced is made clear by the footnote on p 233: "This ingenious explanation was first suggested by Dr. De La Rive. —See Journal of the Royal Institution, Vol. I, p. 259." It is no accident that Dr. De La Rive was a Genevan friend of Alexander Marcet, distantly related by marriage, and who shared his study exile in Edinburgh. She ascribes all flames to the burning of hydrogen. She does explain that the novel gas lighting uses inflammable coal gas or hydro-carbonate and she describes how the gas is produced industrially. Gas lighting as "one of the happiest applications of chemistry to the comforts of life, and even to the morals of large cities …. Gas lights are excellent policemen" (p 239). But she adds that application to illuminating homes had "not yet been found desirable."

Mrs. B produces soap bubbles of hydrogen, to acclaim. Caroline: "Now a bubble ascends; it moves with the rapidity of a balloon. How beautifully it refracts the light!" Thunder and lightning are ascribed to detonations of hydrogen, and finally Sir Humphry Davy's safety lamp is described in detail (p 248). It was invented in 1815 and used from about 1816, and, of course, this is an addition compared to 1807. It effectively prevented the detonation of what was termed hydro-carbonate by chemists or fire damp by miners, and for this invention Davy was publicly thanked and honored throughout Europe. Mrs. B is effusive about its value, but she also mentions Mr. Tennant's contribution to its early development, though she ignores others. The need for such an apparatus had long been recognized, and Leonard Horner had written from Edinburgh to Dr. Marcet in 1815 about another proposal for a safety lamp (27). Caroline expresses the situation very well. "This is indeed a most interesting discovery, and one which shows at once the immense utility with which science may be practically applied to some of the most important purposes" (p 250). It is striking that nowhere in this context does Mrs. B mention methane and inflammable marsh though methane was discovered by Volta as early as 1778.

Conversation 9, On Sulphur and Phosphorus

Here Mrs. B starts by saying that she will consider these elements, their compounds with oxygen, and their properties as acids. This echoes the Lavoisier concept of acids being oxygen compounds. She describes sublimation of sulfur using an alembic, though she does not demonstrate it, but she does burn sulfur and dissolves the resulting gas in water to generate an acid "because it [sulfur] unites with oxygen, which is the acidifying principle." This causes Caroline to ask why water isn't an acid. The rather unsatisfactory reason is because hydrogen "is not susceptible to acidification." Although Mrs. B follows Lavoisier's acid hypothesis, she admits that Sir H. Davy has shown (p 258) that halogens possess to some, though insignificant, degree the same property as oxygen, of being able to generate acids, which is new compared to 1807. Acidification, she says, always implies previous oxidation. Acidic character requires a higher degree of oxidation than simple oxide formation, but she correctly distinguishes between the two degrees of oxidation associated with sulfurous and sulfuric acids. Caroline, under instruction, fills a gas bottle with oxygen ("Very well; you have only let a few bubbles escape, and that must be expected on a first trial.") and this is then used to burn sulfur in order to make sulfuric acid. It is notable that in this text, as in other texts of the time, no distinction was made between sulfur dioxide and sulfurous acid. Sir H. Davy had shown that submitting sulfur to the action of the Voltaic battery generates hydrogen at the cathode, which raised the question of whether it contained hydrogen rather than being an elementary substance (p 261), but sulfur and hydrogen can also react to form sulfuretted hydrogen gas, as found in "Harrowgate waters" (in 1807 or "Harrogate waters" by 1837, as it is spelled today). The analysis of waters from various different sources was another of Dr. Marcet's chemical interests (28). Caroline finds sulfur boring, and wants to move on to phosphorus.

It appears that phosphorus may also contain hydrogen, though it is considered to be a "simple body" (p 264). Mrs. B explains that phosphorus was known to Brandt (he isolated it in 1669 from a large volume of urine while searching for the philosopher's stone), Kunckel (who discovered Brandt's recipe for phosphorus in about 1678), and Boyle (he was involved in the commercial production of phosphorus in London by 1680), but she is too refined to discuss its source, though she reveals that it is extracted "by a chemical process" (29). However, even Emily is overwhelmed when Mrs. B burns phosphorus in oxygen. "What a blaze! I can hardly look at it. I never saw anything so brilliant. Does it hurt your eyes, Caroline?" "Yes: but still I cannot help looking at it." The product is phosphoric acid, but exposure of phosphorus to atmospheric oxygen yields phosphorous acid (p 267). The girls are delighted with phosphorescence, matches, and the spontaneously inflammable phosphoretted hydrogen gas [phosphine] ("phosphorated" in 1807), supposedly the origin of the Will-of–the-Wisp [also known as marsh gas]. After a short discourse on nomenclature, phosphoret of lime [calcium phosphide] is also used to make phosphine, but this is done outside the house, because the smell "is so extremely fetid that it would be intolerable in the house." The detonating bubbles of phosphine excite Caroline, but she does not understand the chemistry. Mrs. B thinks the explanation is too complex for Caroline to understand (p 273). "It is the consequence of a display of affinities too complicated, I fear, to be made intelligible to you at present." Nevertheless, the fact that both sulfur and phosphorus are stated to be found widely in nature promises more excitement in the future for the assiduous student.

Conversation 10, On Carbon

Some of Davy's work which was not included in 1807 is described here in 1837. Mrs. B states that Davy believes that purest form of carbon then attainable must contain hydrogen, and that 100% pure carbon would probably turn out to be a metal (p 277). Davy knew that carbon is widespread in nature, and he popularized the concept of the natural carbon cycle originally postulated by Lavoisier and Priestley (30). Mrs. B states that carbon may be produced pure as charcoal, by a process with which Emily, at least, is familiar: "I have seen the process of making common charcoal." Caroline is startled to learn that the diamond in Mrs. B's ring is also carbon: "Surely you are jesting, Mrs. B?" Mrs. B increases the wonderment: "There are many other substances, chiefly consisting of carbon that are remarkably white. Cotton, for instance, is almost wholly carbon." Caroline is amazed, "That, I own, I could never have imagined!" There follows a discussion of the difference between analysis and synthesis and their value to the experimentalist, but Mrs. B doubts whether chemists will ever be able to synthesize animals and plants. "…the principle of life, or even the minute and intimate organization of the vegetable kingdom, are secrets that have almost entirely eluded the researches of philosophers; nor do I imagine that human art will ever be capable of investigating them with complete success" (p 279). The combustion of carbon to give carbonic acid gas, and even Tennant's demonstration of the combustion of diamond announced in 1797 are described in detail. The combustion of diamond was actually first investigated by Lavoisier but in Tennant's case it was assisted in part by Alexander Marcet himself, as other personal correspondence shows. The generation of Seltzer water, its value and its properties are also described (p 289). The fact that a burning flame may be visible is again ascribed to the presence of some hydrogen. Helpfully, the lead in lead pencils is not really lead but a carburet of iron (p 294).

The occurrence of carbon in graphite and steel and the decomposition of water by hot charcoal are also demonstrated. Finally, the widespread occurrence of carbon in what we would today term organic compounds is described, though how carbon, oxygen and hydrogen could make so many different materials was beyond the chemical theory of 1837.

Conversation 11, On Metals

The metals are treated in various classes, a beginning of the kind of classification that would lead ultimately to the Periodic Table. In *Conversation* 1 metals (including ammonium) had already been classified as those forming alkalis upon oxidation, those forming lime or earths upon oxidation, those malleable metals occurring naturally, and brittle metals. The Voltaic battery features in this *Conversation*, whereas in 1807 the use of the Galvanic pile to oxidize metals was the sole mention of electricity. The *Conversation* begins with the statement that the metals that form alkalis on oxidation will be discussed later because they were more mysterious and of recent discovery, which prompts Caroline to say that the mystery makes them more exciting. Mrs. B reprimands her. "You are not aware, my dear, of the interesting discoveries made by Sir H. Davy respecting this class of bodies. By aid of the Voltaic battery …" (p 301). So, back to the boring well-known metals, such as copper, lead and iron. Their oxidation in the atmosphere and in furnaces is treated at some length. Caroline seems a bit blasé about all this, perhaps because her father seems to own a lead mine in Yorkshire. This may be an oblique reference to Jane's friends, the Cleaver family, who lived in Yorkshire, and are mentioned in her personal correspondence. Emily wonders whether white lead "with which houses are painted" is lead oxide, and is told that it is a carbonate (p 305). After mention of the other oxides, Mrs. B shows the girls how to use a blowpipe (p 307), and though the girls would like to burn gold in this way, Mrs. B tells them that gold, silver and platina cannot yet be burnt by a blowpipe, though it can be done with sparks from a Voltaic battery. The characteristic colors emitted by metals upon oxidation which she mentions (p 305) are an interesting forerunner of spectral analysis.

One of Jane's sources of information at this time were the popular public lectures of Davy and, later, of Faraday at the Royal Institution in Albemarle Street, London. She tells her pupils that "You will see these experiments performed in the most perfect manner, when you attend the chemical lectures at the Royal Institution." Jane knew Davy personally, but her relationship with Faraday was very special. He clearly respected her greatly, and he recounted that, when he was apprenticed as a bookbinder, reading *Conversations on Chemistry* after work was a major influence upon his decision to take up science. On June 7, 1847, Faraday wrote another note to Jane from the Royal Institution, to which he had ordered that she be admitted whenever she so wished, in which he addressed her as "Dear Mistress" and closed with the sentence: "These come with my duty from your devoted and affectionate pupil."

The fact that "platina becomes incandescent by exposure to a current of hydrogen gas, even when the temperature of the metal is lowered by a frigorific mixture eight or ten degrees below the zero of Fahrenheit," is one of several "singular phenomena [which] remain as yet without satisfactory explanation" (p 313). After this exciting diversion, the problems of oxidation, rusting, and reduction of metal oxides are dealt with at length. Mrs. B always gives the current rationalization of the phenomena she describes. "I imagine that it is because lead cannot decompose water that it is so much employed, in the form of pipes, for its conveyance." Lead pipes for carrying water had been used for at least two thousand years, from Roman times. Mrs. B: "Certainly; lead is, on that account, particularly appropriate to such purposes." The toxic properties of soluble lead compounds were already well known long before 1837.

The action of acids on metals is also ascribed to oxidation (p 320), because Lavoisier's theory of oxygen as the ultimate source of acidity was still accepted in 1837. Mrs. B drops some nitric acid onto metallic copper, which causes Caroline to remark: "Oh, what a disagreeable smell!" Salt formation follows, but "you will be careful to remember that metals are incapable of entering into this combination with acid, unless they are previously oxidated." The girls crystallize iron(II) sulfate, much to Caroline's delight. They learn of soldering and plating, and talk of hot springs and comets. They discuss mercury, and how to solidify it, and this gives Mrs. Marcet the chance to mention once again her husband's device for producing cold by harnessing the evaporation of diethyl ether, though he had died long before, in 1822.

The discussion of the caustic nature of acids leads onto consideration of verdigris and poisons, and then Mrs. B pulls a masterstroke. She sprinkles some water and some copper nitrate that they had made previously on some tin foil, and suddenly folds the tin up and presses it into a lump. Caroline: "What a prodigious vapour issue from it! —and sparks of fire, I declare!" (p 336). After a brief excursion into invisible or sympathetic ink, Mrs. B finishes with a paean extending over several pages to Sir H. Davy and his use of the Voltaic cell to discover the alkali metals, which she believes only the illiberal, ignorant and narrow-minded would regard as simple curiosities (p 337). The students experiment with reactive materials such as sodium and potassium, which especially enchant Caroline. The chemical preparation (in about 1808) of potassium in large quantities by Thénard and Gay-Lussac is mentioned (p 344). Later on this same page Mrs. B speaks of Davy's great skill in investigating the chemistry of this metal even though he could prepare only "a few atoms of this curious substance." This was phrase was probably the use of common language rather than a reflection of atomic theory. Davy is also stated to have ascertained that ammonia also contains oxygen, and to be derived from a metal (p 345), even though Berthollet had shown by 1785 (see Volume II, p 37) that this was not the case. Evidently Davy was still convinced that the formation of ammonium salts was the result of a reaction between an acid and the oxide of some unknown metal, analogous to the alkali metals he himself had isolated. Mrs. B concludes the volume with further praise of Humphry Davy "Thus in the course of two years, by the unparalleled exertions of a single individual, chemical science has assumed a new aspect …. In geology new views are opened…. it is reasonable to suppose that the interior of the earth is composed of a metallic mass … The eruptions of volcanos, those stupendous problems of nature, admit now of an easy explanation. For if the bowels of the earth are the grand recess of these newly discovered inflammable bodies, whenever water penetrates into them, combustions and explosions must take place; and it is remarkable that the lava which is thrown out is the very kind of substance which might be expected to result from these combustions."

This extraordinary and erroneous claim closes Volume I of the 1837 edition. However, the 1807 version contained *Conversations* which were transferred to Volume II by 1837. Volume II deals with compound bodies, in a sequence which follows Lavoisier's classification of bodies.

Conversation 12, On the Attraction of Composition

Mrs. B now discusses "the attraction of composition, or chemical attraction or affinity." She lists six "laws of chemical attraction" (pp 1-8), most of which are generalizations that still hold today. Attraction occurs "only between the most minute particles of bodies." These minute particles are not here defined, and Mrs. B does not mention Dalton, whom she possibly met, or his ideas, and it is notable that she always tries to avoid quantitative questions involving matters such as yields and compositions. Modern chemists often do not realize that Dalton's ideas concerning atomic theory and published in 1805 had very little immediate impact. The theory was, in any case centuries old. It was a theory which did little to illuminate real chemistry practice at the time, even if it was the concern of some philosophers. Wollaston had published his Table of Chemical Equivalents in 1814, and had taken some time to develop it but he did not readily adopt atomic theory. Avogadro was already promulgating ideas about gaseous molecules by 1811 and Berzelius was an early adherent of Dalton's theory. Jane and Alexander Marcet must have discussed it with Berzelius in 1812, and perhaps also with Dalton. In 1837 a mention is made of chemical atoms, and the law of constant proportions, by weight for solids and by volume for gases, is related to their existence on pp 12-14. Such atoms are not further divisible by mechanical means. However, as Mrs. B states on pp 14 and 15: "Philosophers have not yet been able to give us any decisive information upon this point ["the singular uniformity in the law of combination"] ... we may suppose that the smallest particles or portions in which bodies combine (and which we may well call chemical atoms) are capable of uniting together ..."

Compound bodies are stated to include oxides, acids and salts, and Mrs. B explains the nomenclature of salts, as exemplified in names such as nitrate of copper and sulfite of potash. Mrs. B acknowledges measuring the force of attraction between different chemical entities was a problem, but she presents a set of relative affinities, based upon observations of selected displacement reactions. Caroline: "I confess I do not understand this clearly." Mrs. B's explanation is based upon the reaction of nitrate of lime and sulfate of soda yielding sulfate of lime and nitrate of soda (p 9) and illustrated by a diagram. The reaction takes place because of the different relative affinities of acids and alkalis, though how this was studied in practice is not clarified. Nevertheless, Caroline thinks it is now very clear, though she queried the use of the words quiescent and divellent (p 10). Quiescent forces are those that tend to stop compounds reacting, whereas divellent forces are those that promote reactivity. The problem of affinity was a considerable worry to chemists of the period, and Berthollet published at least as early as 1799 the idea that chemical combinations are affected not only by relative attractions but also by the proportions of the materials involved in the preparative reaction, by the heat evolved, and by other circumstances. These views were challenged by several investigators such as Proust in 1806, and Mrs. B acknowledges that Berthollet's ideas are not consistent with the law of definite proportions (p 12). Of course this law was clearly explained by the theory of indivisible chemical atoms, Mrs. B was evidently of the opinion that chemical theory was becoming too difficult for her immature students to master. A footnote on page 16 mentions that Dr. Wollaston had produced a table of chemical equivalents (in 1814), but "we must not run the risk of entering into difficulties which might confuse your ideas, and throw more obscurity than interest on this abstruse part of the philosophy of chemistry."

The *Conversation* finishes with some interesting electrolysis experiments, purporting to show decomposition of salts into the acids and alkalis from which they were formed. The material in this *Conversation* did not appear as a separate *Conversation* in 1807, though some of it was presented elsewhere in that earlier version.

Conversation 13, On Alkalies

The three alkalies are potash, soda and ammonia. They all affect the color of vegetable dyes such as turmeric. Potash is obtained primarily from wood ash. Caroline wants to use potash for laundering clothes, but needs to be told that it is too caustic (p 26). There follows a disquisition on nomenclature. Mrs. B states that even Lavoisier who established the new nomenclature thought it more prudent to use established names for some substances even if more explicit names could be coined. Customary usages might have to be retained. Emily infers that carbonate of potash is formed by the union of carbonic acid with potash. This earns a pat on the head: "you see how admirably the nomenclature of modern chemistry is adapted to assist the memory" (p 27). Would that this were always still the case! However, a disquisition on Lavoisier and his colleagues' nomenclature is then introduced. A footnote adds that despite the admirable systematics, some acids contain hydrogen and some alkalies contain oxygen. Nevertheless, Caroline, when told how potash can give rise to saltpetre correctly exclaims: "then saltpetre must be nitrate of potash?" (p 33).

Soda combines "with a peculiar acid" to form common salt. Like potash, soda gives rise to glass and soap. Finally ammonia, or volatile alkali, is identified with hartshorn. Mrs. B opines that the name ammonia arises from "*Ammonia*, a region of Libya" though this is probably not the case (p 24). Since sal ammoniac is made from ammonia and muriatic acid, Caroline rightly says that it should be called muriate of ammonia. Berthollet "a celebrated French chemist" has shown "a few years since" that passing electric sparks through heated ammonia gas produces about four parts of nitrogen to one part of hydrogen by weight and one part of nitrogen to three arts of hydrogen by volume (p 37). Ammonia is a product of putrefaction of both animals and of plants and it forms an amalgam [a compound with metallic mercury] in an "extremely curious experiment" (p 38).

Conversation 14, On Earths

The nine earths are silex, alumina, barytes, lime, magnesia, strontites, yttria, glucina, and zirconia (p 44), the last three being very new to chemistry. The list of earths of 1807 also contains the name "gargonia" which had disappeared by 1837. The alkaline earths are named as barytes, magnesia, lime and strontites (p. 49). The girls confuse chemical earths (natural metal oxides with basic properties) with soils. Once this is sorted out, the discussion moves on to crystallization and precious stones. The devout Mrs. B never once questions the geological age of the earth or the modern geology that was beginning to emerge in Mrs. Marcet's time. "The characteristics of earths are insipidity, dryness, unalterableness in the fire, infusibility, &c." Caroline immediately asks how silex [silica] fits this pattern, as in the fire it forms glass. This is ascribed to the fact that it is normally not pure.

The earths are then treated in order, which provokes Caroline to say "I confess that the history of earths is not quite so entertaining as that of simple substances" (p 53). Apparently Mrs. B agrees, and the rest of the *Conversation* is a cursory gallop through the earths: silex, alumine (a constituent of clays with a non-systematic name, as Caroline notes, though it is sanctioned by history), barytes, lime (used in medicine to counter stomach acidity, and which, in a furnace, gives rise to quick-lime, that Mrs. B treats with water, to Caroline's delight: "how the quick-lime hisses! It becomes excessively hot! —It swells, and now it bursts and crumbles to powder …", p 58), magnesia (identified by Tennant and used as a medicine, like the related Epsom salt: and as Caroline must observe "and properly called sulphate of magnesia, I suppose!"), and strontian or strontites (identified in 1791-2 by Dr. Hope (31), a student of Black, and professor of chemistry and medicine at Edinburgh from 1799 until he died, and another close friend of Dr. Marcet from his Edinburgh days, p. 65). It was Davy who isolated the element strontium, though this is not mentioned here.

Conversation 15, On Acids

This *Conversation* is completely reorganized in 1837 when compared to 1807, and it starts with a definition of acids. "They all change vegetable infusions to a red colour: they are all more or less sour to the taste; and have a general tendency to combine with earths, alkalies, and metallic oxides" (p 66). The nomenclature is described, in a manner of which Lavoisier would have approved. The terminations -ous and -ic had already been described in 1807. Mrs. B states that the only members of the class of the forty known acids that don't quite fit the oxygen theory are muriatic and fluoric, for they had yet to yield their free bases. In fact Scheele had isolated chlorine in 1774 and Davy had proposed it to be an element in 1810, though fluorine was first isolated by Moissan as late as 1886. Acids are divided into three classes, those of known and simple bases (the mineral acids); those of double bases, of vegetable origin; and those of triple bases, or animal acids (p 70). These are listed in 1837 as lactic, caseic, prussic, formic, bombic, cetic, sebacic, margaritic, oleic, zoonic and lithic. Some of these names are retained today, but the identities of most were not understood, just like the organic agents involved in digestion, chime and chyle, which were assumed to be distinct compounds. The action of acids on material such as wood is described by Mrs. B as involving the transfer of oxygen, just like combustion (p 75).

Conversation 16, Of the Sulphuric and Phosphoric Acids; and of the Sulphates and Phosphates

This 1837 version is similar to that of 1807, though reorganized, and again it begins with nomenclature (p 76). Sulfuric acid was once obtained by dry distillation of vitriol (iron(II) sulfate) and so was called oil of vitriol, but Mrs. B says she has changed the label on the bottle obtained from the chemists (p 77) to sulphuric acid to forestall any questions! However, it is evident that the differences between sulfurous and sulfuric acids and that between phosphoric and phosphorous acids is due the different degrees of oxidation of the original sulfur and phosphorus.

If it were possible to remove all the water from sulphuric acid, it should then become a solid, and the girls note the evolution of heat when the strong acid is diluted with water (p 78). It decomposes vegetable matter, such as wood, and then Caroline causes a diversion: "I have very unintentionally repeated the experiment on my gown, by letting a drop of acid fall upon it, and it has made a stain, which, I suppose, will never wash out" (p 79). It will burn a hole, says Mrs. B, but that doesn't stop Caroline next dropping some on her hand. Mrs. B tells her to wash her hands immediately though Caroline says: "It feels extremely hot, I assure you." After that there is a lecture on how to handle acids, and it is recommended that one's fingers should always be wet, in order to dilute any acid spilt on them!

Mrs. B describes the lead acid process for the manufacture of sulfuric acid (and at the same time, some sulfurous acid), its use "in a state of great dilution" as a medicine. A very dilute solution mixed with an aromatic substance, presumably to make it palatable, appears to have been the mysterious elixir of vitriol which was sometimes prescribed by Dr. Marcet to his patients. Meanwhile, Emily has a spot of mulberry juice on her gown, and this is removed with sulphurous acid that merely bleaches the vegetable dye, and does not destroy the fabric (p 85). Caroline asks where is sulphurous acid to be found, and Mrs. B answers that "We may easily prepare some ourselves simply by burning a match." Stain removal is effected by dampening the stained material and then holding a lighted match under the stain, so that the vapor of the burning match which contains sulfurous acid (or more properly, sulfur dioxide) ascends to it. This was apparently a common way to remove stains, as Emily says, but Mrs. B ensures that the girls appreciate the chemistry involved.

Finally, Mrs. B enumerates the salts of sulfuric acid, their occurrence and their uses, especially that of writing ink (iron sulfate plus gallic acid). Phosphoric acid is dismissed cursorily. It can be made from bones, in which it is combined as calcium phosphate.

Conversation 17, Of Nitric and Carbonic Acids; and of the Nitrates and Carbonates

The 1837 version is also similar to that of 1807 version, though reorganized. Caroline objects to the smell of nitric acid (p 96), and were she not headed off with an apology, would have complained about its name, as she did later (p 98). It always contains water, and has never been obtained pure and its composition had been determined both by "the celebrated Mr. Cavendish" in 1785 after passing an electric spark through moist air (10 parts of nitrogen to 25 parts of oxygen) and Sir H. Davy in 1800 who reported the nitrogen:oxygen ratio as 1:2.389 (p 97) [which actually corresponds to a weight ratio of these elements close to NO_2] (32). In neither case does Mrs. B make clear whether she is referring to weights or gaseous volumes, but what she terms nitric acid is probably principally derived from nitrogen dioxide. What Mrs. B refers to as the caustic properties of nitric acid are demonstrated by its reaction when poured over dry, warm charcoal, which bursts into flames (p 96). There follows an interesting discussion on nomenclature and how this acid was obtained before oxygen and nitrogen could be combined using the electric spark. This was from a salt of potash called nitre. Caroline: "Why is it so called? Pray, Mrs. B, let these old unmeaning names be entirely given up, by us at least; and let us call this salt nitrate of potash." Apparently this riles Mrs. B. She says the old names have to be used until the newer ones are more widely adopted, and then she describes how nitric acid is produced from the potash, in a form diluted in water "and commonly called aqua fortis, if Caroline will allow me to mention the name" (p 98).

Pure nitrous acid is a gas and then described, though to modern chemists this gas seems suspiciously like a nitrogen oxide. Nitrous air is more properly called nitric oxide gas. Mrs. B converts some to nitrogen dioxide, which Emily finds "very curious," but she rationalizes the observation correctly. Mrs. B then converts nitrous oxide gas into nitrous acid gas. Nitrous air (otherwise nitric oxide gas) apparently reacts with air to generate an orange color "like nitrous acid" (p 102). The girls claim to understand all this, even if to modern minds the exposition seems rather complicated. Then Mrs. B mentions Sir H. Davy and another modification, gaseous oxide of nitrogen, otherwise exhilarating gas, now known as nitrous oxide, or, conventionally, laughing gas. Caroline wants to try it, but she is not allowed to do so, even though they prepare some by heating ammonium nitrate. The final subject in this area is nitre, or saltpetre, or nitrate of potash, and gunpowder and its detonation, and some other nitrates. Silver nitrate (lunar caustic) was apparently used by surgeons to destroy animal fiber (p 111), presumably to avoid using the knife! In this period even nitric acid was used medicinally, often to treat syphilis, though is ingestion probably did little to cure the patients. What is evident from this discussion to a modern chemist is that the precise identities of the oxides of nitrogen were not all clearly identified by 1837, though Mrs. B does describe how exhilarating gas can be prepared by heating nitrate of ammonia (p 106).

Carbonic acid gas and carbonates are next. Priestley's observation that the gas can promote plant growth is mentioned (p 120), though his name is not. By 1837

Priestley was long gone, but his unpopularity as a non-Conformist preacher who supported the ideals of the French and American revolutions may not have been entirely forgotten in some British circles! Mrs. B describes the widespread occurrence of carbonates in rocks and animal and plant nature as well as the use of what she terms carbonic acid in Seltzer water and mineral waters (p 120).

Conversation 18, On the Boracic, Fluoric, and Muriatic Acids; On Chlorine; and on Muriates — On Iodine and Iodic Acid — On Brome

According to Mrs. B in 1837, boracic acid was apparently imported for industrial purposes "from the remote country of Thibet" as a sodium salt, often called borax (p 122). Despite the acid initially being considered "undecompoundable," in 1808 Humphry Davy (and also some un-named French researchers, actually Thénard and Gay Lussac) decomposed the acid using either the Voltaic battery or metallic potassium to yield the basis, called boracium by Davy, but now called boron. Boron burns in oxygen, and Mrs. B even mentions what analysts might now call the borax bead test (but no more is reported on this acid.

Fluoric acid is obtained from fluor, found in Derbyshire, and it was identified (as early as 1771) by "Scheele, the great Swedish chemist," who was a co-discoverer of oxygen (p 125). Mrs. B describes the preparation of the acid by treating the mineral fluor with sulfuric acid and distilling the mixture into a glass receiver which becomes etched. It is doubtful whether she would have undertaken this herself, for she mentions the want of a suitable container. Caroline wants to etch glass with it, but she forgets that a glass bottle would not be able to hold it. The acid seems to contain a little water, and so it is called hydro-fluoric acid. The acid consists of hydrogen and an unknown principle Sir H. Davy termed fluorine. He could not break it down further, even using potassium (p 126).

Muriatic acid is a gas which may be liquefied by "impregnating it with water." Again, Sir H. Davy could not obtain the basis, but "The celebrated chemist Scheele, while examining the action of muriatic acid on oxide of manganese discovered that a peculiar gas was disengaged," and termed by French chemists "muriatic acid gas," and even oxymuriatic acid gas. Finally "in the year 1811, Sir H. Davy proved it was a simple body" not containing oxygen, and named it chlorine. This is all new compared to the 1807 version. Only the subsequent discovery of brome (1826) and iodine (1811) finally convinced all the chemical community of this fact.

Chlorine is the only material other than oxygen to be able to support combustion (p 130). Caroline keeps her handkerchief to her nose to avoid the smell while phosphorus is exposed to chlorine, and she then exclaims: "Look, Emily, it burns almost with the same brilliancy as in oxygen gas." Mrs. B even burns gold leaf in chlorine. The girls are told that chlorine is used as bleach and as a disinfectant in fever hospitals and prisons. This offends Caroline: "But I think the remedy must be nearly as bad as the disease, the smell of chlorine is so dreadfully suffocating." The remedy, apparently, is to keep one's mouth shut and to wet one's nostrils with "liquid ammonia." However, the vapor of nitric acid is to be preferred for such purposes (p 136)!

The oxides of chlorine and the salts of muriatic acid or "as it is now frequently called, hydro-chloric acid" are then described. Gunpowder is discussed, but the existence of chlorine oxides, though probably observed by Faraday and others, was too contentious for consideration in 1837. Mrs. B then offers to show what happens when you mix potassium chlorate, phosphorus and sulfuric acid "on condition that you will never attempt to repeat it by yourselves" (p 141). The girls apparently agree not to try and are very impressed with this burning of phosphorus.

The discussions of iodine and brome, both of which are inspected in the free form as provided by Mrs. B, are relatively short, and the *Conversation* finishes with a description of the work of Mr. Faraday ("this celebrated chemist") on the liquefaction under pressure of chlorine (1823, p 146) and many other gaseous materials, though not yet air or oxygen.

Conversation 19, On the Nature and Composition of Vegetables

From this *Conversation* onwards what would today be recognized as chemistry is lacking. This involves what are termed organized bodies. Organized bodies "bear the most striking and impressive marks of design" (p 150), but they require an unknown principle called life in order to function. The girls discuss the characteristics of life, and Emily remarks critically: "Yes, Caroline, you have told us what life does, but you have not told us what it is" (p 151); and that sets the pattern of the discussion. Mrs. B describes sugar and sugar candy, starch (which may also be converted in part to sugar, according to "some foreign chemists"), gum Arabic, gum senegal, honey, bread and gluten, various oils and waxes, resins and varnishes, tannin, and vegetable dyes and mordants. Their natures, origins and uses are described at some length, but with little about their real constitutions. Without irony, Mrs. B tells how the sugar-beet industry in Europe arose as a result of "Bonaparte's prohibitory system, which deprived his subjects of the use of West Indian produce…" (p 158). There is also a reference to a Dr. Peschier of Geneva, who detected potash in plants.

Mrs. B notes that all these materials contain hydrogen and carbon in various proportions, plus some oxygen (p 183). Otherwise this *Conversation* is really a listing of materials, their occurrences and uses. It finishes with two lists, the first of vegetable acids (p 184), the names of some of which, for example, oxalic (from a name for wood sorrel, oxalis) and succinic (from the Latin name for amber) are still in use today. Other names such as kinic and boletic acids are no longer immediately recognizable. Their modern names are now quinic and fumaric acids, their sources being Peruvian bark and a variety of the fungus boletus, respectively. The second, short list is of native vegetable alkalis, which seem to be principally narcotics and alkaloids (p 188). Some materials listed here, such as strychnia and quinia were not mentioned in 1807, and Mrs. B adds a footnote that such alkalis were first given names such as quinine and strychnine, etc., but these have since been renamed quinia and strychnia, etc., names consistent with their nature as alkalis! Finally and ironically, Mrs. B closes the *Conversation* with a discussion of the antipyretic quinine (p 189).

Conversation 20, On the Decomposition of Vegetables

Caroline relates that the previous *Conversation* has left her unsatisfied. "What I wish particularly to know is, how do plants obtain the principles from which their various materials are formed …" Mrs. B replies that "This implies nothing less than a complete history of the chemistry and physiology of vegetation," and a footnote refers the reader to Mrs. Marcet's *Conversations on Plant Physiology*, a book which was yet to be written in 1807. In 1837 Caroline was advised to rely on this current *Conversation* for the time being.

Decomposition occurs when plants die, eventually reaching "putrefaction, which is the final state of decomposition." New plants then take up the principles released by these processes. Mrs. B lists four kinds of fermentation which occur in nature, some of which are employed in making products such as wine, beer and bread. Emily has seen the fermentation of wine in Switzerland (p 201) in which sugar gives rise to alcohol but there is no real chemistry in the modern sense. Mrs. B distils some port wine to demonstrate the production of alcohol. Emily asks earnestly "And, pray, from what vegetable is the favourite spirit of the lower orders of people—gin—extracted?" The answer is juniper berries (p 207).

The physiological effects and chemical and physical properties of alcohol are seriously discussed (p 209). It is correctly noted that alcohol burns in air to yield "a small quantity" of carbon dioxide and "a great proportion of water" (p 214). This inaccurate statement is as close as the text gets to a quantitative discussion. Removal of "a certain proportion of carbon" from alcohol using acids generates ether (p 215), a reaction which had been known to alchemists for perhaps three hundred years. Mrs. B shows how a hot platinum wire can glow with white heat when bathed in alcohol vapor in air, which is, as she says, an effect observed by Davy (and others) by 1817, though she does not mention the concept of catalysis, which had been recognized as a general phenomenon first by Berzelius, but as late as 1836. Some modern authorities suggest that ether was not used medically as an anaesthetic until the 1840s, but its properties had been recognized by authorities such as Paracelsus. Mrs. B answers a question from Caroline by stating that ether is used medicinally and is "one of the most effectual antispasmodic medicines," though in excess it can intoxicate (p 217).

Acetous fermentation includes yeast fermentation in bread making, and a process is described for making alcohol, based upon the fact that an ounce of alcohol is produced in the fermentation of every quartern loaf. Mrs. B states that "the final operation of Nature" is putrid fermentation. It is notable that earlier in this chapter (p 195), before the discussion of fermentation, there are hints at a natural cycle of materials in nature ("No young plant, therefore, can grow unless its predecessors contribute both to its formation and support: and these furnish not only the seed ... but likewise the food by which it is nourished.") Such a cycle was proposed a little later by Liebig (1852) to account for the occurrence of nitrogen in both plants and animals.

Conversation 21, History of Vegetation

This *Conversation* is slightly expanded compared to the 1807 version and deals with soils and manures. There is much description and little chemistry. Mrs. B agrees with Emily that an important function of vegetation is to convert carbon, hydrogen and oxygen into a form suitable to feed animals. This is Nature's principal objective (p. 229). There is a long discussion of seeds and germination and the function of manure, with no real understating of chemistry and chemicals involved. Today this material might be considered to me more appropriate to a treatise on botany and agriculture. Caroline wonders why animal products produce better manure than vegetable products which contain more materials which plants require. This is because animal products contain more nitrogen than the vegetable and are more complex, and therefore decompose more rapidly (p 233). Caroline again has conceptual problems. "But Mrs. B, though experience daily proves the advantage of cultivation. A certain quantity of elementary principles exists in nature, which it is not in the power of man to augment or diminish" (p 235). The consequence is that the more of these that are contained in animals that eat plants, the fewer plants will be able to grow. Apparently, Caroline's misconception arises because there is much more of these principles in nature than plants and animals need. "Nature, however, in furnishing us with an inexhaustible stock of raw materials, leaves it in some measure to the ingenuity of man to appropriate them to its [sic] own purposes" (p 236). Emily wonders whether producing carbonic acid by combustion of coal might not increase vegetable growth, but Mrs. B points out that another consequence is London smoke, which was notorious then (p 237), and for more than a century after. The last great London fog was in 1952.

Agriculture is seen as a beneficial process, able to support industry and workers for the benefit of all even though, though, as Emily remarks, "Health and innocence are frequently sacrificed to the prospect of a more profitable employment" (p 238). It is remarkable that statements similar to these are still being made today.

The final part of the *Conversation* is a very descriptive account of seed germination and the functions of leaves. Mr. Senebier of Geneva has shown that plants reared by lamplight close their petals when the lights are extinguished. Plants whilst growing produce oxygen which is apparently derived from their chief sustenance, water (p 246). Priestley observed such oxygen evolution by 1774, perhaps earlier, but again his name is not mentioned. Animals can then use the oxygen. Emily remarks on the "harmony of nature" and Mrs. B comments on "the admirable design of Providence which makes every different part of creation thus contribute to the support and renovation of the other" (p 247). It may be more than an accident that the name of the non-Conformist Priestley is ignored in all this discussion, whereas Sir H. Davy is continually alluded to.

The *Conversation* finishes with a description of woods, resins, and growth, flowering, and deciduous and evergreen trees. The dispensations of wise Providence and Divine Wisdom are referred to more than once.

Conversation 22, On the Composition of Animals

This is the "last branch of chemistry" (p 259). The fundamental principles of animals are oxygen, hydrogen, carbon, and nitrogen, forming just gelatine, albumen and fibrine, the basis of all the parts of the animal system, an idea which the girls find surprising as animals are so complex (p 260). Phosphorus and some metals are also found in animals, especially in bones.

Bones and gelatine are related, and gelatine is clearly prized. Emily is surprised that the "common people" don't use bones to make gelatine (p 266), but Mrs. B reminds her that "There is a prejudice amongst the poor against a species of food that is usually thrown to the dogs." In any case, the best method for extracting gelatine uses too much fuel to adapt to the lower classes, though it is used by some charitable soup establishments. Bones are also used industrially to make hartshorn and sal ammoniac, originally imported from Egypt, but now exported to the Levant (p 267). This leads to a consideration of glue and leather and of cooking, which may be regarded as a variety of chemistry.

Albumen is effectively what we would now term protein, and it contains a little sulfur. Animal oil contains nitrogen, unlike vegetable oils. Animal acids are often formed by decomposition of animals. Prussic acid can be obtained from blood and caustic alkali, but also in other ways and from other sources. Prussic acid (or hydrocyanic acid) and cyanogen have been analyzed by M. Gay-Lussac (in 1815), and since they contain no oxygen, Sir H. Davy thinks the acid properties may be due to the presence of water (p 274). This question of the source of acidity was also posed in 1807, with the comment that not everyone accepted the oxygen/acid explanation of Lavoisier. This has been omitted by 1837 though overall the *Conversation* has been enlarged. The colors produced by prussic acid with metal oxides and with solutions of iron are described, especially Prussian Blue, and the degree of oxidation of its iron content is investigated (p 276).

Conversation 23, On the Animal Economy

This discussion of animalization, the way in which food is assimilated and converted to tissue, is very like the 1807 version. Caroline asks whether the disease rickets is due to a deficiency of phosphate of lime (p 281). Mrs. B states it is due to too rapid growth of muscles or poor digestion. Emily suggests it is due to bad nursing. Anyhow, exercise is good for muscular development. Then come arteries and veins, and lymph, and chyle, and blood, which is a very complex substance. "Females are furnished with another system of absorbent vessels, which are destined to secrete milk for the nourishment of the young" (p 286). The word breast would certainly not have been acceptable in 1837, and probably a reference to cows and udders would not have been regarded as in good taste. Finally nerves are mentioned, all joined ultimately to the brain. "Every organ of sense is a peculiar and separate ornament and the skin finally conspires to render the whole the fairest work of creation" (p 292). In this *Conversation*, discussion of chemistry is again conspicuous only by its absence.

Conversation 24, On Animalisation, Nutrition and Respiration

This is very like the 1807 version. Digestion occurs in the stomach, and the process and the subsequent assimilation of suitable matter into chyme, chyle and blood is outlined (p 296). The mechanism of breathing, using a mechanical model for illustration, is described, but the purpose ascribed to the circulation of the blood seems to be the "nourishment of every part of the body." Respiration involves the absorption of oxygen and the emission of carbonic acid gas, the bulk [volume] of the two being equal. The lungs supposedly purify the blood by oxidizing using oxygen all the impurities scavenged by the blood during its circulation (p 305). The quantities of gas involved for a normal adult are equivalent to eleven ounces of solid carbon in 24 hours (p 308). Perspiration is rather like transpiration of plants. Again, there is little chemistry in this *Conversation*.

Conversation 25, On Animal Heat and on Various Animal Products

Emily starts by saying how similar respiration seems to be to combustion (p 314). Mrs. B approves of the idea, but Caroline is shocked "A combustion on our lungs! that is a curious idea, indeed!" The problem that Mrs. B admits is that this heat evolution cannot be taking place in the lungs and she does not know exactly how carbon and oxygen can be converted to carbon dioxide in the body, because it is unlike a direct combustion, but it does produce heat. Perhaps light is involved and she does know that "It has been calculated that the heat produced by respiration in 12 hours … is such as would melt 100 pounds of ice" (p 315). This is the source of animal heat, and there follows a discussion of the effects of exercise, fever and climate on body temperature, normally constant. Mrs. B describes Sir Charles Blagden's new experiment of sitting in an oven at a temperature near that of boiling point of water and suffering no discomfort apart from "profuse perspiration" and also the experiment of M. De la Roche in Paris. He covered himself with resin, apart from his forehead, and remained in an even hotter oven, when his forehead "sent forth a copious stream of water" (p 320). This last experiment was already described in the 1807 version.

Even fish, which generate much less heat than animals, need oxygen dissolved in the water in order to breath, and birds breath more air in proportion to size than animals, because flying is so strenuous. There are some generalizations about the muscular strength of different kinds of animals. Milk, butter, cream and then animal products such as spermaceti, ambergris, wax, lac, musk, civet and castor are discussed. Animal matter decays in only a single step, putrid decay. In 1807 Mrs. B described a process in Bristol for manufacturing spermaceti, leather and phosphorus via the putrid fermentation of horse corpses under water. In 1837 she notes that this was not a commercial success (p 336).

And finally (p 336), a sermon from Mrs. B: "To GOD alone man owes the admirable faculties which enable him to improve and modify the productions of nature, no less than those productions themselves. In contemplating the works of creation, or studying the inventions of art, let us, therefore, never forget the divine Source from which they proceed: and thus every acquisition of knowledge will prove a lesson of piety and virtue." There is no chemistry in this *Conversation*, but Nature is clearly wonderfully designed, for the general benefit of mankind.

Because of the continuous revision, each edition of this book is a mirror of the state of chemistry of its time. Academic chemistry grew out of medicine, and this was very evident in the interests of Dr. Marcet, Jane's husband, who studied chemistry after exposure to Dr. Black's lectures when he arrived in Edinburgh to study medicine. Eventually he became more interested in chemistry than in medicine. The texts of *Conversations* are a reflection as much of his interests as of those of Mrs. Marcet. They contain a lot of descriptive matter, and precious little chemistry. However, the book also conveys a religiosity that was apparently Jane's and was surely characteristic of comfortable upper-class people of the period. The text reflects a disdain for people of the lower classes perhaps stronger than might have been expected from someone exposed to the rather patronizing but charitable influences of her Swiss husband and his compatriots from Geneva. The Genevan education system was adapted to the needs and requirements of all members of society, including those of the "lower classes."

The Novelty of *Conversations on Chemistry*

The above comparison of an early and a late version of *Conversations* is unique. It is difficult for us today to appreciate the impact that this book had in Britain, the United States, and even Europe. The contents of successive editions changed as the science of chemistry developed, and a consensus as to the breadth of the subject gradually grew. These editions provide a guide to the state of chemical science at the time each was published. For example, the thirteenth of 1837 notes that the tenth edition received a new *Conversation* on the steam engine, in the eleventh oxymuriatic acid became chlorine, possibly as a result of Davy's influence, and the twelfth had a revised *Conversation* on Electro-Chemistry. The approach even in 1837 is completely descriptive, non-mathematical and without a single atomic symbol or equation. This is equally true of Thomas Thomson's huge four-volume textbook for serious chemists, *A System of Chemistry* (33) which was published in 1802. Textbooks such as this were already available when *Conversations* first appeared in 1806, but were considerably less easily portable, let alone digestible. As late as 1860, Muspratt's two-volume treatise of over 2000 pages contained very few formulae (34). The style of Jane Marcet's writing is very different from that of a formal text book or reference work, being a joy to read even today. Nevertheless, this popular text was actually used as a textbook, often by medical students, confirming that *Conversations* was both comprehensible and up-to-date. Despite the different audiences to which they appealed, the organizations of the material in both *System* and *Conversations* are not very different. It is perhaps surprising that *Conversations* was used so widely and for so long in the United States, although many authorities there felt it necessary to amend, correct and expand the text, rather than writing their own books. That Mrs. Marcet treats Dalton's atomic theory as just an unproven theory shows how little influence it initially had upon practical chemistry.

Chemistry and medicine grew from a common source, as exemplified by the influential teachings of Joseph Black and his contemporaries in Edinburgh. Evidently the physicians who followed chemistry were eager to use the newer materials isolated by chemists in medicinal treatments, even if they had no idea of what these materials were likely to do. Some were certainly poisonous. Alexander Marcet was interested in kidney stones, termed calculi, and treatments for such inflictions, required often by gentlemen of quality, was apparently based upon the idea that such stones must be essentially mineral in content and therefore soluble in acids. This relationship of biology and chemistry is evident in many parts of the exposition purveyed by *Conversations*.

Conversations contained not only engravings based upon Mrs. Marcet's own drawings, but also descriptions of experiments, most apparently carried out by her in the laboratory she used in her father's house in St. Mary Axe, in London. This must have been set up by her husband, who later constructed a laboratory in their newer house in Russell Square. That Jane also included experiments in her text was not unusual for books of this kind. *A Grammar of the Principles and Practice of Chemistry*, apparently written by the Rev. David Blair, similarly contains no formulae but does describe experiments for the student to perform (35). The name Blair may be a pseudonym, and modern reproductions ascribe the book to its original publisher, Richard Phillips.

While Volume II, which initially tries to concentrate on chemical facts, is less fun and of less attraction than Volume I, one can begin to appreciate, even after almost two hundred years, why *Conversations on Chemistry* had such an impact. First, the dialogue format is between people who have some kind of individuality; they are not just ciphers. Caroline is bubbly and not inhibited in expressing her feelings, whereas Emily is a serious student. Many of those reading the book would have been able to identify with either or both Emily and Caroline. These characters were probably based upon two daughters of Sir John Sebright (4).

Secondly, despite the reluctance of the Marcet figure, Mrs. B, to claim any expertise for herself, the material contained in the book represented a large part of the contemporary corpus of chemistry. In a society in which the writing of school textbooks was not yet a widely recognized activity, teachers must have found this invaluable. Thirdly, many of the experiments seem to be derived from demonstrations at the Royal Institution. They would often have required considerable amounts of expensive equipment and experimental skill, and would have appealed most to teachers in institutions that could supply both. This might also explain the tendency for US copiers to add experiments that were more appropriate to a home environment. Certainly some of the British contemporary rivals did the same in their books. In any case, it must have been tempting to US writers to edit the text to make the references to purely British circumstances more palatable to US readers. Finally, Mrs. Marcet has managed to convey the excitement of research and the wonder of the new discoveries, and it is probably the girls Emily and Caroline rather than the didactic Mrs. B. who realize this. One can see perhaps a reflection of the young Jane Marcet in Caroline, delighting in the spectacle, drama, and value of the new chemistry, and in Emily a reflection of her studious husband, always trying to explain things. That the whole production is dressed in female clothes also argues for a much more enlightened philosophy of middle-class society than was then common. The religious, social and political attitudes displayed by Mrs. B reflect those of many upper middle-class ladies of the period, and confirm much that has been discovered from study of the Marcet archive in the Biblithèque de Genève (36).

The text of *Conversations* suggests that Emily and Caroline are not sisters, whatever the relationship of the persons upon whom they were based. They are probably of a similar age. Though Caroline's father is said to own a lead factory in Yorkshire, one guesses from the way she says this that Emily's father does not. Emily had travelled, at least to be able to have seen winemaking and charcoal manufacture. Caroline does not say she has also done so. Both girls wore muslin dresses even in 1837, though their clothes are not otherwise described. Nevertheless, the tutor and students together form a group of individuals whose excitement and attitudes still come through to us after more than two hundred years.

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About the Author

G. J. (Jeff) Leigh is an Emeritus Professor at the University of Sussex. After a lectureship at the University of Manchester and a year working in Munich with E. O. Fischer, he spent the rest of his employed career at the Unit (later Laboratory) of Nitrogen Fixation in Sussex, from where he published over 200 papers on the chemistry of nitrogen fixation. He first came upon

Conversations on Chemistry in 1964 in a second-hand bookshop, and was intrigued by the fact that this book had been written as early as 1806 by a woman who was not a recognized natural philosopher. He has since researched her life intensively, and unearthed a considerable amount of new material about her, including a large number of personal letters, about which he is currently writing a further paper.

Conference: The Laboratory Revolution

The University of Groningen is presenting a conference titled "The Rise of the Laboratory and the Changing Nature of the University, 1850-1950" on 26-27 October 2017, at the University of Groningen, The Netherlands. The conference is part of the program "History of the University of Groningen (1614 to the present)."

Laboratories are the ultimate place where knowledge is created. What originally had been the workplace of chemists and alchemists, by the end of the nineteenth century had become a standard element in the infrastructure of science. The rise of the laboratory revolutionized the sciences in many ways and continues to do so. This development has been studied over the past decades by many historians, but the tremendous impact the rise of the laboratory had on the university is less well studied. In the nineteenth century, simple lecture halls were replaced by purpose built science laboratories, that could dominate the city scape. Even academic disciplines that on the face of it needed no laboratory space to develop, like astronomy, psychology and linguistics, each acquired their own laboratories. Also metaphorically, the laboratory became the paradigmatic site for scientific and scholarly research, as is shown by the historians, who liked to compare their libraries to laboratories. Finally, the nature of the academic community was tremendously changed by the rise of the laboratory, each laboratory becoming a small, self-contained community of professors, technical assistants, students, and administrative personnel. The conference 'The Laboratory Revolution' intends to bring together scholars from different backgrounds to study how the laboratory changed both science and the university. By merging the expertise of historians of science and scholarship, historians of architecture, social and cultural historians, and historians of the university, the organizers hope to create a better understanding of the revolution brought about by the rise of the laboratory – a revolution that is still going on.

Keynote Speakers include

- Antonio Garcia Belmar (Alicante University)
- Klaas van Berkel (University of Groningen)
- Ernst Homburg (Maastricht University)
- Alan Rocke (Case Western University)
- Geert Vanpaemel (University of Leuven)
- Kaat Wils (University of Leuven)

For further information: www.labrevolution2017.com

CARBON DIOXIDE IN SELF-RISING FLOUR AND BAKING POWDER: A STUDY IN APPARATUS, SCHEIBLER TO CHITTICK

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An important piece of apparatus frequently used by chemists concerned with the composition of baking powder and self-rising flour (hereafter BP and SRF) is one that is able to determine the amount of carbon dioxide (hereafter CO_2) contained in these products. Knowing the amount of CO_2 available to produce properly raised baked goods gives a clear indication of the products' quality and likely performance as a commercially saleable product.

This article traces the evolution of a relatively simple piece of laboratory equipment which to the present time consists mainly of a graduated manometer, or large U-tube, connected to some kind of reaction vessel in which the sample under test can be treated with a suitable acid (or sometimes water) in order to release the CO_2 which is then measured volumetrically.

This apparatus is known as the Chittick and this article traces its development from its earlier relative invented in the 1860s, as a means of determining CO_2 impurity in the sugar refining industry, to its present role in BP and SRF analysis.

"You Can Only Know What Baking Powder Is by Analysing It."

So claimed the Recorder in a notorious legal case of the Norfolk Baking Powder of 1880 (1). The same dictum could have been applied to self-rising flour since both products had by this time attained a commercial market place (2). Exactly when analysis began as a service to the manufacture or use of BP and SRF is difficult to ascertain; however, according to Chirnside and Hamence (1974), the appointment of Public Analysts followed from the first Adulteration Act passed in 1860 (3). Also, whenever a commercial product was made, particularly in blended powdered goods, there no doubt came a need to ascertain the accuracy of the manufacturing procedures or processes used. To this end the services of chemists would be drawn into this industry and once established the exchange of chemical knowledge was made available through scientific societies, their publications and related trade journals etc.

Chemists and their apparatus experience mutual development. It seems appropriate therefore to give some account of the entry of chemists into the branch of analysis concerned with food before considering the development of their apparatus for the determination of CO_2.

One important chemist concerned relatively early with the adulteration of food was F. C. Accum (1769-1838) who, in his *A Treatise on Adulterations of Food* (1820), devoted an entire chapter to the adulteration of bread by such chemicals as magnesium carbonate and ammonium carbonate, but mainly alum (4). He cited a *Times* report of October 1819, where mere possession of alum (a favored adulterant) brought legal redress (note on p 131):

> … a baker, was convicted … of having in his possession a quantity of alum for the adulteration of bread, and fined in the penalty of £5. and costs, under 55 Geo. III. c. 99.

The need for analysis of food arose mainly from the medical profession's concern over food adulteration, particularly in commercially processed food where fraud or mere errors of processing might exist. It is no surprise therefore that medical professionals first promoted analytical interests. According to Clare and Clare (2012), it was Thomas Wakley (1795–1862), founder of the *Lancet*, who encouraged A. H. Hassall in 1850 to investigate this subject (5), the results of which initiated legal intervention by means of a Parliamentary Select Committee of 1855 resulting in "An Act for Preventing the Adulteration of Articles of Food and Drink 1860" (6). Meanwhile, Hassall's book *Adulterations Detected* (7) had been published in 1857 and was followed by a further act in 1872 entitled the "Adulteration of Food and Drugs Act." Local boroughs soon had the right, although not the legal obligation, to appoint Public Analysts as advisers to the regional Medical Officer of Health.

Chemists quickly formed their own society and journal, *The Analyst* (8), from which this article has frequently drawn. The year 1876 thus marked the beginning of food product analysis by professionally qualified chemists who, it should be remembered (9):

> … started with almost no knowledge of the composition of food and equally almost no knowledge of reliable methods of analysis.

Prosecutions occurred as the appointment of Public Analysts increased. Liverseege (1932), under the heading of adulteration in Effervescent Foods and Drugs, cited only four samples of 76 submitted in the period 1900-1928 were deficient in CO_2 content (10). Adulterants such as alum and calcium sulfate, often in high concentrations, resulted in prosecutions. Those in Britain arising from low CO_2 content included (11):

> *Lowestoft*. Total carbonic acid 4.1%, available carbonic acid 0.85%, instead of 8% of total carbonic acid gas, of which 90% should be available. It was practically devoid of available carbonic acid, the essential ingredient. Fine £2 (*Grocer*, 1907, July 27, Aug. 3; *B.F.J.*, 1907, 138).
>
> *Lambeth*. Available carbon dioxide 2.4%, instead of at least 6%. …
>
> *Newcastle-on-Tyne*. …The ingredients were only sufficient to yield 2.6% of carbon dioxide, instead of 6% as a minimum…. Case dismissed (*Grocer*, 1916, Oct. 14; *B.F.J.*, 1917, 16).
>
> *Mansfield*. Carbonic acid gas 4.33% instead of 8% … Dismissed (*Grocer*, 1917, Dec. 8).
>
> *West Ham*. Available carbon dioxide 1.1% and of very little value as a baking powder. Fine and costs 61s. (*Grocer*, 1923, June 16).
>
> *Wolverhampton*. Carbon dioxide 1%, whereas a reasonable percentage was 8% ... Paid costs 53s. 6d. (*Grocer*, 1929, June 8).

Six to eight percent appears to have been an acceptable CO_2 content which is much below present day levels (up to 18%). There was no mention of SRF in this section.

The most important characteristic of BP or SRF is ability to generate CO_2 under conditions of use involving moisture and heat. This property demands accurate measurement—particularly in the case of SRF where the percentage composition of CO_2 is relatively low compared with the bulk of the product. Furthermore, both products can lose CO_2 during storage depending on moisture present within the products at the time of manufacture or taken up afterwards.

Measurement of gas volume has a long history in the annals of science but of course baking powder came into being long after these original researches. Page (2013) identified chemical aspects as part of the early development of BPs and SRFs (12), but it is unlikely that chemists were routinely employed by BP manufacturers in that period.

The eighteenth-century natural scientist Joseph Black (1728-1799) published *Experiments upon Magnesia Alba, Quicklime, and Some Other Alcaline Substances* in 1756 (13) which described decomposition of carbonates to liberate CO_2 using accurate quantitative means (14). Whilst this may appear to have little direct parallel with BP analysis of today, it nevertheless showed that Black faced considerable difficulty in determining CO_2 content by weight. What follows in this article is an attempt to trace the development of the apparatus and methods used to determine the CO_2 content of BPs or SRFs mainly by volume.

One early pioneer, though not at the time concerned with BP or SRF, designed a volumetric means of measuring the volume of gas liberated from the carbonate impurity in bone char, a substance frequently used in sugar refining (16). That invention belongs to Dr. Carl Scheibler (Figure 1, 1827-1899), whose *Calcimeter* is fully described below.

Figure 1*. Carl Scheibler (1877). © SDTB: Historisches Archiv. Bestand Zucker-Museum (15).*

Analytical Apparatus: A Gasometric Method

The name of Carl Scheibler occurs in chemical literature and the earliest extant copy of his instructions regarding his invention of an apparatus for the sole purpose of measuring released carbon dioxide from carbonate salts when reacted with acid appears in a publication of 1865. This is entitled *Anleitung zur Gebrauche des Apparates zur Bestimmung des kohlensauren Kalkerde in der Knockenkohle, &c*. Dr. C. Scheibler, Berlin, 1865 (17). The title translates as *Instructions for the Use of the Apparatus for Determination of Carbonate of Lime in Bone Char as well as the Volumetric Quantitative Analysis of Carbonate Salts*. No earlier editions of this small book have been found but an 1865 copy is held by the Universitätsbibliothek at the Technische Universität Braunschweig (18). On its title page it is described as a "third edition, enlarged and corrected," thus indicating two earlier editions, one of which may have been 1862. It is impossible to say whether the other edition came before or after 1862. There is also an 1874 edition held by the German National Library of Science and Technology.

An early textbook citation by Fresenius (1865) described Scheibler's apparatus fully and its method of use and in a footnote referred to the 1862 booklet by Scheibler (19):

> "Anleitung zur Gebrauche des Apparates zur Bestimmung des kohlensauren Kalkerde in der Knochenkohle, &c.," von Dr. C. Scheibler, Berlin, 1862. (on p. 711)

Scheibler's reputation as inventor and chemist rested more upon his fame regarding sugars than on the creation of a relatively simple apparatus for measuring gas volume; nevertheless he deserves recognition for what became known as Scheibler's Apparatus. His life is documented in the *New German Biography* (20), which shows his considerable contribution to sugar chemistry and refining but omits his invention of the gas volume apparatus.

Fresenius' (1865) comprehensive account described the importance of analysis of bone black (sometimes referred to a bone earth), for this material is used in both the "preparation of beetroot sugar, and in the refining of cane sugar" (p 710). The process of recycling used bone black also made a demand for analytical control. According to Fresenius, Scheibler's apparatus gained popular use in German sugar manufactories and the account ends, "The process is very expeditious, and in careful hands yields excellent results" (p 714).

Five years later the apparatus was reported in William Crookes' journal, *The Chemical News,* in an article by William Arnot (21). This writer placed Scheibler's apparatus firmly in the context of sugar refining as a means of determining the amount of calcium carbonate in bone char (22). Other industries, such as cement manufacture, found use for this apparatus (23) as a means of quantitatively determining calcium carbonate present as an impurity, but its main application lay in assessing the value of the bone-char used in sugar refining and decolorization (24):

> The almost daily use, for some years, of Dr. Schiebler's [*sic*] expeditious instrument for the estimation of carbonic acid in carbonates, and the invariably consistent results obtained, have made it quite a favourite with the author of these notes. Believing the instrument to be far too little known, he would seek to call attention to its value, especially to those who have the charge of sugar refineries, where the frequent estimation of calcic carbonate in animal charcoal is a desideratum.

Arnot also mentioned Fresenius' description of the instrument adding that "a perusal of the original German instructions will be found profitable" (25).

Crookes gave a full account of Scheibler's apparatus in his analytical textbook, *Select Methods of Chemical Analysis* (26):

> **Volumetric Estimation of Carbonic Acid in Solid Carbonates, Animal Charcoal, &c.**—Dr. Schiebler [*sic*] has devised a very perfect instrument which is adapted for the estimation of the quantity of carbonic acid contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily estimating the quantity of carbonic acid contained in animal charcoal. The principle upon which the apparatus is founded is simply this:- That the quantity of carbonic acid contained in carbonate of calcium can, according to well-known stochiometrical [*sic*] rules, be used as a measure of the quantity of that salt itself; and instead of determining, as has been usually the case, the quantity of carbonic acid by weight, this apparatus admits of its estimation by volume. It is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish, while, moreover, the operator need scarcely possess any knowledge of chemistry. The analytical results obtained by means of this apparatus are very correct, provided care be taken to use the needful precautions (p 390).

From the diagram of Scheibler's apparatus shown in Fresenius' textbook (Figure 2) the actual working of the apparatus becomes obvious.

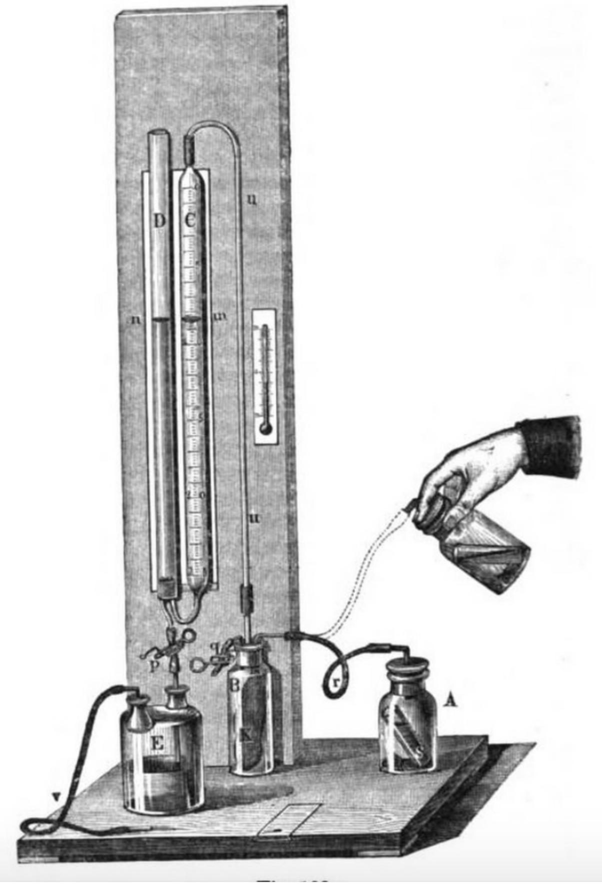

Figure 2. *Scheibler's Apparatus from Fresenius (19).*

The reaction vessel is on the right and contains the sample plus a loose tube of the acid which when the whole is suitably inclined brings about the reaction. The liberated CO_2 enters a thin india-rubber bladder (27), and the displaced air then depresses the liquid in the right-hand graduated tube (having earlier adjusted both tubes to zero). The levels in both tubes achieve equality by drawing off sufficient liquid into the left-hand vessel in order to attain this state. After the determination the liquid can be returned to the zero marks by blowing through the mouth tube shown. Both tubes are connected to each other acting as a manometer. The graduated tube shows the amount of CO_2 liberated from the weighed sample. Another leading analytical textbook of the period, Sutton's *Volumetric Analysis* (1871), included an account of Scheibler's apparatus (28).

The immediate publicists of Scheibler's apparatus were Fresenius and Crookes and it is surprising that neither paid greater attention to the inflatable bladder within the middle container. Although Scheibler perhaps devised this as a means of avoiding the possible dissolution of CO_2 (or other gas) into the burette liquid—it was clearly a thin-walled bladder (*postpapierdünnem Kautschuk mündet*) as thin as writing paper—neither of these commentators considered the consequences should the balloon happen to fill to more than its "uninflated" or flaccid state. Any additional gas would cause elastic resistance and in so doing the pressure in the bladder would be greater than its surrounds. Such a situation would have inevitably produced an inaccurate burette reading.

The possibility of CO_2 dissolution into the reaction acid had certainly been anticipated by Scheibler who devised a correction factor. Fresenius (1865) also remarked on this point (29):

> Scheibler has determined the small amount of carbonic acid which remains dissolved in the 10 c.c. hydrochloric acid at the mean temperature, and he directs to add 0.8 c.c. to the volume of carbonic acid read off. Lastly, the volume being reduced to 0°, 760 mm. and the dry condition, the weight is found.

The point was ignored in Crookes' account of 1871 but in his later editions of *Select Methods* he recommended the adjustment caused by 'retention' of CO_2 rather than absorption. He also suggested a means of confirming the correction by carrying out two determinations using pure $CaCO_3$; in the first using 10 cc of acid and in the second only 5 cc and extrapolating accordingly.

Modifications

An important modification was made by Edward Nicholson in 1874 (Figure 3). This removed possible errors arising from the balloon or bladder, such as over-inflation, by completely removing it. Nicholson also ignored the possible absorption of the gas into the burette displacement solution (30). Dissolution into the reacting acid however remained a necessary factor which Scheibler believed he had fully accounted for.

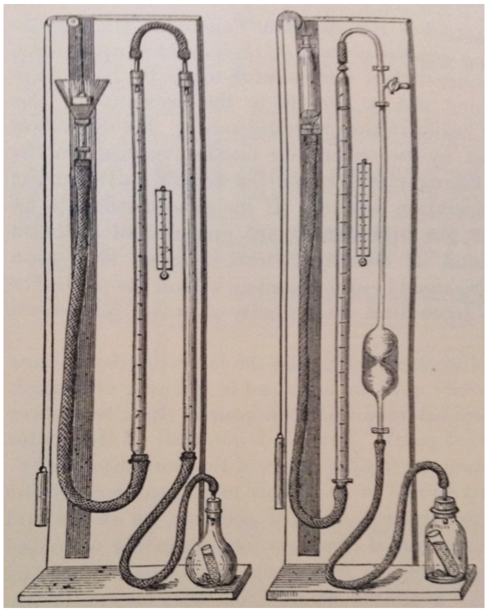

***Figure 3**. Nicholson's Apparatus of 1874 (31).*

Nicholson's new apparatus, which retained the essential features by Scheibler, was reported in *Chemical News* (31). In his short article it appears that he was connected with the Army Medical Department in India and as a consequence had grave doubts as to the efficacy of the india-rubber bladder used by Scheibler. Because of the Indian environment he expressed reluctance to import the apparatus if only because "very thin india-rubber would probably arrive in a glutinous condition." For this reason his modified design removed this possibility and satisfied his need for a quick and accurate method for CO_2 determination.

Nicholson provided a sketch of his apparatus; the left-hand side shows his actual modification for use in India, and the other for construction in "other countries where the manufacture of apparatus is carried on."

Instead of using Scheibler's second graduated measuring tube with reserve bottle and blowing tube he constructed a reservoir capable of moving vertically in order to maintain equality during liberation of CO_2. The india-rubber diaphragm was thus no longer needed and he assumed there would be no significant "diffusion taking place beyond the double bulb during the short time which the operation requires."

Though much resembling a modern Chittick apparatus, discussed later, Nicholson retained Scheibler's separate reaction vessel with its vial of acid, not realizing that the acid addition could be made easier by merely connecting a separate exterior burette and subtracting the volume used from the actual gas as measured.

A further attempt to improve and make more convenient the use of Scheibler's apparatus appeared in 1877 in *Journal of Chemical Society* (32) in which the authors, Pruen and Jones, mention "Scheibler's well-known calcimeter" but describe their own modified form as a "carbometer" (Figure 4).

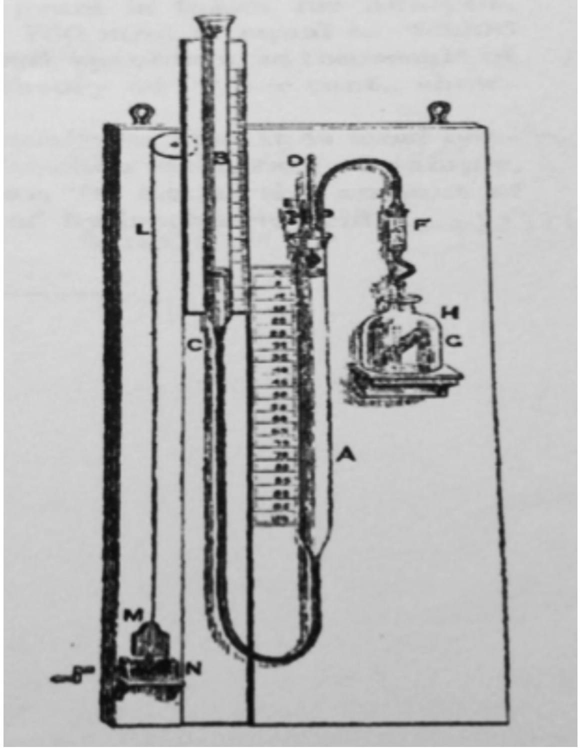

***Figure 4**. The Carbometer of Pruen and Jones (32).*

Using their apparatus they carried out analyses of calcium carbonate in which allowance was made for dissolution of CO_2 into the acid component. This was made on the basis of using "hydrochloric acid, 1 c.c. for each decigram of sample, and to calculate, according to Scheibler, [0].08 c.c. as the amount of carbonic anhydride dissolved in each c.c. of hydrochloric acid" (33).

By this means results were obtained of 43.99% against a theoretical content of 44.00%. $CaCO_3$.

In addition to these experimental results the authors describe their major improvement in design of the apparatus by suggesting "two equal and graduated glass tubes, one (A) stationary, the other (B) [the leveling tube] capable of moving in a vertical direction" (similar but offering a slight improvement to the earlier Nicholson apparatus). This advantage becomes obvious and useful inasmuch as there is no necessity to withdraw an amount of liquid equal to the volume of CO_2 generated—as was necessary in Scheibler's original design. By having the ability to move the leveling tube up or down the levels can easily be brought to equality.

Crookes' *Select Methods* did not mention Nicholson's modification of 1874 until 1905 (34), by which time the further changes made by Pruen and Jones in 1877 had been reported resulting in an apparatus much resembling that of the present time. However, all three innovators retained the awkwardness of the separate acid tube within the reaction vessel.

There were several other published articles related to Scheibler's original apparatus some of which are discussed below. One example, reported by Collins (1906), suggested a means of improving temperature control and disregarded the earlier modifications discussed above (35).

In his article Collins referred to two earlier authors (36) who claimed that with very small amounts of calcium carbonate, 0.5% and below, Scheibler's apparatus "becomes unworkable, for all the gas produced remains in the reacting acid." Collins appears to accept these observations but nevertheless regards Scheibler's apparatus as very vulnerable to temperature variations when compared with other means of gas analysis. To counter this possible source of error he suggested: "… the simplest and most efficient means of obtaining these ends [temperature control] is to bodily sink the apparatus under water, …" (37). This unwieldy arrangement, surprisingly, appeared in Sutton's *Volumetric Analysis* even as late as 1935 (38).

In considering the solubility of carbon dioxide in the aqueous acid, Collins provided correction tables and complicated gas equations—much in agreement with Scheibler. Both authors (Scheibler and Collins) also commented on the solubility of CO_2 in the burette water. A further consideration was that of the effect on vapor pressure "of unknown amounts of calcium chloride and other salts" particularly when testing soils, and Collins devised correction tables for when such salts were thought to be present.

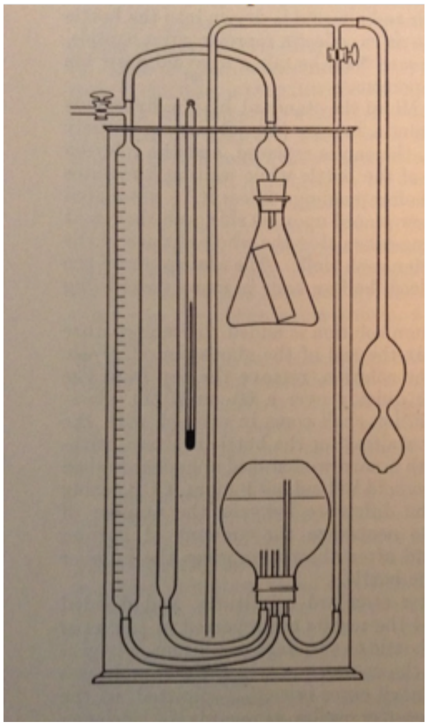

***Figure 5**. Collins' Submerged Apparatus (38)*

A further criticism of Scheibler's apparatus appeared in 1898 in the *Journal of the Society of Chemical Industry* (39) in which the author, Arthur Marshall, also points to possible dissolution of carbon dioxide into the acid used in the reaction to liberate the gas (and presumably also the displacement solution in the measuring burette and leveling tube). He points out that because the total volume of gas in the apparatus is substantial, any errors from incorrect barometric and temperature readings could influence accuracy. He claims that a change or error of one degree centigrade could result in an error of 2 cc. of measured gas. Whatever remedies this author had in mind they did not result in any major changes to the existing design but nevertheless reflected contemporary technical concerns.

A publication of 1899 by Catlin (40) promoted the work of Eben Horsford's 1850s development of phosphates for use in baking powder and also commented on Scheibler's apparatus. Catlin pointed out that because of its inability to measure large quantities of gas this restricted its use to the determination of CO_2 in bone-char only. To overcome this limitation Catlin proposed the incorporation of a reservoir into the burette or manometer but oddly ignored the easier option by the analyst to use a smaller sample. Nevertheless, the suggestion had value and implied that Scheibler's apparatus was in use for baking powders at that time.

Absorption Methods

Determination of CO_2 can be achieved by liberating the gas followed by its quantitative absorption. One instance where a method of this kind was first specifically applied to BP is explained in an article by C. A. Crampton (1890) (41). The analytical method he chose was that attributed to A. E. Knorr (Figure 6). This depended upon absorption of the CO_2 into weighed potash bulbs and was a method given in the first edition in 1920 of *Official and Tentative Methods of Analysis* of the Association of Official Agricultural Chemists (A.O.A.C) (42).

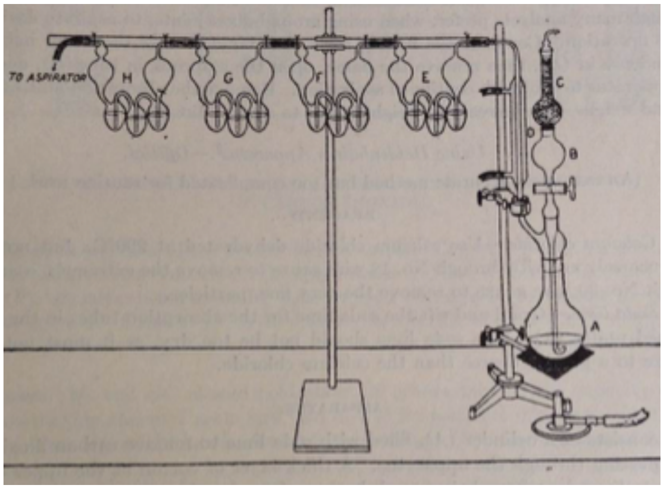

***Figure 6**. Knorr's Apparatus (42)*

Absorption methods remained of importance although cumbersome and time consuming compared with the future gasometric methods employing Scheibler's principle in design. One earlier writer in 1914 (43) gave Knorr's apparatus as the only method at that time for determining both total and available CO_2 in BP. These terms became of importance in Britain when government legislation set controls on CO_2 content in BP and SRF. (See below.)

Crampton's paper above remains of value firstly because it confirms contemporary interest in analysis of baking powder at an early time (1890) and secondly for his use of terms which only somewhat later gained common usage. For example he mentions two distinct measurements, the first, using acid to determine the *total* amount of CO_2 present, and secondly, by the addition of water only to determine what he called available CO_2 content. In other words (44):

> …it is the quantity [of CO_2] which would be actually liberated by the acid ingredient of the powder when it is used in baking, and therefore represents the actual *value* of the powder for aerating purposes, ...

Two published papers, separated by eleven years (1904 and 1915), are of significance regarding the measurement of liberated CO_2, for they give some indication of the developing interest in the analysis of SRF and BP. Both articles are by Thomas Macara (45), the second of which, not only from its title but also from the opening sentence, suggest that analysis of these products was already established for "it is customary to estimate the total and available carbonic acid." Both articles describe the same apparatus (Figure 7), which employed a large decomposing flask connected to an absorption flask containing excess baryta as a saturated solution of barium hydroxide. The liberated CO_2 from the reaction vessel passes over into the baryta solution to form an insoluble precipitate of barium carbonate which by using appropriate indicators can be titrated with standard acid.

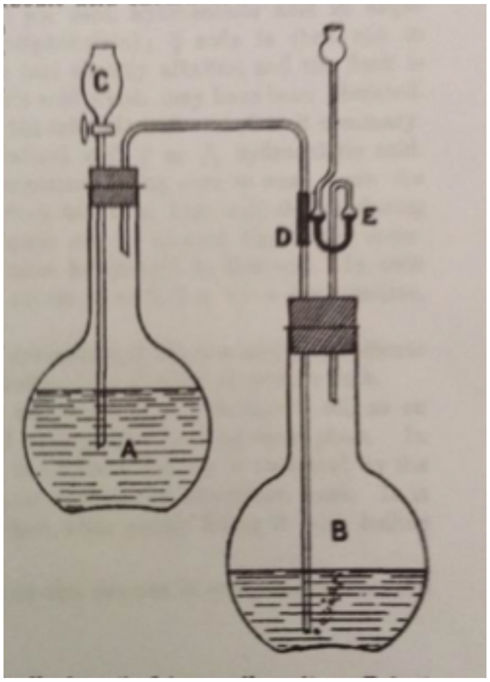

***Figure** 7. Macara's Apparatus (Ref. 45, 1904).*

Macara's description appears somewhat convoluted, however, and his experimental results ambiguous. His method involved firstly precipitating barium carbonate and by several titrations reaching a point of determining the carbonate with acid to methyl orange end point. A simpler method would have been to introduce a known volume of standard baryta into the absorption flask and to titrate the unused remaining baryta with standard acid to phenolphthalein after the reaction was completed.

Nevertheless, Macara's 1915 paper throws light on a growing interest in analysis of BP and SRF and confirms that analysis of these products was established before the time of his writing. The future legislation concerning this trade will be seen to increase the need for reliable analysis.

Macara's terminology is worthy of examination. For example, his opening sentence 'it is customary to estimate the total and available carbonic acid," suggests that such analytical differentiations and their procedures were already in being (although no such terminology is evident in his earlier paper of 1904). He attempted to define these terms more accurately by stating that total CO_2 results from reaction of the BP or SRF with acid, and that available carbonic acid is generally assumed to be that liberated on adding water only to the mixture. However, for some unstated reason he assumes an excess of bicarbonate is usual in baking powders—but there is no reason to believe that makers of BP or SRF were not aware of the desirability of a chemical reaction leading to neutrality. Remember that Crookes spoke of "well-known stochiometrical [*sic*] rules" in 1871 (46) leading to a neutral and complete reaction. Any possible excess of $NaHCO_3$ was perhaps due to faulty weighing or an erroneous recipe by the manufacturer or blender, resulting in an unexpected measure of available CO_2. Thus, Macara believed that available CO_2 ought to be that amount liberated during the entire course of baking. This takes into account the effect of any acid present in the flour, milk or other components in the recipe. From this perspective Macara suggested a modified definition of available CO_2, namely on the basis of total amount of gas liberated from the normal acid-alkali reaction, (47):

> … *plus* that liberated by any acid present in the flour, milk, or other ingredients used, together with that liberated by the action of heat on the excess [if present] of bicarbonate.

He thus proposed a new term, "apparent" available CO_2 (by boiling with water only) and for its determination by his method described earlier in 1904 (48). He further suggested a method "for the estimation of the non-available carbonic acid [residual CO_2], by adding acid to the residue [in the reaction vessel] and boiling into another absorption flask" (49).

It will be seen later that legislation regarding BP and SRF adopted these definitions and because of the framing of new legal requirements changes occurred in definition. Whilst total CO_2 remained as that volume liberated by adding an excess of acid, a new determination came into being entitled residual CO_2. This was the amount of CO_2 generated from an aqueous dispersion of the SRF or BP held at boiling point for a fixed time period and then treated with acid. The true available CO_2 was then judged by subtraction of one from the other.

Before considering the currently used gasometric method embodied in the apparatus known as the Chittick, one novel method devised in 1914 is worthy of comment—if only because its title confirms practical interest in the analysis of BP. The principle of the apparatus depended upon generation of CO_2 in a reaction flask and then leading the gas to a saline-filled glass cylinder where the displaced solution was collected in a conventional measuring cylinder. One could reasonably assume too many variables in this apparatus, but nevertheless the author wrote (50):

> simple in principle, requires an apparatus simple to construct, and manipulate, consumes little time and gives reasonably accurate results.

In the early 1920s there was a growing interest in more convenient methods of CO_2 determination in BPs caused perhaps from the awkwardness of the two existing official absorption methods (Knorr and Heidenhain) adopted by the American Association of Official Agricultural Chemists (51). This was reflected in a 1920 meeting of this association reported by Robinson and Bandermer (1922) in which an obscure gasometric method, based on a modification of an existing method of CO_2 determination in blood plasma, was suggested for use in BP analysis (52). The complexity must have completely ruled out this method but nevertheless the article showed active interest to find a convenient gasometric or volumetric method applicable to BPs.

The Chittick Apparatus

This apparatus now known as the Chittick was reported in the *Journal of the Association of Official Agricultural Chemists* in 1923 (53) but received its formal approval as a "Gasometric Method.—Tentative" in the 1925 edition of the AOAC's book of methods (54) and is shown in Figure 8. The journal entry shows Chittick's submission:

> A volumetric method and apparatus for determining the carbon dioxide content of baking powder. (Submitted by J. Raymond Chittick). (p 453)

Chittick provided instructions on the determination of residual CO_2 by reacting the sample fully with water followed by reaction with acid in his apparatus, thus obtaining an available CO_2 content by subtraction from the total content. The report ends in the recommendation that the accuracy of the method "be compared with the official absorption methods before they [volumetric methods] are recommended as tentative methods."

In 1930 three authors, Chittick, Dunlap and Richards (55), published a paper in answer to criticism of the apparatus made by Hertwig and Hicks two years earlier (56). They claimed inaccuracies of the Chittick method related to vapor pressure of the acid solution. The two groups based their arguments on different publications of the Chittick method (57), but there appears to be no significant difference of method between them.

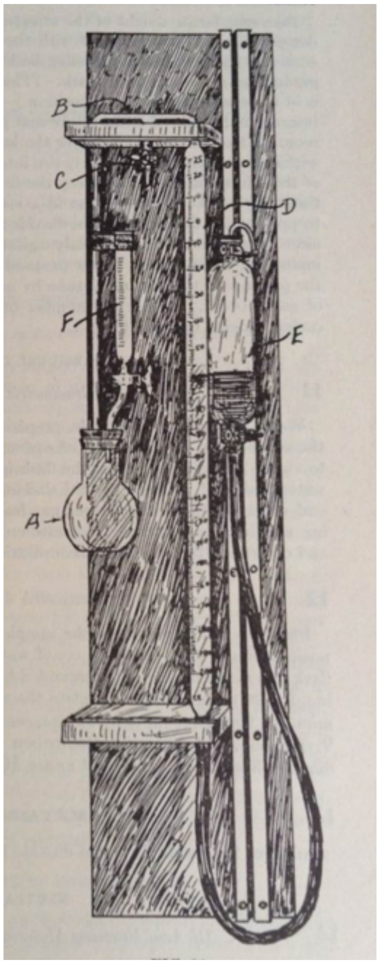

Figure 8. *Chittick Apparatus (AOAC 1925, Ref. 54)*

Chittick *et al.* began their reply by describing the essentials of the method (58):

> … the method depends on the liberation of the carbon dioxide from a baking powder by the addition of an excess of sulphuric acid and collecting the gas liberated (or its equivalent volume of air). This gas volume is then reduced by calculation to the standard temperature of 0°C. and 760 mm. pressure. Knowing the weight of one cubic centimetre of carbon dioxide under these conditions as well as the weight of the sample taken, the percentage of carbon dioxide in the sample can be calculated.

However, Hertwig's and Hicks' criticism claimed inaccuracies in the Chittick method, not addressed by the AOAC, insofar as the vapor pressure of the added acid must cause an increase in measured volume of gas.

This appears to have been the only major criticism of Chittick's design although the solubility of CO_2 into the reacting and displacement solutions had often received attention even from the time of Scheibler's earlier first account in 1862. Their criticism demanded attention and it was incumbent upon Chittick and his colleagues, as instigators of the method's adoption by the AOAC to respond in the way now described. It was probably the first occasion in which vapor pressure had been publicly discussed in connection with the apparatus. Chittick's response concurred with the criticism insofar as (59):

> … when a given volume of dilute sulphuric acid is added to the dry reaction flask, the gas-measuring tube volume will read greater than volume of acid added to the flask, and that this increased volume is due to the vapor tension of the acid.

However, he tempered this fact by pointing out that:

> The strength of the sulphuric acid does not remain the same, … and we have the complex result of the vapour tension of the dilute acid plus the various salts that may be present. This condition undoubtedly does produce a vapour tension but certainly we cannot assume it as being equal to that produced by the acid per se.

Hertwig and Hicks had claimed an increase in the gas volume of "about 3 to more than 5 cc." (56).

Chittick *et al.* had carried out an extensive program of analyses based on BP samples of accurately known composition and CO_2 content. Indeed this was at the heart of their rebuff to Hertwig and Hicks (who lacked such supporting evidence for the method). All parties acknowledged the presence of a vapor tension, but Chittick claimed the added existence of a compensating factor which must have accounted for the accurate results they consistently obtained in their program of analysis.

Chittick's reply therefore rested upon this compensating factor, and claimed (59):

> This is actually the case and the compensating factor appears to be the amount of CO_2 that remains dissolved in the liquid in the reaction flask.

To illustrate this factor Chittick determined the amount of residual CO_2 remaining in the reaction flask by first aspirating away any gas above the liquid and then by connecting the flask to a Knorr's apparatus. On the results so obtained Chittick claimed (60):

> … it bears out the point that there is a factor in the CO_2 dissolved in the liquid in the flask which compensates for the vapour tension of the liquid itself …

Working with highly purified $NaHCO_3$ these three authors each conducted determinations of CO_2 in BPs of known composition under varied controlled conditions. Having in mind that vapor pressure is reduced with lowering of temperature and that solubility of CO_2 in the flask increases, their results showed these factors working together, and so reducing the gas volume. They claimed therefore the Chittick method's accuracy, even in different hands, and that Hertwig's and Hicks' assertion that a correction factor was necessary was without foundation. Hence (61):

> Whatever vapour tension effect is produced by the liquid in the reaction flask is closely compensated for (in the working temperatures generally experienced in the laboratory) by the CO_2 dissolved in the liquid.

Chittick's arguments in response to Hertwig and Hick's criticism therefore rests mainly upon the fact that the apparatus recorded a quantity of liberated CO_2 exactly equal to that theoretically expected from the prepared sample(s) of BP.

It may appear surprising that Chittick had not earlier considered the effect of vapor pressure and was content to accept the accuracy of the apparatus merely only on the basis of results obtained from accurately prepared BP samples. The apparatus was adopted by the American AOAC though only as a tentative method sometime before 1925 (62) and yet the matter of vapor pressure had not been addressed until raised by Hertwig and Hicks two years later. Of course Chittick's use of an external acid burette, although proving more convenient than by introducing the acid in a separate phial or test tube, made no difference to the effect of vapor pressure.

Little is known about Chittick (63) or the development of his apparatus prior to its adoption by the AOAC, whose early editions of method books do not refer to the apparatus by his name. Nevertheless, the apparatus bears his name to the present time and remains a standard piece of analytical equipment in many laboratories and is available commercially. Of course the role of the AOAC was to offer reliable and accurate methods of analysis without theoretical discussion and it was in order to maintain the "tentative" position and perhaps his own reputation that Chittick *et al.* were drawn into the aforementioned dispute which he so fully answered. It is known that Chittick was in the employ of the Jacques Manufacturing Co. of Canal Street in Chicago—one of very many baking powder companies in America at that time (64), and presumably it was during his employment here that the apparatus was devised.

The Acidic Ingredient

The rate at which a BP or a SRF releases its CO_2 became of interest particularly when the range of available acidic ingredients included acid phosphates. Although sodium bicarbonate ($NaHCO_3$) has always retained its position as the source of CO_2 the acidic counterpart received considerable attention if only because the rate of reaction was found to vary from one acid to another, thereby offering the user, the baker, more operational scope in the baking procedure. This subject was highlighted in a 1939 journal notice of a presentation by R. S. Potter and H. H. Bagnall (65), who erroneously dated the use of cream of tartar and monocalcium phosphate as patented by Horsford in America (66).

Acid sodium pyrophosphate was also discussed by these authors, who confirmed its availability commercially as a slow-acting acid but caused "certain difficulties in determining 'available carbon dioxide'" in BPs (67). Potter's and Bagnall's experiments showed that the standard method set by the AOAC (meaning the gasometric using the Chittick apparatus) failed to give sufficient accuracy. These authors also expressed criticism of methods involving absorption into baryta solution followed by titration. They therefore suggested that the means to determine available CO_2 should be more directly related to the complete baking cycle. Though sound in principle it should be remembered that much earlier the AOAC had clearly defined available CO_2 (68):

> Available Carbon Dioxide.—Official.
>
> Subtract the residual carbon dioxide from the total carbon dioxide.

Potter and Bagnall tested four different BPs using different acid ingredients to give a theoretical CO_2 content of 14%. The Chittick method registered 11.6%-

13.3%, while a baryta absorption method gave near theoretical results only when testing samples containing quick-acting ingredients. BPs containing slow-acting acidic ingredients registered about half of theoretical. Because of these poor results the authors recommended a method that involved heating the sample in water to 100°C, drawing the liberated gas through 0.3-N baryta, and determining the amount by titration with HCl. The results were consistent within 0.1 ml. of 0.5-N HCl "irrespective of the nature of the acid ingredient" and "it was concluded that the incomplete evolution of gas was due to the weak acidic properties of cream of tartar and sodium pyrophosphate in dilute solutions" (69).

It should be noted however that these authors, finding an uncertain result from the Chittick apparatus, were in fact only initiating the reaction with water (as in the actual baking process). Potter's and Bagnall's results, based on known theoretical CO_2 contents involving BPs employing different acidic ingredients, clearly showed the Chittick apparatus was not suitable for tests merely employing water to bring about the reaction. It must be noted however, that these authors were somewhat behind the times inasmuch as the 1925 AOAC *Official and Tentative Methods of Analysis* had (p 306) described reliable means of determining residual CO_2 content—even by using the Chittick apparatus! Nevertheless, they illustrated the relationship between solubility or "strength" of the acidic ingredient and rate of reaction.

Potter and Bagnall made their presentation in 1939 just before World War Two influenced the analytical procedures for BP and SRF. It should be noted that the Chittick apparatus, with only minor adjustments, can be used to give an indication of rate of reaction in BPs and SRFs. By standardizing the agitation of the reaction vessel and controlled addition of water the timed evolution of CO_2 can easily be recorded graphically.

Some Legal Aspects

Analysis is a quantitative pursuit and as such seeks to relate its findings to the compositional requirements set by the manufacturer of commercial products such as BP and SRF, or those standards as decided by governmental legislation. The analytical figures sought by industry may not always be entirely compatible with the aims decided by government regulations. It therefore seems worthwhile to examine how legislation, its context and mode of enforcement, influenced analytical techniques in the BP and SRF industry.

In 1944 two statutory orders regarding the amount of CO_2 evolved from these products came into being (70). Both dictated that available carbon dioxide in BP should be not less than 8% and residual carbon dioxide not more than 1.5% (Golden Raising Powder to yield not less than 6% available carbon dioxide and not more than 1.5% residual carbon dioxide). For SRF the available CO_2 should not be less than 0.45% and total CO_2 not more than 0.65%.

These regulations arose from wartime shortages and were used as a means of limiting the consumption of food phosphates. However, both regulations were ultimately revoked (71), although a 1970 Food Standards Committee report suggested that the trade favored the continuation so far as baking powder was concerned.

The analytical methods given in these orders were somewhat inadequate and contained no reference to the Chittick apparatus. Available CO_2 content was calculated as the difference between total and residual without any specific complete analytical methods quoted. Any consequent trade dissatisfaction following these regulations was considered later by a government subcommittee which included public analysts and industrial chemists.

According to an editorial article in the *British Food Journal* (1946) greater standardization of method was a major requirement by trade chemists, Public Analysts and consultants in view of "meagre instructions for the determination of available carbon dioxide" and consequent poor standardisation from one laboratory to another (72). In fact the new order that followed in 1946 contained little improvement and still made no mention of the Chittick apparatus. Indeed, the new order concerned itself mainly with CO_2 content although the committee's demand to abandon the upper limit of 0.65% total CO_2 in SRF was accepted. It was of course because of the possible need to control phosphate usage that the 1944 order came into being although it also safeguarded the customers' interests. Nevertheless, the new order of 1946 for SRF specified no limit on total CO_2 but stated "… flour shall yield not less than 0.40 per cent. of available carbon dioxide" followed by the most basic instructions of analytical method. This gave wider scope to manufacturers in that, without an upper limit, they could, where necessary, formulate to take into account loss of CO_2 in storage. The change also removed any problems arising from the addition of chalk (*Creta Praeparata*) to milled flour following the legal requirements of 1943 in order to increase calcium levels in the diet (73). This of course increased the amount of CO_2 measured by the Chittick apparatus (as total CO_2). The value of the residual content determination in SRF therefore became of greater significance in order to arrive at a true available CO_2 content and thus avoid possible prosecution. Fortification of flour with vitamins and calcium remains a requirement to the present time.

Argument over available CO_2 content persisted, however, and the 1944 earlier order specified a minimum of 0.45% whereas the manufacturers wanted 0.35% CO_2 in the belief that this was generally sufficient for most baked goods. Arguments flowed to and fro with the submission of cakes and other baked items as support from both sides. The committee finally agreed with the Ministry on a figure of 0.4% available CO_2 cited in the new order of 1946 (74).

Both 1944 and 1946 orders made analytical demands. One single total CO_2 figure was insufficient for a manufacturer to avoid prosecution, thereby giving importance to the determination of residual CO_2.

The 1946 order still did not specify the full analytical method. The preparation of the sample prior to analysis and the choice of method remained with the analyst. Of course it is not the responsibility of legislative bodies to devise and instruct on analytical procedures. One method, not mentioned earlier in this article appears in the official orders (1944 for both BP and SRF) is merely referred to as "by means of reduced pressure."

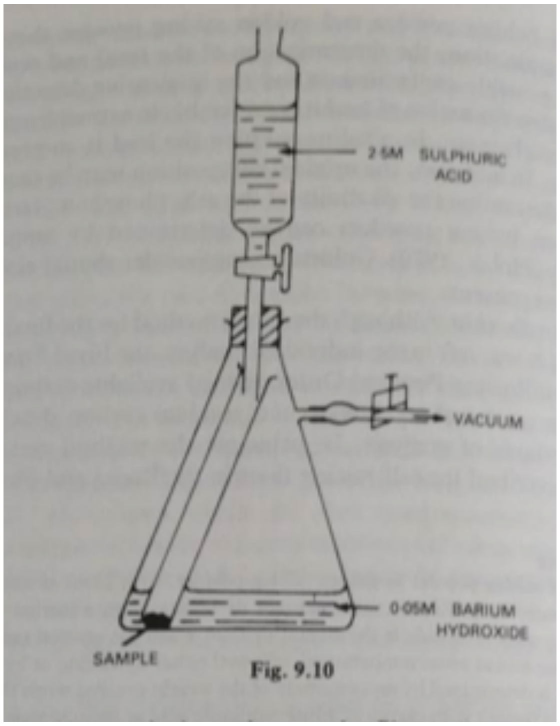

Figure 9. *Determination of CO_2 under reduced pressure (75).*

Pearson's (1991) (75) illustrates this method (Figure 9). It is self-explanatory inasmuch as the reaction flask is first evacuated, allowing evolved CO_2 to react with the standard baryta solution which after a lengthy standing time is back titrated.

In summary the three general methods consisted of

1. gasometric (Chittick)
2. gravimetric (absorption into soda-lime tubes, though considered insufficiently accurate).
3. volumetric (absorption into baryta solution and titration).

For most modern laboratories dealing with BP and SRF analysis, the Chittick is the choice of apparatus

Figure 10. *An everyday working Chittick. (Courtesy of Kudos Blends Ltd.)*

(Figure 10) mainly for total CO_2 determination, and it is regarded as the standard method. Relatively easy to operate and giving reproducible results, the aspect of solubility of the CO_2 in the reaction liquid and any vapor pressure present is usually ignored in line with Chittick's argument discussed above.

Because of the legislative changes discussed above the so-called residual CO_2 remained a requirement during the period of regulation and hence the volumetric method, involving absorption of CO_2 into baryta solution followed by titration, was of importance as a means of obtaining the available CO_2 content (by difference) and so avoiding prosecution. The diagrammatic presentation of this apparatus for residual CO_2 determination was given by Kent-Jones and Amos (76) over many editions of their text book is shown in the Figure 11. Industrial laboratories tended to make their own modifications of this apparatus, for example Kent-Jones and Amos (1967) appear rather over- cautious regarding the inflow of CO_2-free air. The absorption vessels can be easily simplified in order to achieve equally reliable but easier titration.

A current of air is drawn through the residual CO_2 apparatus as shown in the diagram by connecting an aspirator to the second absorption bottle and titration of the baryta standard solution contained therein after evolution of CO_2 from the main reaction flask. This apparatus and the Chittick remained the mainstay of many industrial bakery-related laboratories during the period of legislative regulation; the Chittick however still holds a position of high importance in this area of analysis.

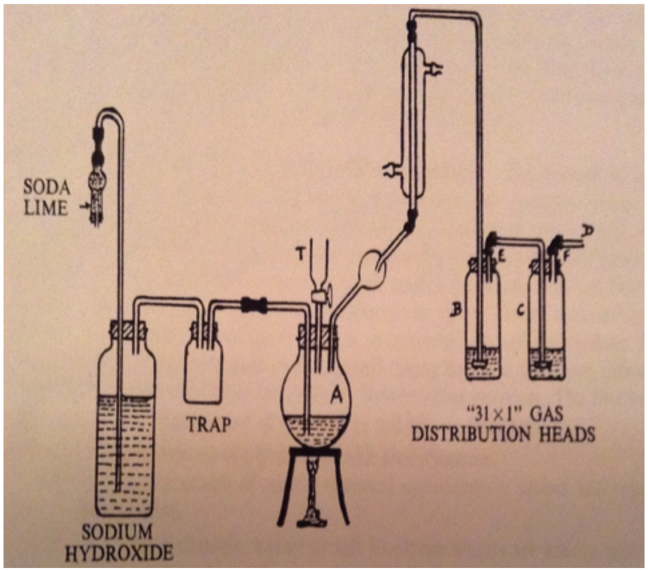

Figure 11*. Residual CO_2 Apparatus (76).*

Conclusion

Journal articles, in particular by Crampton (41), suggest that analysis of BP was practiced as early as 1890 and possibly before. That such early interest existed is further shown by the 1914 paper of H. W. Brubaker whose apparatus, though designed for the determination of CO_2 in BPs was also, rather unexpectedly, used for the enlightenment of girls in household chemistry (50)!

The exact dating of Chittick's design has proved difficult and requires further research but its entry into the published AOAC methods of 1925 and its earlier journal reporting of 1923 clearly show that it was well established in that period. No records have been found which describe the circumstances under which J. R. Chittick developed the apparatus as we know it today. His employment by a notable BP manufacturer no doubt influenced his achievements. The development of Chittick's apparatus followed from the earlier designs of others influenced by Scheibler's original model. Of course Scheibler was only concerned with its use in his own specialized field of sugar manufacture as a means to determine carbonate impurities in bone char.

It is not obvious why Scheibler used a "thin balloon" in his apparatus but his reason may have been to avoid possible dissolution of the liberated gas into the burette or manometer liquid. It could be asked however why he did not realize that once saturated with CO_2 no further dissolution would occur. Perhaps his cautious approach arose from the belief that this CO_2-saturated liquid might alter during periods of disuse or because of changes in ambient laboratory conditions. Of course early collection of gases often employed animal bladders and perhaps Scheibler was merely acting within tradition.

This article has illustrated several important modifications to the early apparatus of Scheibler, often not adopted, but usually following his principles of design. Absorption methods have been discussed in this article but these never reached the ease of performance given by the gasometric apparatus from the time of Scheibler to Chittick. Arguments regarding the accuracy of the Chittick apparatus have sometimes influenced its early development, but, as is often the case in industrial analysis, if the measured quantity (of CO_2) matches that of a known prepared sample then further enquiry takes second place.

The modern apparatus in any bakery analytical laboratory would be immediately recognized by Scheibler, though no longer bearing his name. One element of surprise would no doubt have arisen from today's manufactured price of around £2,500 compared with £3 for Scheibler's original model. The piece has not changed dramatically although its ease of use is greatly improved since its first invention. The apparatus has retained its main principles through a period of unprecedented instrumentation in industrial analysis as a consequence of the present electronic age (77) and still consists of a reaction vessel connected to a manometer.

Like few other specialized pieces of laboratory equipment the Chittick apparatus has not been replaced by a modern electronic alternative and remains an essential laboratory piece.

Acknowledgments

I am grateful to Frank Moll-Seiler, Librarian, Universitätsbibliothek, TU Braunschweig for information regarding Scheibler and the portrait of Scheibler, courtesy of © SDTB: Historisches Archiv, Bestand Zucker-Museum (15).

I express thanks to the Royal Society of Chemistry for permission to reproduce illustrations from *J. Chem. Soc*., 1877, (Pruen and Jones' apparatus), and from *Analyst*, 1904 and 1915, (Macaro's apparatus). Permission to reproduce AOAC illustrations has been given by AOAC INTERNATIONAL.

I am grateful to the staff and chemists of Kudos Blends Ltd. Cleobury Mortimer, DY14 8SY. UK, and the Bodleian Law Library, Oxford, Official Papers Librarian, Hannah Chandler, and staff of the Radcliffe Science Library.

Professor W H Brock is thanked for his reading of this manuscript.

References and Notes

1. A report of this legal, if humorous, case was reprinted as, "The Norfolk Baking Powder Case," *Analyst*, **1880**, *5*, 21-33. See also, "Alum in Bread," *Br. Med. J.*, **1880**, *1*(995), 138.
2. F. G. Page, "Baking Powder and Self-rising Flour in Nineteenth-Century Britain: The Carbon Dioxide Aerations of Henry Jones and Alfred Bird," *Bull. Hist. Chem.*, **2013**, *38*(2), 140-154. Henry Jones first made SRF in 1845 although its legal status came into being much later. See Bread Amendment Acts 1922. Amendment of 3 Geo.4.c.cvi. and 6&7 Will.4,c.37, so as to permit sale of self-raising flour.
3. R. C. Chirnside and J. H. Hamence, *The "Practising Chemists": a History of the Society for Analytical Chemistry, 1874-1974*, Society for Analytical Chemistry, London, 1974, p 6.
4. F. C. Accum, "Adulteration of Bread," in *A Treatise on Adulterations of Food and Culinary Poisons* …, London, 1820, 2nd ed., pp 125-144.
5. P. Clare and M. Clare, "The Life and Times of Alfred Henry Allen, Sheffield's first Public Analyst," *J. Assoc. Public Analysts*, **2012**, *40*, 39-59.
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8. The first issue of *Analyst* included the *Proceedings of Public Analysts,* which appeared on 31 March 1876. Remarks in the opening notices state "The ANALYST appears, primarily, as the organ of the 'Society of Public Analysts,' and, secondly, as the representative of Analytical Chemists in general." Also, "…to publish all cases of prosecution for adulteration, and such parliamentary and other proceedings as may appear to touch the interests of Analysts in general." *Analyst*, **1876**, *1*, 3a.
9. Ref. 5, p 49.
10. J. F. Liverseege, *Adulteration and Analysis of Foods and Drugs: Birmingham Methods and Analyses of Samples. Review of British Prosecutions During Half a Century*, Churchill, London, 1932, ch. XXIX, 433-446.
11. Ref. 10, pp 439-440.
12. Ref. 2 (Page).
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15. The artist is thought to be Ernst Trepper (1843-1890), a disciple of Anton von Werner. The picture is dated as 1877. Signature and Year are in the lower left corner.
16. Bone char is produced by charring animal bones in limited air supply. The product may contain up to 10% carbon.

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18. The book resembles an instruction manual of 27 pages with 7 additional tables and measures 13.5 cm by 20.8 cm, and it is from this source that this article draws. Digitised copy at http://www.digibib.tu-bs.de/?docid=00059656 (accessed Mar. 26, 2017).
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22. M. G. Tissandier, "Methods of Analysis and the Composition of Various Chemical Manufacturing Products," *Chem. News*, **1870**, *19*(530), 26. Analyses of bone-black (animal black) used in sugar refining in 1870 showed levels of 12% to 15% CaCO$_3$. See also T. Graham, "Effect of Animal Charcoal on Solutions," *Quart. J. Sci. Lit. Art*, **1830**, *7* [new ser.], 120-125: "In 1810, M. Figuier, Professor of Chemistry at Montpellier, discovered that animal charcoal discoloured with much greater power [than wood charcoal]. It has subsequently been used very extensively by the sugar refiners of France in clarifying their syrups" (p 121).
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25. W. Arnot, "Notes & Queries," *Chem. News*, **1870**, *19*(April 1), 156: "…for a general description of the apparatus consult 'Fresenius' (4th edition, [1865], page 711). The apparatus I work with was purchased in Berlin, but is, I think, supplied by Dr. Schiebler [*sic*], Stettin, [Szczecin, Poland] for 20 Thalers (about £3), complete."
26. W. Crookes, *Select Methods in Chemical Analysis (Chiefly Inorganic),* Longmans, London, 1871, pp 390-396.
27. Described by Crookes (Ref. 26, p 391), as like the "well-known inflated india-rubber balloons sold as toys."
28. F. Sutton, *Volumetric Analysis: A Systematic Handbook of Volumetric Analysis*, Churchill, London, 1871, 2nd ed., p 364. Not unexpectedly, Scheibler is not reported in the first edition of 1863. In later editions the author reported the modifications recommended by Collins (Ref. 35).
29. Ref. 19, p 713. It appears from the later Fresenius, 1876 edition that Scheibler had altered this correction factor to 3.2 cc. In a footnote (p 345) Fresenius expressed uncertainty and pointed out this factor's dependence on, for example, the salt concentration in the acid solution and referred the reader, "Compare SCHEIBLER'S later directions and [E.] DIETRICH, Zeitschr. f[ur] anal. Chem. 3, 165."
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36. A. D. Hall and E. J. Russell, "A Method for Determining Small Quantities of Carbonates," *J. Chem. Soc. Trans*., **1902**, *81*, 81-85. A. Amos, "A Method for the Determination of Carbonates in Soils," *J. Agric. Sci.*, **1905**, *1*(3), 322-326.
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a similar one by Heidenhain (considered far too complicated for routine work) were both described as "official." These were time consuming in use and predated the gasometric volumetric method (described as tentative) which appeared five years later in the second edition of 1925, (pp 305-306).

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45. T. Macara, "A Rapid Accurate Method for the Volumetric Estimation of Carbon Dioxide," *Analyst*, **1904**, *29*, 152-153. T. Macara, "Notes on the Estimation of Carbonic Acid in Self-raising Flours and Baking Powders," *Analyst*, **1915**, *40*, 272-275.
46. Ref. 26, p 390.
47. Ref. 45 (1915), p 272.
48. Ref. 45 (1915), p 273.
49. Ref. 45 (1915), p 274.
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51. The Association of Official Agricultural Chemists (AOAC) was originally founded in 1884, under the auspices of the U.S. Department of Agriculture. The original aim was to formulate standard methods of chemical analysis of fertilizers but this gradually incorporated other areas such as animal feed and dairy products and after 1906 all foods and drugs. In 1965, the organization changed its name to the Association of Official Analytical Chemists (AOAC). This was again changed in 1991 to AOAC INTERNATIONAL.
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58. Ref. 55. This description agrees with that given in *J. of A. O. A. C.,* 10, (1927), 36, to which the authors refer.
59. Ref. 55, p 475.
60. Ref. 55, p 478.
61. Ref. 55, p 480.
62. The first edition of *Methods of Analysis* was published in 1920. The preface described the vigorous process by which a method or apparatus was "tentatively" adopted by a referee whose report appeared in the *Journal* of the AOAC, and that "… a method can be made official only after the most thorough series of tests, not alone for accuracy, but for ease of operation as well."
63. J. Raymond Chittick was born in the early 1880s in the state of Iowa (US Census data). The Iowa Official Register for 1906 lists him as a member of the chemistry faculty at Highland Park College in Des Moines. He joined the American Chemical Society in 1908, according to a 1935 ACS directory. The Iowa Official Register for 1913-1914 lists Chittick as Chief Chemist under the Dairy and Food Commissioner. He moved to the Chicago area, where he worked for Jaques Manufacturing Company, makers of KC Baking Powder. Jaques was given as Chittick's affiliation in AOAC reports in the early 1920s, and according to *The Cook's Book* (a 1933 recipe book published by Jaques, available online at http://archive.lib.msu.edu/DMC/sliker/msuspcsbs_kcba_jaquesmanu8/msuspcsbs_kcba_jaquesmanu8.pdf (accessed Apr. 30, 2017)) he was Chief Chemist. After retirement, he moved to La Jolla, California, where he died in 1950 ("Necrology," *Chem. Eng. News*, **1950**, *28(45)*, 3911).
64. *Bulletin National Research Council*, vol. 3(1) Dec. 1921, Washington DC. This lists Jaques Manufacturing Co., 16th and Canal Sts., Chicago. (Manufacturers of K. C. baking powder) Research Staff: J. R. Chittick and 3 chemists. Research Work: "One-third time of 2 on leavening materials." Chittick is recorded as Director of Research elsewhere. Chittick's joint author F. L. Dunlap is also listed.

65. *J. Soc. Chem. Ind.,* **1939**, *58*, 76-77.

66. There are eighteen patents in Horsford's name (some jointly with G. Wilson) but the one of significance here is probably no. 75,336, dated March 10, 1868, regarding the manufacture of phosphates and extracting phosphoric acid from bones.

67. No clear date has been confirmed for the first use of pyrophosphate but its first manufacture and sale by Albright and Wilson in the UK occurred about 1917. See R. F. Threlfall, *The Story of 100 Years of Phosphorus Making, 1851-1951*, Albright & Wilson, Oldbury, UK, 1951, pp 198-199.

68. Ref. 54, p 306.

69. Ref. 65, p 77.

70. In Statutory Rules and Orders, 1944 Volume II Comprising the Title Emergency Powers (Defence), London, HMSO (1945), Baking Powder and Golden Raising Powder, 1944 no. 46, p 509; Self-Raising Flour 1944 No. 44, p 515; both orders dated January 14, 1944.

71. Revoked in 1984 by The Bread and Flour Regulations 1984 (SI 1984/1304), Schedule 7, Regulation 16, (revocations) in Statutory Instruments, 1984, no. 1304, on p. 4071, following the recommendation of the Food Standards Committee Report on the Pre-1955 Compositional Orders Concerning Baking Powder and Golden Raising Powder etc. p 8, HMSO London, 1970. There were additional revocations in 1995 (SI 1995/1302) and again in 1998 (SI 1998/141).

72. *Br. Food J.*, **1946,** *48(4)*, 149-158.

73. The Calcium Flour Order became mandatory for the addition of chalk to flour. According to E. N. Greer, J. D. Mounfield and W. J. S. Pringle, "The Estimation of Added Calcium Carbonate (Creta Praeparata) in National Flour," *Analyst*, **1942**, *67*, 352-355, the amount added was 7 oz. of chalk to a 280 lb sack of flour. This would add only 0.07% CO_2 (approx.) to the total amount. Small though this was it could have been of significance to a SRF manufacturer.

74. Statutory Rules and Orders, 1946, no. 157, vol. II, pp. 26-27, HMSO, London.

75. R. S. Kirk and R. Sawyer, *Pearson's Composition and Analysis of Foods*, 9th ed., Longman, Harlow, Essex, 1991, p 339.

76. D. W. Kent-Jones and A. J. Amos, *Modern Cereal Chemistry*, 6th ed., Food Trade Press, London, 1967, p 640, and other editions.

77. See Ref. 14, p 291.

About the Author

After retiring from the chemical industry in 1989, the author gained a M.Sc. degree at the Oliver Lodge Laboratory of the University of Liverpool. His studies of early analytical chemistry under the supervision of Professor W. H. Brock resulted in his earning a doctorate from the University of Leicester in 1999. This present article and a previous one in this journal regarding self- rising flour and baking powder, originated from his early employment with Albright and Wilson Co. and involvement with the development of food phosphates.

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AFTER THE REVOLUTION: NIKOLAI MATVEEVICH KIZHNER (1867-1935) IN SOVIET MOSCOW

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Nikolai Matveevich Kizhner (Николай Матвеевич Кижнер, 1867-1935) (1) is familiar to most students who have completed an introductory course in organic chemistry as the Kishner of the Wolff-Kishner reduction (2, 3). Rather fewer organic chemists, however, know that he also discovered the related, platinum-catalyzed, base-promoted decomposition of pyrazolines to cyclopropanes, now known as the Kishner cyclopropane synthesis (4). Both of these discoveries were made while Kizhner was Professor of Organic Chemistry at Tomsk Technological Institute, in the city of Tomsk, in Siberia.

The first decade of his independent career was an extremely eventful period in Kizhner's life. Not only did he discover the two reactions that bear his name, but, during the Revolution of 1905, he joined the fight of the students at Tomsk against the heavy hand of the central government over the universities. As a result of his activities, he was exiled from Tomsk in February, 1906, only to be reinstated in May, 1907. Remarkably, he did all these things after he had fallen victim to a gangrene of the extremities that resulted in amputation of his right leg above the ankle in 1904. Even more remarkably, he discovered the two reactions that bear his name after 1910, when his left leg, also, had been amputated above the ankle, confining him to a wheelchair. It is not difficult to imagine that the support of his wife, Sofia Petrovna Kazantseva, whom he had married while a student in Moscow, and son, Boris Nikolaevich, (b. 1894), were critical to his continued success during these difficult periods of his life.

Kizhner was finally forced out of his position as Professor in May 1912, although he gave his poor health as the official reason for his resignation (5). Since the Chair (*kafedra*) of Organic Chemistry also carried with it the perquisite of a professorial apartment in the building, his resignation from the *kafedra* meant that he also had to move out of his apartment; this was enforced in July 1912.

Kizhner left Tomsk with a great deal of regret: it was at Tomsk that he had established his first laboratory and taught his first students, and it was at Tomsk that he had made the discoveries that established him on the international stage. After his ouster he would still talk fondly of his first laboratory. But Tomsk had also revealed the darker side of Russian society at the time—the major reasons for Kizhner's ouster were anonymous accusations of disloyalty to the Tsar, and the petty enmity of Leonid Ivanovich Lavrent'ev (Леонид Иванович Лаврентьев, 1835-1914), a trustee (curator) of Tomsk educational district, who considered him a dangerous "free thinker." The position of trustee was a powerful one that gave the holder direct access to the Minister, and Lavrent'ev used it: in 1906, he had orchestrated the exile from Tomsk of several professors, including Kizhner and the Director of the Institute, Efim Luk'yanovich Zubashev (Ефим Лукьянович Зубашев, 1860-1928), and his efforts against these two "disloyal" professors continued after their reinstatement. In 1912, as the pressure mounted from Lavrent'ev's undermining his position at the Technological Institute, and veiled threats of action against his family by the ultra-conservative gangs known as "Black Hundreds" (6), Kizhner formally resigned his position, officially for reasons of health. One (perhaps unintended) consequence of his resignation for health reasons was that he was awarded a full pension after just over a decade of work at Tomsk.

His resignation notwithstanding, Kizhner remained at the Technological Institute for the 1912-1913 academic year at the request of his faculty colleagues there. During this year, he taught a course in organic chemistry on contract from the Board. But, the loss of the professorial apartment close to his laboratory added a physical hardship to what was clearly a psychological hardship. Kizhner left Tomsk in 1914, never to return. One of his students, Georgii Vasil'evich Khonin (Георгий Васильевич Хонин, 1878-1952), later became Dean of the chemistry faculty at Tomsk Polytechnic University.

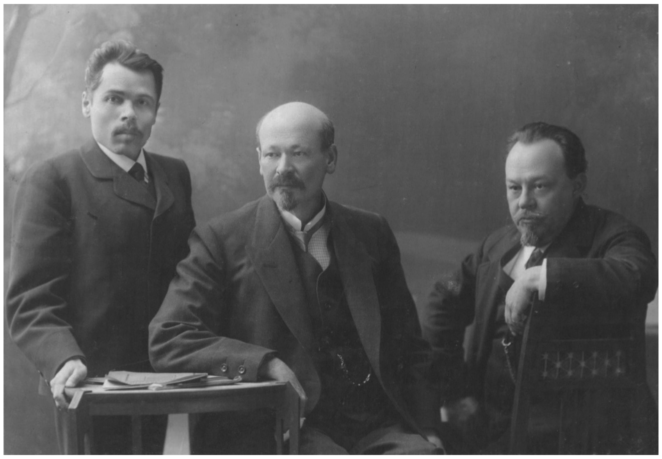

Figure 1. *Members of the Chair of Organic Chemistry at Tomsk Technological Institute ca. 1910: (l-r) Laboratory Assistant (later Professor) Georgii Vasil'evich Khonin (1878-1952), Professor Nikolai Matveevich Kizhner, and an unidentified member. Photograph courtesy of Tomsk Technological Institute.*

To gauge the loss to Tomsk by the departure of this eminent and productive scientist, one need only look at what he accomplished in his last two years there—the two years after he had lost his professorship and was on an annual appointment. In 1912-1913, Kizhner published eleven papers in the *Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva* (4b-g, 7), the flagship Russian chemistry journal, and three more in 1914 (8). Even with the plethora of journals available to chemists today, publishing fourteen papers, all but one with a single author, in less than three years would be a remarkable feat. It must surely stand as an astonishing accomplishment by a chemist at the beginning of the twentieth century (9)—especially a disabled chemist working in an era when there were no special accommodations for disability!

The details of Kizhner's career after his departure from Tomsk are not easy to assemble. One source that contains vivid details of his character is the biography of Russian dye chemist Nikolai Nikolaevich Vorozhtsov (Николай Николаевич Ворожцов, 1881-1941) by Vladimir Mikhailovich Rodionov (Владимир Михайлович Родионов, 1878-1954) (10); Rodionov knew and worked with Kizhner.

In 1914 Kizhner returned to Moscow, where he had spent the happier days of his youth—the year that he won the major Butlerov Prize (the Academy's highest award in organic chemistry). There he hoped, as he put it, to find a place in a laboratory where he could work "for the good of his soul" (10). All who have written biographical memoirs of Kizhner seem to be in agreement that he was fanatically devoted to his science and that it was unimaginable that Kizhner could be happy without his beloved laboratory. At the time of his arrival in Moscow, higher education in the capital was in turmoil thanks to the heavy-handed and reactionary actions of the Minister of Education, Lev Aristidovich Kasso (Лев Аристидович Кассо, 1865-1914; Figure 2). Kasso was a lawyer who had been educated abroad (in Paris, Heidelberg, and Berlin) before returning to the Russian empire to teach civil law. Between 1892 and 1908, he had taught, in turn, at Dorpat University (1892-1895), Khar'kov University (1895-1899), and Moscow University (1899-1908), and then had become Director of the Imperial Lyceum (1908-1910). In September 1910, he was appointed the Chief Administrator of the Ministry of Education, and in February 1911, he was raised to the position of Minister of Education.

As Chief Administrator, and then Minister, he was ruthless. He crushed the student movement and prohibited student unions, he outlawed student meetings, and he intensified the after-school surveillance of students. He greatly exacerbated the existing division between the government and the professoriate by dismissing progressive professors and students from the universities (11). In 1910, Moscow University lost about one third of its best instructors, who resigned their positions en masse following Kasso's summary dismissal of three of their leaders, Rector Aleksandr Apollonovich Manuilov (Александр Аполлоноивич Мануйлов, 1861-1929),

Figure 2. *Minister of Education, Lev Aristidovich Kasso (1865-1914) at his desk in 1913.*

Deputy Rector, Mikhail Aleksandrovich Menzbir (Микчаил Александрович Мензбир, 1855-1935), and Prorector, Pyotr Andreevich Minakov (Пётр Андреевич Минаков, 1865-1831), who had, all three, protested police action against the students. In 1912 he expelled all the women students from the Higher Medical Courses in St. Petersburg, ostensibly for their participation in political rallies and their political unreliability. One consequence of Kasso's actions was the rapid rise in importance of the Shanyavskii People's University.

Figure 3. *Science philanthropist, General Al'fons Leonovich Shanyavskii (1837-1905)*

This university had been founded in 1909 by a bequest from science philanthropist, General Al'fons Leonovich Shanyavskii (Альфонс Леонович Шанявский, 1837-1905; Figure 3) (12). As an unofficial university, Shanyavskii could not confer degrees, but it offered courses that were as rigorous as those offered at Moscow University, and its faculty was held in high esteem. Despite its unofficial status, this institution became quite influential, and a number of future Academicians received at least part of their education there. The Russian Revolution of 1917 led to the nationalization of the university in 1918, with control passing to the state, and with its full merger with Moscow State University (thus completing the circle) in 1920.

When Kizhner arrived in Moscow, the renowned pyridine chemist, Aleksei Yevgen'yevich Chichibabin (Алексей Евгеньевич Чичибабин, 1871-1945; Figure 4), helped him obtain an appointment at the Shanyavskii Moscow City People's University. At Shanyavskii, Kizhner was provided with a single room where he could do his experiments, and he obtained modest support from the Society to Promote the Success of the Experimental Sciences and Their Practical Applications (5e). This society had been founded in 1909, thanks to the merchant and philanthropist, Khristofor Semyonovich Ledentsov (Христофор Семёнович Леденцов, 1842-1907; Figure 5), who bequeathed all his wealth for its formation. To put this bequest in perspective, it amounted to a sum

Figure 4. *Aleyksei Yevgenievich Chichibabin (1871-1945). Photograph from RGAKFD (Rossiiskii Gosudarstvennyi Arkhiv Kinofotodokumentov).*

exceeding that which Alfred Nobel bequeathed to establish the Nobel Prizes. Of course, given the cash-strapped nature of the nation after over a decade of war and civil war, one of the first acts of the Soviet government was to seize these funds, so the Ledentsov awards never had the chance to rival the Nobel Prizes. In addition to the Ledentsov funds, Kizhner used a substantial portion of his professorial pension to equip his laboratory and support his science.

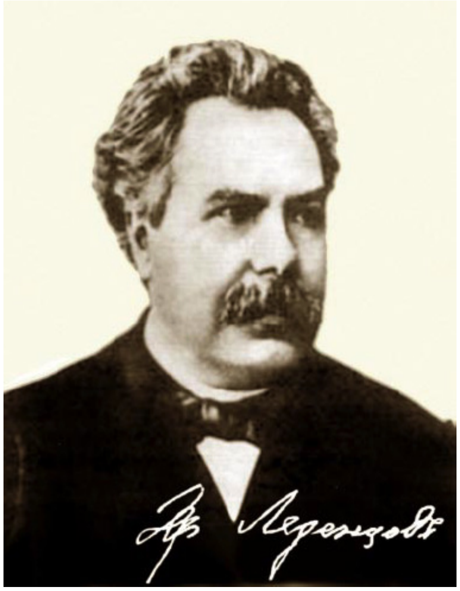

***Figure 5**. Merchant and philanthropist, Khristofor Semyonovich Ledentsov (1842-1907)*

Rodionov (10) paints a vivid picture of Kizhner as an antagonist:

> Arguing with N. M. Kizhner was interesting. [During the argument] it would seem as if he thoroughly hated you, but that was not correct. After the dispute was over, he once again became the good-natured man he was, and would offer to play a game of chess with you. He loved the game, but it excited him so much that his partners found pretexts not to play with him—he had high blood pressure and all this excitement was dangerous.
>
> ... N. M. Kizhner was an interesting conversationalist, and his stories about living and working in Moscow with Markovnikov gave a vivid picture of the late ‘90s. I still remember his story about how he had to steal back a water bath that Markovnikov had taken from his bench...

Kizhner was comfortable at Shanyavskii, and his first year there was productive. In 1915, he published five papers (13) in the *Zhurnal*, but this proved to be the last of his years of high productivity (at least, when measured in terms of the numbers of research publications). He had arrived in Moscow just three years before the Russian Revolution, and the Revolution had an immediate, quantifiable impact on the careers of many Russian scientists, Kizhner included. His first paper in the *Zhurnal* after the Revolution appeared in 1918 (14); his next papers did not appear for another six years (15).

In the Fall of 1916, Kizhner agreed to teach a short course, “The chemistry of strained cyclic compounds,” in which he presented the work of—among others—his mentor, Vladimir Vasil’evich Markovnikov (Владимир Васильевич Марковников, 1838-1904; Figure 6), another of Markovnikov’s students, Nikolai Yakovlevich Dem’yanov (Николай Яковлевич Демьянов, 1861-1938; Figure 7), and, of course, himself, on small-ring compounds (5e). It was notable for its predominant focus on the contributions of Russian chemists to the field, which had begun with the synthesis of cyclopropane itself by Gavril Gavrilovich Gustavson (Гаврил Гаврилович Густавсон, 1842-1908; Figure 8) by a modification (16) of the original procedure (17), developed by Austrian chemist, August Freund (1835-1892). Magidson (5e) reported that his lectures were distinguished by conciseness, clarity, objective coverage and generalization of material that was very new for the time; they were attended not only by students from Shanyavskii, but also by many prominent Moscow Professors and Docents. Unfortunately, no notes of the original course that he taught have survived. At the same time, he continued his studies of the two reactions that he had discovered while at Tomsk.

***Figure 6.** Vladimir Vasil’evich Markovnikov (1838-1904)*

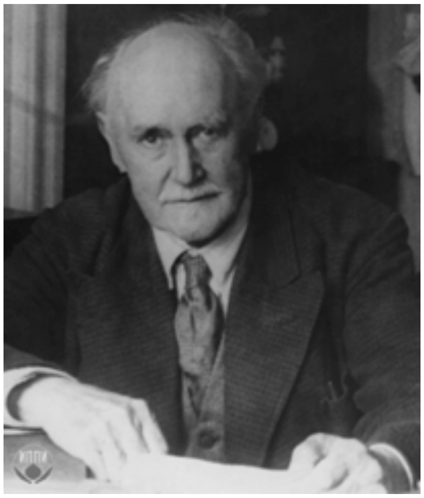

***Figure** 7. Nikolai Yakovlevich Dem'yanov (1861-1838)*

***Figure 8**. Gavril Gavrilovich Gustavson (1842-1908)*

Despite the surgery that saved his life, his gangrene of the limbs would periodically recur, which meant that at times he was in his laboratory with painful sores on the bottoms of his legs. He also, according to some reports, lost at least some of his fingers at this time (5e), and yet he was still able to make his own apparatus, including such things as thermometers and barometers. Kizhner was an active laboratory worker at Shanyavskii, moving about on crutches or in a wheelchair. His physical disabilities meant that the daily journey from his home to his laboratory was a severe physical ordeal for him. Kizhner viewed chemistry as an experimental, not a theoretical science—he distrusted theoretical work not based on experimental observation, so, despite the torment that it became, he still spent long hours in the laboratory, repeating experiments to ensure reproducibility. He demanded similar dedication to these principles from his students, but they still viewed him as "an extremely charming man and a delicate soul," rather than an overbearing taskmaster, and as a gregarious lover of art, music, and conversation (5e). He was a voracious reader, not only of chemistry, but also of literature. One of his favorite authors was the Russian satirist, Mikhail Yevgrafovich Sal'tykov-Shchedrin (Михайл Евграфович Сальтыков-Щедрин, 1826-1889), and he would frequently quote from his works (10).

By 1918, both Moscow and St. Petersburg were under Bolshevik rule; by the end of the Russian civil war in 1923, Russia was a Soviet state. The consolidation of power by the Soviets in the capitals led to the implementation of Soviet economic schemes, and to a sea change in the direction of Russian science. The exhaustion of many of Russia's resources by the decade of war and civil war from 1914-1923 meant that the new rulers of the state were faced with a collapsed economy requiring rebuilding. This, in turn, led to a major shift in the focus of the scientific efforts in Russia from basic to rigidly defined, applied research, with the limitations that this entails.

Kizhner's first work for Soviet Russia after the nationalization of the Shanyavskii People's University was in the testing laboratory of the new Government Commissariat Department, where he could apply his skills as an analyst. However, within a year, he had agreed to lead the aniline dye industry in Russia as Director of the Central Laboratory of the Aniline Trust (AnilTrest), although according to Rodionov (10) he refused any administrative obligations that he felt he could not carry out due to his health problems. In fact, those very health problems gained him a private room (quite unusual in Soviet Russia) in the central laboratory to live in with his wife, due to his difficulties moving about on crutches. In 1919, the "Russian Joint Stock Company of the Chemical Industry in 1914" (also known under the name "Russkogo-Kraska," or "Russian Paint") was nationalized, and became the state-owned enterprise, "Glavanil" (or "Main Anil"). This company was an important part of the Russian dye industry. Kizhner carried out this thankless task well, and under his guidance the Soviet dye industry flourished.

***Figure 9**. Laboratory Building of the Russkogo-Kraska, 1914, which became Glavanil after nationalization in 1919.*

The job at Glavanil again showed Kizhner's fanatical dedication to his science. Another of his students, V. A. Izmailskii, wrote about his time living with Kizhner, from 1919-1922 (5f). He writes that due to his amputations, Kizhner could only carry out scientific work while he lived in the laboratory—the trips to and from his apartment on Arbat Street in Lefortovo to the Glavanil laboratory were simply too arduous. As a consequence, Kizhner would leave the comforts of the apartment that he shared with his wife, and live on an oilcloth sofa in his laboratory. He would drink his tea from beakers, and would occasionally heat up the food that the "tireless" Sofia Petrovna would bring him.

At this time, Soviet industry was almost at a standstill for want of raw materials, and the dye industry was no exception. However, there were stockpiles of a few important industrial chemicals left over after the war—naphthalene, phthalic anhydride, anthranilic acid, toluene, and xylene; and the possibility of manufacturing chloroacetic acid still existed. The central government proposed that Kizhner investigate the synthesis of indigo from these raw materials, especially *o*-xylene (5f). The synthesis of indigo and its derivatives was to be a major focus of the remainder of his career: under the Soviet regime, Kizhner's research became very applied.

The job of directing the national aniline dye industry placed a huge burden on Kizhner's shoulders. He remained the dedicated chemist that he had been in Tomsk, and he continued to study the synthesis of cyclopropanes (12, 18), and the reduction of carbonyl compounds (15, 19), but the rate at which he now published was dramatically reduced by the time taken by his administrative duties—between 1918 and his death, he published only thirteen more papers abstracted by *Chemical Abstracts*.

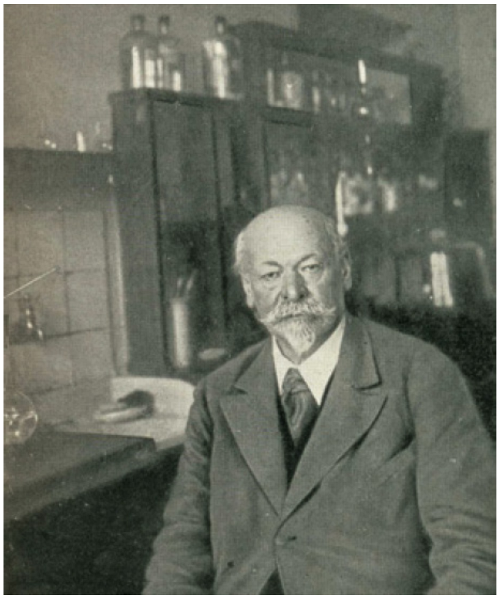

***Figure 10**. Kizhner (1867-1935) in his laboratory at AnilTrest, Moscow, around 1930.*

During this period, the bulk of his work, which concerned aniline dyes (e.g. the Fast Violet B analogues in Figure 11) and sulfur dyes (e.g. sulfur black) was seldom published (only two of his dye papers (20) were ever abstracted by *Chemical Abstracts*), and when it was, it was in specialized trade journals such as *Anilkrasochnaya Promyshlennost* (*Aniline Dye Industry*). Much of the work was tedious, and involved the careful study of the minutiae of the commercial manufacture of dye intermediates. Even so, students still sought to work with Kizhner, who was appreciated for his great knowledge and his willingness to talk about chemistry with any of the students.

One example of Kizhner's attention to detail is provided by his study of the hydrolysis of dinitrochlorobenzene for use in the production of Sulfur Black (21). Kizhner found that allowing the solution to become strongly basic during the base hydrolysis of 2,4-dinitrochlorobenzene led to displacement of one of the nitro groups instead of the chloro group (Figure 12), thus giving dyes of an inferior and inconsistent quality. Based on his work, he was able to design production protocols that gave a superior product. We have not been able to determine where (or if ever) Kizhner published this work, but his protocols were incorporated into the production of the dye in the west, although without attribution (21). His development of a method for the isomerization of *m*-dinitrobenzene to the *ortho* isomer by means of sodium metabisulfite is another example of his attention to detail in even the most mundane facets of the dye industry. The remainder of his papers concerned his continuing basic research, as well as other problems in applied chemistry.

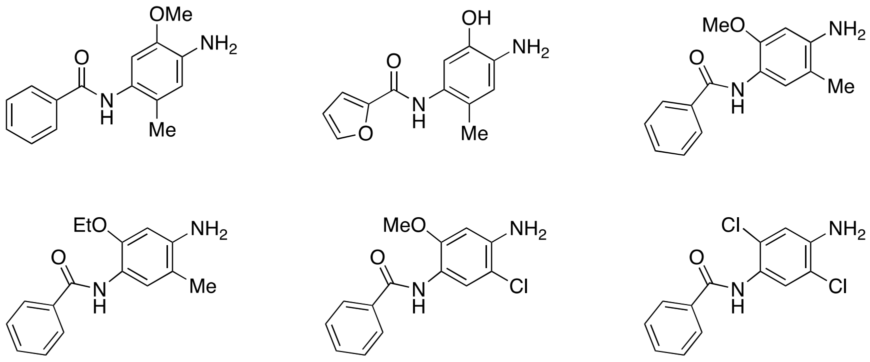

Figure 11. Some Fast Violet B analogues synthesized by Kizhner and his students

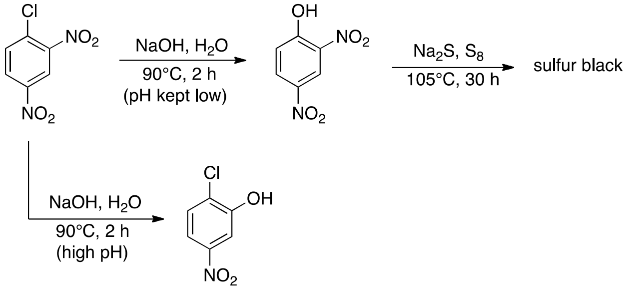

Figure 12. Kizhner's discoveries affected the manufacture of Sulfur Black T by noting that carefully maintaining the pH was critical in obtaining the correct phenolic precursor to the dye.

Among Kizhner's later work was the separation of isomers of xylene by exploiting the differing rates of formation and desulfonation of the monosulfonic acids (Figure 13), described in three papers over the course of a decade (15c, 22). This work provided a simple method for the production of the *o*-xylene needed as starting material for the manufacture of indigo. The work was important in the dye industry in another way, because the particular isomer of an aromatic moiety within the dye molecule affects both the chemical stability and the exact shade of the dye. Kizhner's xylene papers exhibit the hallmarks of his typically meticulous approach to experimental organic chemistry.

Thus he noted, for example, that the *meta* isomer of xylene is sulfonated much more rapidly than the other isomers (in 30 minutes, 100% of the *meta* isomer dissolves in concentrated sulfuric acid, while only 68% of the *ortho* isomer, and 64% of the *para* isomer dissolve under the same conditions in 30 minutes; Kizhner also noted that after 2 hours, 82% of the *ortho* xylene had dissolved, while 32% of the *para* isomer still had not reacted). Interestingly, the sulfonic acid from *p*-xylene hydrolyzes (desulfonates) much more rapidly, thus allowing one to separate *o*-xylene from *p*-xylene. He also observed that the sulfonic acid from *m*-xylene hydrolyzes faster than that of the *para* isomer. These observations provided the basis for a much more reliable method for separating the isomers than fractional distillation, for example.

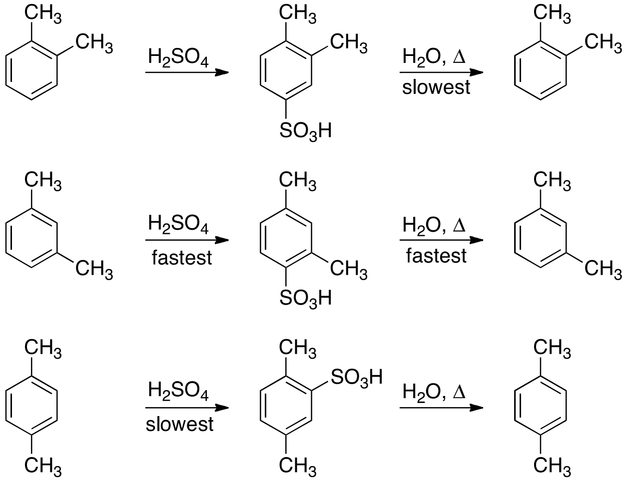

Figure 13. Sulfonation reactions used by Kizhner as a means to separate xylene isomers.

The change in Kizhner's scientific focus and output did not mean that he ceased to work on his fundamental organic chemistry projects, but only that he changed the focus of his energy. He still continued working on his previous projects involving hydrazine derivatives. During his Moscow years, he published papers on cyclopropane synthesis in 1918 (14) and 1929 (18). His work on the reduction of carbonyl compounds with hydrazine also continued slowly.

In 1929, Kizhner was elected a Corresponding Member of the U.S.S.R. Academy of Sciences, and in 1934 he was elected an Honorary Academician. When the U.S.S.R. Academy of Sciences moved to Moscow, in

1935, he was offered the opportunity to lead an independent department in the Institute of Organic Chemistry. He accepted this invitation, despite his health problems, and spent the last few months of his life organizing his new laboratory, and working with enthusiastic, young colleagues. The laboratory had begun to produce publishable results when Kizhner was struck down. A scientist to the bitter end, on November 28, 1935, he had completed a Dumas nitrogen analysis and, apparently in good health, returned to his home—as usual, after sundown. By 10 o'clock that same night, he had died of a heart attack.

Unfortunately, we do not know if Kizhner was an official member of the Communist party, but we can infer at least some of his attitudes. In many ways, he was a replica of his mentor, Markovnikov. To begin with, both had little truck with authoritarianism. Markovnikov was one of the seven Professors at Kazan University who had resigned their positions over the Lesgaft Affair. Pyotr Frantsevich Lesgaft (1837-1909), who had joined the faculty of Kazan University in 1868, was a highly popular and progressive professor and an outspoken supporter of women's rights. By 1871, his promotion to *ordinarius* had twice been blocked by the Trustee of the Kazan Educational District, Pyotr Dmitrievich Shestakov (1826-1889), whose conservative views were antithetical to those of Lesgaft. Shestakov had also humiliated Lesgaft by interfering with his courses, and when the University Council did not take what he viewed as suitable action, Lesgaft made the internal scandal public by venting his rage in the local newspaper. Unfortunately for him, Shestakov wielded more power, so he was fired from his position and banned from further teaching. Markovnikov and six other Professors in the Natural Science Division resigned their positions in protest. After he had moved to Moscow, Markovnikov still bristled at authority, and this led to his compulsory retirement in 1893, at the statutory quarter century after his first academic position under the arcane rules of the Ministry of Education.

Like many of Markovnikov's students, Kizhner admired his mentor, and absorbed many of his progressive views. In 1902, Kizhner opposed mass expulsions of striking students, maintaining that it should be sufficient to suspend them from their student status so that they could still attend classes, and so that they would not be separated from the science. In 1905, Kizhner organized strikes by faculty and students, and he gave revolutionary speeches to gatherings both off and on campus. Obviously these activities—including his refusal to discipline striking students—did not sit well with the Trustee of the Educational District, and this led to his internal exile from Siberia to St. Petersburg. He returned to Tomsk after his reinstatement, but the ill will of the conservatives continued, and eventually they were able to force his retirement "for medical reasons." Two years later, he left Tomsk under a veiled threat against his family by right-wing groups (5h).

As described above, in Moscow, Kizhner joined the Shanyavskii People's University, a progressive-leaning university founded by the Professors fired from Moscow University by Kasso. Following the Revolution, Kizhner was moved into industrial research. It is noteworthy that he spent the rest of his life—until 1935—in Moscow. In the late 1920s and early 1930s, there were arrests of chemists, and it was in this era that Vladimir Nikolaevich Ipatieff (1867-1952) left Russia in 1930, following the arrests of several scientists. The previous year, Chichibabin had also left Russia for France, never to return. The fact that there is no hint of Kizhner being the subject of any investigations by the Soviet authorities suggests that he enjoyed the government's favor. In any case, it is clear that Kizhner was a political progressive with strong revolutionary leanings.

References and Notes

1. Russian uses the Cyrillic alphabet, and so names must be transliterated to the Roman alphabet. The exact transliteration used depends on the language into which the transliteration occurs, and even this is not a constant within the same language. In keeping with our previous practice (D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer-Verlag, Heidelberg, 2012) throughout this paper, the BGN/PCGN romanization system for Russian is used as the most intuitive for English speakers. In citations of articles in western journals, names are given as transliterated by the journals. The Roman alphabet transliteration of Kizhner's name is addressed in our previous papers (Refs. 5h, 5i). Following the Russian Revolution, the Russian alphabet and rules of spelling underwent a simplification. The transliterations used here are, to the extent possible, based on the modern spelling.
2. (a) N. M. Kizhner, "Kataliticheskoe razlozhenie alkilidengidrazinov, kak metod polucheniya uglevodorodov [The Catalytic decomposition of alkylidenehydrazines as a method for the preparation of hydrocarbons]," *Zh. Russ. Fiz.-Khim. O-va.,* **1911**, *43*, 582-595. (b) N. Kizhner, "O kataliticheskom razlozhenii alkilidengidrazinov: St. 2-ya [On the catalytic decomposition of alkylidenehydrazines: 2nd part]," *Zh. Russ. Fiz.-Khim. O-va.,* **1911**, *43*, 951-962. (c) N. Kizhner, "32. O razlozhenii alkilidengidrazinov. Perekhod ionona psevdo ionona i sootvetstvuyushchie uglevodorody, $C_{13}H_{22}$ [32. On the decomposition of

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3. V. Suntsov and D. E. Lewis have prepared English translations of Refs. 2a and 2b and an introduction to the translations: (a) “25. The Catalytic Decomposition of Alkylidenehydrazines as a Method for the Preparation of Hydrocarbons (Abridged),” *Bull. Hist. Chem.,* **2015**, *40*, 64-68. (b) “27. On the Catalytic Decomposition of Alkylidenehydrazines. (Second Part) (Abridged),” *Bull. Hist. Chem.,* **2015**, *40*, 69-73. (c) V. Suntsov and D. E. Lewis, “Introduction to an English Translation (Abridged) of Kizhner’s Pioneering Papers on Decomposition,” *Bull. Hist. Chem.*, **2015**, *40,* 61-64. Unabridged versions of the translations can be found as supplemental information for these papers at http://www.scs.illinois.edu/~mainzv/HIST/bulletin/bull15-vol40-2-supplemental-p61-73.php (accessed Mar. 15, 2017).

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Vladislav Suntsov was born in Russia, and moved to the United States in 2007. He graduated from the University of Wiscosin-Eau Claire in May, 2013, with a major in biology, and a minor in chemistry. During his undergraduate years, he carried out research in organic synthesis and the history of chemistry with Dr. David E. Lewis. He is now completing his medical education at the Arizona College of Osteopathic Medicine.

David E. Lewis is Professor of Chemistry at the University of Wisconsin-Eau Claire, and a former Chair of HIST. He earned the D.Sc. from the University of Adelaide in 2012. He is the author of *Advanced Organic Chemistry* (Oxford University Press: New York, 2016), which was released in 2015. A collection of his papers in the history of chemistry was translated into Russian and released as a bilingual book (Kazan University Publishing House) in April 2016.

HIST Plans Symposium on Archaeological Chemistry

The Division of the History of Chemistry (HIST) is planning a symposium on archaeological chemistry to be held at the spring meeting of the American Chemical Society in Orlando, FL, March 31-April 4, 2019. The tentative title of the symposium is "Archaeological Chemistry: Art and Archaeology in the Ancient and Medieval World." Papers on any subject that address this general topic, especially those that integrate chemistry with archaeology, those directed at answering social, political, and economic questions about ancient cultures, and those that incorporate the use of new technologies, are welcome. Please communicate your interest in participating in the symposium along with a tentative paper title and possible co-authors to either of the co-organizers: Seth Rasmussen (Seth.Rasmussen@ndsu.edu) or Mary Virginia Orna (maryvirginiaorna@gmail.com).

CARBIDE CHEMISTRY AND OPARIN'S THEORY ON THE ORIGIN OF LIFE

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The first and foremost question concerning the origin of life on our planet (abiogenesis) is the synthesis of complex organic compounds (sugars, amino acids, proteins, nucleic acids, etc.) without the help of a living cell. The problem was apparently solved in the 19th century by the first organic synthesis, Wöhler's preparation of urea in 1828 (1), but this is not that simple. To regard Wöhler's synthesis as "a chemical legend" (2) is an exaggeration, as it is also an exaggeration if we take it as a revolutionary discrediting of vitalism (3) and judge it as "in the true sense of the word an epoch-making discovery" (4). The truth is that there are no really crucial experiments, for science actually progresses "in an organic and evolutionary manner" through many small incremental changes and frequently simultaneous discoveries (5).

Products of biogenic and abiogenic synthesis are frequently the same, but their chemistry is different. "It must be noted, however, that the chemist employs in his syntheses altogether different means than the living cell," (6) wrote A. I. Oparin (1894-1980), the founder of the first modern theory of the origin of life. This raises a primary question about the origin of life: does inanimate nature employ the same means as a chemist? This was and still is a great enigma because there were no "halogens [i.e., derivatives of chlorine, bromine, etc.], mineral acids, strong alkalies, high temperatures and pressures, and various other powerful agents" (7) in prebiotic nature.

Oparin goes on to assert that prebiotic organic chemistry proceeded without these powerful agents, and of course without enzymes, but incredibly slowly. Therefore it is a bit misleading to propose that abiogenic synthesis occurs on the modern Earth, but remains unnoticed for it is immediately consumed by living organisms, as Darwin speculated in his famous letter to Hooker written in 1871 (8):

> But if (and oh what a big if) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc., present, that protein compound was chemically formed ready to undergo still more complex changes, at the present day, such matter would be instantly devoured or absorbed, which would not have been the case before living creatures were formed.

Conditions on Earth were quite different in those remote times when life had come into being than they are at present. More recent theories, starting from that of Urey and Miller (9) assume that the primary organic synthesis occurred in the primordial, undoubtedly reducing atmosphere consisting of carbon monoxide and dioxide, methane, ammonia, water, hydrogen, and the like, mostly by free-radical photochemical reactions. Oparin's theory took a different course, though. Oparin also assumed the primitive Earth's atmosphere was reducing, but the first organic compounds were produced by hydration of hydrocarbons (to summarize it in the simplest possible terms), which in turn were originated by volcanic and other tectonic activities from carbides.

Carbide Technology

The idea that hydrocarbons were originated from carbides and subsequently transformed into more complex compounds by reaction with water, as Oparin put it, has close resemblance to a chemical technology used in his time, namely in utilization of calcium carbide (10) for the production of organics. Curiously, that substance was prepared by the chemist associated with the first organic synthesis, Friedrich Wöhler in 1862, by heating an alloy of zinc and calcium with charcoal to a high temperature (11). However, the real father of calcium carbide as well as acetylene technology was Thomas L. Willson, who accidentally invented a method for its production in 1892, trying to reduce calcium oxide with charcoal (12). By the end of the century it was "produced commercially in many places—notably at Niagara Falls, New York, where the requisite electric current to produce the high temperature needed (4500 Fahrenheit) can be readily and cheaply obtained" (13). It became the raw material for almost all the products of organic chemical industry, especially Buna synthetic rubber, via reactions of acetylene (14).

Acetylene gas was a miracle of the age for "The illuminating power of acetylene, in a proper burner, is greater than of any other known gas; the flame is absolutely white and of great brilliancy; its spectrum closely approximates that of sunlight, and consequently it shows the same colors as daylight" (13). Not less important was its reaction with water at 300°C on an iron oxide catalyst, producing acetaldehyde, described in 1915 by Russian-French chemist Aleksei Yevgen'yevich Tchitchibabin (Chichibabin) (15, 16). This and similar reactions were, according to Oparin, crucial for the formation of complex organic compounds on the early Earth (16):

> Considerable quantities of various oxidation products of hydrocarbons, such as alcohols, aldehydes, ketones, and organic acids must have originated as result of such transformations on the Earth's surface. In the above described reaction, as Tchitchibabin points out, if the heated moist acetylene gas contains ammonia, it is possible to observe with the naked eye the formation of a crystalline precipitate of an aldehyde-ammonia; i.e., under these conditions ammonia very rapidly combines with the acetaldehyde formed by hydration. Similarly, other oxidized derivatives of hydrocarbons (the above mentioned alcohols, aldehydes and acids) can enter into variety of reaction with ammonia, giving rise to ammonium salts, amides, amines, etc.

It is clear that Oparin used the hydration of acetylene as a key reaction for the abiogenic formation of organic compounds. This is not at all surprising because the same reaction led to a number of products in acetylene-related chemical industry, but at lower temperatures and with a different catalyst (Hg_2SO_4). But acetylene has not been produced only by reaction of calcium carbide with water. In 1859 French chemist Marcel Morren synthesized it in an electric arc between carbon electrodes in an atmosphere of hydrogen (17), and in 1931 it was demonstrated that methane, heated to 1000°C was converted to acetylene without any catalyst (18), a process which is now widely employed for its production. The reaction was, according to Oparin, also instrumental in abiogenic synthesis, but methane as well as other hydrocarbons were originated by reaction of carbides with hot water vapor.

Abiogenic Origin of Hydrocarbons

Oparin founded his carbide theory of abiogenic synthesis mostly on the Mendeleev's theory of the inorganic formation of petroleum. After his visit to American oil fields, at the session of Russian Chemical Society of October 15, 1876, Mendeleev launched a hypothesis that hydrocarbons were originated from iron carbides by the action of water vapor according to a somewhat cumbersome equation (19):

$$3\ Fe_mC_n + 4m\ H_2O \rightarrow m\ Fe_3O_4 + C_{3n}H_{8m}$$

"As the igneous rocks were folded, cracks must have been formed which at the crests opened outwards while at the depression they opened inwards," says Mendeleev. "Both these types of cracks became in time filled in, but the more recent the origin of the mountain the more open must these cracks be, and water must have entered through them into the Earth's interior to such depths as would be impossible normally from a plane surface" (20). Oparin expressed his disbelief in Mendeleev's explanation because "it would be difficult to imagine how drops of liquid water could possibly reach the glowing mass of carbides, from which they were separated by more than a thousand kilometers' (about 600 miles) thickness of igneous rocks," (20) both of them ignorant of the existence of the Earth's mantle (moho), discovered by Croatian seismologist Andrija Mohorovičić in 1910 (21). They namely supposed that the interior of Earth (barysphere) was composed of melted iron containing dissolved carbon, above which a rock layer (lithosphere) was formed (19). However, Oparin accepted Mendeleev's theory in general terms assuming that "Hydrocarbons must have originated on the Earth by a similar process during the remote past of its existence, when carbides were erupted onto its surface and were acted upon by the superheated aqueous vapor of the atmosphere of that epoch," leading to the final conclusion (his italics): "*Carbon made its first appearance on the Earth's surface not in the oxidized form of carbon dioxide but, on the contrary, in the reduced state, in the form of hydrocarbons*" (22). This hypothesis contradicts modern theories of the origin of life, which propose the primordial Earth's atmosphere was composed mostly of carbon monoxide and dioxide (23), which were the primary source of organic carbon (24), as was speculated even in Oparin's time (25). However, there are also theories which find its primary source in tectonic processes and extraterrestrial material (26).

Oparin's theory was supported by many experiments with carbides in these times. The first such experiment seems to be that of Schretter who in 1841 obtained a liquid resembling naphtha by action of diluted acid on cast iron, and this reaction was further studied by Hahn and Cloëz (27). These experiments were known to Mendeleev who repeated them. He was also informed of the more elaborate experiments of his former student K. B. Haritchkov (1865-1921), an eminent Russian oil chemist (28), who, at the end of the 19th century, produced hydrocarbons by action of water vapor and hot water solutions of magnesium chloride, magnesium sulfate and sodium chloride on cast iron containing 3% carbon (29).

The problem of prebiotic synthesis of nitrogen compounds Oparin solved in a similar way. He namely hypothesized that they were produced from ammonia, that was in turn produced by action of water and water vapor on nitrides. Nitrogen needed for their synthesis was provided by thermal decomposition (at about 1000°C) of nitrogen(II) oxide which further combined with free metals, especially iron in the Earth core (30). This hypothesis was confirmed by the finding of free nitrogen and ammonia in volcanic gases, as well as nitride mineral osbornite (TiN) in chondrites which "may reflect the dominant form of nitrogen in early Earth" (31). These new findings are in line with Oparin's hypothesis that the dominant reaction was that of iron(III) nitride with water converting it to ammonia. Oparin wrote, "Thus, it can be assumed with a high degree of probability that *nitrogen, like carbon, first appeared on the Earth's surface in its reduced state, in the form of ammonia* (31, his italics)."

Oparin did not go further to elaborate prebiotic chemistry in detail; he simply assumed that by reaction of aldehydes and ammonia in the primordial ocean many compounds resembling those found in living beings were formed, including sugars (by the formose reaction, discovered by Butlerov in 1861 (32)), pyruvic acid (by reaction of acetaldehyde with carbonic acid), etc. (6):

> We cannot follow the extremely varied and numerous processes of evolution of organic matter in detail, and for our purpose this would be superfluous. We can certainly establish the general trend of these transformations and changes on the basis of our knowledge of the properties of these compounds.

Conclusion

In the carbide theory of prebiotic synthesis lies more or less conscious belief that for its purposes nature uses human technology. The notion is both naive and reasonable. It is naive because the laws of nature are immutable in contrast to technological procedures which are constantly developing and adapting to the needs of humanity (33). It is however reasonable because it leads to the use of new ideas, methods and approaches to solve old problems.

As virtually all organic chemical industry rested on calcium carbide and its water product (acetylene), it was quite natural to "believe" that abiogenic synthesis started with the same or similar substances. This is the first root of Oparin's theory. The second is undoubtedly the growing interest in petroleum, with the first oil well in the world drilled in Canada 1858, immediately followed by the 1859 well in Pennsylvania (34). In this respect we also have to understand Mendeleev's interest in the origin of petroleum because he was engaged in the research of coal and oil deposits of Russia, which had begun to transform itself from a rural into an industrial nation (35).

Mendeleev's theory of abiogenic formation of oil was forgotten after the advent of biogenic theories (36) until Thomas Gold resurrected it in 1992, as a part of his theory of the origin and propagation of life. Gold proposed that the first organisms were originated and developed in the pores of rocks deep in the Earth's interior thriving on "hydrogen, methane and other fluids percolating upward" (37). But from another perspective, the problem of prebiotic synthesis ceased to be in the focus of modern scientists. The last bastion of vitalism, that abiotic ("inorganic") nature is poor in organic compounds, i.e., carbon compounds, has fallen by the finding of millions of organic compounds in carbonaceous chondrites, of which 683 were positively identified (38). In addition, nearly two hundred different organic molecules were detected in interstellar gas (39). The apparent chemical complexity of biotic in contrast to abiotic nature turned to be the consequence of poor analytical methods. However, the organizational complexity of living beings cannot be denied, so new theories of the origin of life are concerned primarily with the development of self-reproducing systems (40).

From another perspective, the carbide theory of abiogenic synthesis points to the fact that every hypothesis, either right or wrong, can have a positive influence on the development of science, or as Joan Oró (1923-2004) put it (41):

> … the irony of Oparin being inspired by Mendeleev's incorrect assumption together with my own independent involvement with the idea to study the origin of life inspired by a biochemically incorrect assumption demonstrates the creative importance of a hypothesis, whether completely correct or not, to develop breakthroughs in the obtention of new scientific knowledge.

This theory "also reveals the role of intuition, serendipity and the tortuous and winding roads of scientific discoveries" (42).

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About the Author

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Ladies in Waiting for Nobel Prizes: Overlooked Accomplishments of Women Chemists

A full-day symposium sponsored by HIST and the Women Chemists Committee (WCC) will be presented at the 254th American Chemical Society (ACS) meeting in Washington, DC, Tuesday, Aug. 22, 2017. Magdolna Hargittai, author of *Women Scientists: Reflections, Challenges, and Breaking Boundaries* (Oxford University Press, 2015) will be keynote speaker. After the symposium the Portal Theatre Group from the Pacific Northwest will present "No Belles," which tells the tale of eight female scientists, six of whom won Nobel Prizes.

"Ladies in Waiting" builds upon the well-received symposium "The Posthumous Nobel Prize in Chemistry," held in March 2016 at the San Diego ACS meeting. That symposium was covered in a popular article in *Chemical & Engineering News* and is now in the process of publication as an ACS Symposium Series book. E. Thomas Strom, organizer of the earlier symposium, joins Vera Mainz as organizers for "Ladies in Waiting."

CUPRENE: A HISTORICAL CURIOSITY ALONG THE PATH TO POLYACETYLENE

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Introduction

The historical importance of polyacetylene was cemented in 1977, when a collaboration between Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger at the University of Pennsylvania revealed that it was possible to achieve metallic conductivity from free-standing films of the conjugated organic polymer when treated with oxidizing agents such as I_2 or AsF_5 (1-8). Although previous studies on oxidized conjugated polymers such as polypyrrole, polyaniline, and polyacetylene (Figure 1) had revealed conductivities in the semiconducting range (6-9), the ability to generate metallic conductivities from an organic plastic seemed to promise a wealth of possible new applications and brought unprecedented attention to these conducting organic polymers. In recognition of this, the 2000 Nobel Prize in Chemistry was awarded to Shirakawa, MacDiarmid, and Heeger for their pioneering work with polyacetylene and their early contributions to the field of conjugated organic polymers (10).

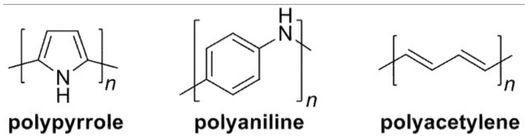

Figure 1. *Conducting conjugated polymers under study between 1963 and 1979.*

Although the most structurally simple of the conjugated polymers, polyacetylene is not nearly as old as other conjugated materials such as polyaniline or polypyrrole (6-9). In fact, it was not until 1955 that Giulio Natta (1903-1979) reported the first successful production of polyactylene (11, 12). As outlined in Figure 2, Natta's methods utilized combinations of triethylaluminum (Et_3Al) and titanium(IV) propoxide ($Ti(OC_3H_7)_4$) to catalytically polymerize the gaseous acetylene to a black crystalline polymeric product (12).

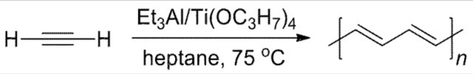

Figure 2. *Natta's catalytic polymerization of acetylene.*

Although not prepared directly from acetylene, oligomeric analogues known as polyenes $(–CH=CH–)_n$ predate Natta's work, with the phenyl-capped series **1a-d** (Figure 3) prepared as early as 1928 (13-16). Such polyenes were typically limited to shorter oligomers (n = 2-10) and were used to correlate physical and optical properties with conjugation length (13-17).

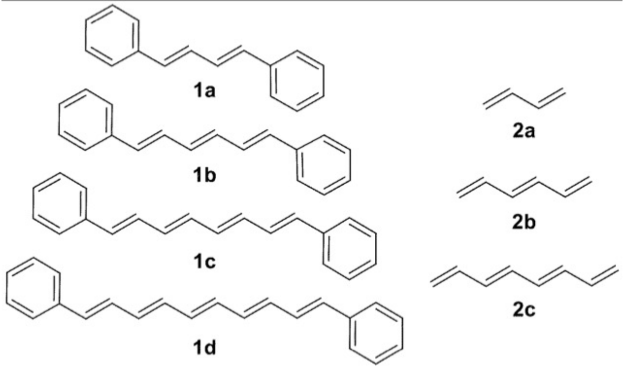

Figure 3. *Early polyene series.*

This is not to say that polymerization attempts did not predate Natta's success in 1955. Prior to all of these efforts, various researchers had investigated the polymerization of acetylene with the earliest reports appearing in the late 1860s (18, 19). These efforts resulted in the production of a resinous material that was ultimately named *cuprene*. The composition and structure of this material was the subject of much debate, however, and to date its history has been poorly detailed (12, 20-22). As such, the current report aims to present the first detailed history of these early polymerization attempts from 1866 through the late 1930s when interest in this material began to decline. This discussion will thus begin with the work of Marcellin Berthelot (1827-1907) in 1866 (18, 19).

Berthelot, Acetylene, and Initial Polymerization

Pierre Eugène Marcellin Berthelot (Figure 4) was born in Paris on October 25, 1827 (23, 24). The son of a medical doctor, he received the *Baccalauréat ès Lettres* required for entrance to the university in 1846. Two years later, he was awarded the *Baccalauréat ès Sciences* and as holder of two Baccalauréats, he was entitled to undertake studies in both the arts and science. He pursued his studies at the Collège de France (23, 24), where he ultimately focused on science and earned the degree of *Licence ès Physique* on July 26, 1849 (23). Berthelot then entered a private school for the practical teaching of chemistry founded by Théophyle Jules Pelouze (1807-1867), former assistant to Joseph Louis Gay-Lussac (1778-1850). At the school, Berthelot supervised the student's work, but was otherwise free to experiment and he published his first two articles in 1850 (23).

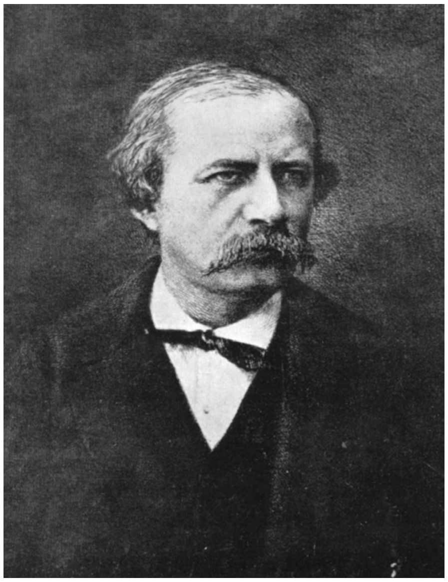

Figure 4. *Pierre Eugène Marcellin Berthelot (1827-1907) [Edgar Fahs Smith Collection, University of Pennsylvania Libraries]*

Berthelot then returned to the Collège de France in February 1851, where he joined Antoine Balard (1802-1876) as his assistant in charge of lecture demonstrations. Finally, he submitted his thesis for the *Doctorat ès Sciences* in April of 1854, after which he registered at the Ecole Supérieure de Pharmacie. He submitted a second thesis for the *Doctorat en Pharmacie* in November of 1858, while also acquiring the diploma of *Pharmacien de Première Classe* (23). Due to the intervention of Jean-Baptiste Dumas (1800-1884), a chair of organic chemistry was created at the Ecole Supérieure de Pharmacie in December of 1859. Coincidentally, Berthelot had just acquired the prerequisites for the position and he thus became the first Titular Professor of the chair and held the position until 1876 (22, 24).

It was in 1860 (25), shortly after assuming the chair of organic chemistry, that Berthelot reported studies on a new carbon-hydrogen gas (26) which he gave the name *acétylène* (25, 27). He was able to produce the gas by passing various organic gases or vapors (ethylene, alcohol, ether, etc.) through a red-hot tube and into an ammonia solution of cuprous chloride (Figure 5). This resulted in the precipitation of a red copper acetylide, which could be collected and then treated with HCl to liberate the acetylene gas (24, 25, 27). In addition to careful characterization of the acetylene gas, Berthelot thoroughly investigated its reactivity via the production of a series of chemical derivatives (25, 27).

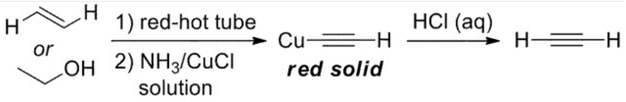

Figure 5. *Berthelot's initial synthesis of acetylene.*

Continuing with these efforts, he then reported in 1862 the production of acetylene via an electric discharge between two carbon rods in the presence of hydrogen (23, 27, 28). As before, the acetylene product was trapped in an ammonia solution of cuprous chloride and the isolated copper acetylide was then treated with HCl to liberate the pure acetylene gas. This now allowed Berthelot to generate large amounts of acetylene, with a reported production rate of 10 mL per min (27, 28).

The following year, Berthelot was entrusted with the lectures on organic chemistry at the Collège de France in addition to his teaching at the Ecole Supérieure de Pharmacie (23). In August of 1864, he then advanced to occupy a new chair of organic chemistry created for him at the Collège. He retained this chair until his death in 1907 (23, 24).

In 1866, Berthelot started a series of studies on the action of heat upon acetylene (18, 19, 24). Upon heating acetylene at extreme temperatures (described as the temperature at which glass softens or melts), Berthelot observed the formation of a mixture of two products which he described as follows (18):

> These consist primarily of two carbides: one volatile and which has the properties and reactions of styrene ... the other almost fixed, resinous, and which appears to be metastyrol.

The term *metastyrol* refers to the product formed by the polymerization of styrene and was thus an early term for polystyrene (29, 30). As such, one could infer that the resinous product here is polymeric material of some form. Analysis of the volatile product, a yellowish liquid, revealed that it consisted primarily of benzene (19).

Berthelot continued this work by heating acetylene in the presence of various species, including elemental carbon or iron. It was found that the presence of these species significantly decreased the temperature required to cause reaction, while simultaneously increasing the overall reaction rate and influencing the nature of the products generated. He ultimately concluded (18):

> In summary, the transformation of acetylene by heat is not comparable to the phenomena of dissociation: it is not the result of a destruction of the affinity that holds together carbon and hydrogen; but it shall be by a very different mechanism, which is not incompatible with the stability of acetylene. What the heat determines here, it's not a decomposition, it is rather a combination of a higher order, developed by the mutual union of several acetylene molecules.

Further studies of acetylene polymerization reactions, however, were not reported until the 1874 work of Paul Thenard (1819-1884) and Arnould Thenard (1843-1905) on the effect of electric discharge on acetylene gas (31).

The Thenards and the Action of Electric Discharge on Acetylene

Arnould Paul Edmond Thenard (32) was born either October 6 (33), December 6 (34), or December 16 (35), 1819 in Paris, the oldest son of the well-known French chemist Louis Jacques Thenard (1777-1857) (33-38). A baron and wealthy landowner (34, 35), Paul was an eminent chemist who submitted his first paper to the Academy of Sciences in 1844 (33-35). Paul married a Miss Derrion-Duplan on October 24, 1842. On January 16, 1847, the uncle of his new wife passed away, leaving her the sole heir to the chateau and land of Talmay, Côte-d'Or. The young couple thus moved to Talmay, where Paul installed a laboratory in the vast commons of the chateau (34). Here, he carried out much of the agricultural chemistry research for which he was known (33-37). The extent of this work resulted in his election to the Paris Academy of Sciences in 1864, where he became one if its most active members (33-36). He was also a member of the French National Society of Agriculture (34).

During the Franco-Prussian War, Paul was taken from his home as a hostage, and transported to Bremen along with several other notables of Côte-d'Or (34-36). His wife followed him (34, 35) and they remained there until the conclusion of peace (35). Paul also served as general counsel for the Côte-d'Or commune of Pontailler until 1871 and was made a Knight of the National Order of the Legion of Honour (35). Paul died as a result of apoplexy at his Talmay chateau on August 8, 1884 (33, 36).

Less is known of the younger Arnould Thenard. He was born in Givry, Saône-et-Loire, to Paul and his wife during the first year of their marriage in 1843 (34). His father initiated him to laboratory life at an early age and he went on to pursue the study of medicine in the service of the French physician and surgeon Auguste Nélaton (1807-1873) (34). After his time with Nélaton, he returned to his father's laboratory to collaborate on various projects. The Franco-Prussian War interrupted his scientific pursuits and he joined the French army to serve as a doctor and liaison through enemy lines (34, 35). After the Battle of Sedan, he moved to Belgium and joined the Armée de la Loire (34). Eventually, he returned to his experimental work, which spanned chemistry, agriculture, and medicine. He was ultimately elected a member of the French National Society of Agriculture (35).

Beginning in 1873, the Thenards began studying the influence of electric discharge on various gaseous mixtures (39, 40). Their initial efforts were supported by the assistance of Edmond Fremy (1814-1894) and Berthelot in order to study discharge tubes containing mixtures of either marsh gas and carbonic acid or carbon monoxide and hydrogen (39). This first report was then followed by a second 1873 paper (40) which expanded the number of gases studied before turning to acetylene in a publication in late January of 1874 (31).

Using a discharge device designed by Arnould, they found that the electric discharge caused a rapid condensation of acetylene (4-5 $cm^3\ min^{-1}$) resulting in a solid deposit on the walls of the unit (31). They described the solid as very hard, with a glassy appearance and a color they compared to the dregs of wine. Analysis of the solid gave a formula consistent with that of acetylene gas (i.e., $(C_2H_2)_n$). No solvent was found that was able to dissolve the material, nor did nitric acid have any effect on the solid. Attempts to separate or purify the material by distillation also failed, resulting in the conclusion that the solid was analogous to bitumen. This view was shared by Berthelot (31).

The work by the Thenards was then quickly followed up with two closely related studies. The first of these studies was by the Belgian P. De Wilde later that same year (41), while the second was three years later by Berthelot himself in 1877 (42).

Additional Discharge Studies of De Wilde and Berthelot

Not much is known about De Wilde (Figure 6), with even his given name being unknown beyond the initial “P” (43). What is known is that he was professor of chemistry at the Agricultural Institute of the State in Gembloux, Belgium (44-47), where he taught general chemistry, analytical chemistry, physics, agricultural technology, and meteorology (46, 47). The Institute had been established in 1860 with G. Michelet as the first professor of chemistry and physics (47). De Wilde replaced Michelet sometime before 1865 (44, 45) and was ultimately replaced by L. Chevron in 1867 (46).


P. DE WILDE

Figure 6. *P. De Wilde (46).*

Beginning in 1865, De Wilde started reporting research on acetylene, with initial efforts focusing on the preparation of acetylene from ethylene chloride or 1,2-dichloroethane (44, 45). He then continued with research into the reactions of acetylene and hydrogen in the presence of platinum black. Although this early work was reported in the Dutch literature, he then published a paper in *Berichte der Deutschen Chemischen Gesellschaft* in which he first presented a summary of his earlier reports, followed by the presentation of new work on the effect of electrical current on various gases and gas mixtures (41). This paper was published in the spring of 1874 and De Wilde began his description of the electrical experiments with a statement that the previous work of the Thenards was the inspiration for his efforts in this area.

De Wilde first studied the effect of electrical current on mixtures of sulfur dioxide and oxygen before moving on to pure samples of ethylene or acetylene (41). In the case of acetylene, he expected to generate benzene and styrene products similar to that found by Berthelot upon heating acetylene at high temperatures, but states that his experiments did not confirm this. Instead, he reported that the current caused the condensation of an oily yellow liquid on the walls of the discharge tube, which solidified after a few hours to produce a hard, amorphous, yet brittle, brown material (41). As with the product of the Thenards, no solvent was found to dissolve the brown material, but De Wilde did find that it burned to leave behind a coal-like residue.

De Wilde’s comment that his efforts did not give the expected products of Berthelot is odd and one can only assume that he was not aware that Berthelot produced a resinous material in addition to the liquid polymerization products. De Wilde stated that he intended to continue studying this interesting solid, but expected the necessary studies to be quite time consuming and thus wanted to report his initial findings (41). De Wilde, however, did not seem to follow up on this initial report.

Berthelot then followed these reports with his own study on the effect of electric discharge on acetylene, three years later in 1877 (42). Repeating the conditions of the Thenards, he verified the accuracy of their report and tried to provide some additional detail. Berthelot described the solid material as a brown polymer with the formula $(C_4H_2)_n$. Heating the material under N_2 caused it to break down exothermically to give styrene, a carbonaceous residue, and other gaseous byproducts. He stated that this reactivity distinguishes it from all other known acetylene polymers (42), but did not directly compare these results to his previous reports of the thermal polymerization of acetylene.

After this flurry of acetylene polymerization studies between 1866 and 1877, no further reports appeared for the next 20 years. This changed in 1898, however, with the report of a new thermal polymerization study by Hugo Erdmann (1862-1910) and Paul Köthner (48).

Erdmann and Polymerization over Copper

Hugo Wilhelm Traugott Erdmann was born in East Prussia on May 8, 1862 (49). Beginning in 1879, he studied chemistry at Halle, Munich and Straßburg under Wilhelm Heintz (1817-1880), Adolf von Baeyer (1835-1917), Emil Fischer (1852-1919), and Rudolf Fittig (1835-1910). He completed his doctorate at Straßburg in 1883 and then habilitated in 1885 under Jacob Volhard (1834-1910) at Halle. He became the director of the Laboratory of Applied Chemistry at Halle in 1899 and was then called to Berlin in 1901 as head of the Laboratory on Inorganic Chemistry of the Institute of Technology. He made significant contributions to both organic and inorganic chemistry, but is best known for coining the term "noble gases." He died in a boating accident on the lake Müritzsee at the relatively young age of 48 (49).

In late 1898, Erdmann and Paul Köthner reported a series of studies involving the heating of acetylene over copper metal (48). They found that although a temperature of 780°C is required to cause the thermal reaction of acetylene, this temperature could be significantly reduced when carried out in the presence of copper. When acetylene was passed over copper powder at 400-500°C, small crystals of graphite were found to form on the copper surface. If the temperature was maintained below 250°C, however, graphite formation was not observed and the production of a light brown solid occurred instead (22, 48). It was found that this material could also be produced in a similar manner, although at a much faster rate, by using copper oxide in place of copper powder.

This light brown material was found to be very light and bulky, with a density of ca. 0.023 g/mL. The material was treated in dilute boiling hydrochloric acid and filtered, after which the colorless filtrate was treated with sodium hydroxide to precipitate yellow copper hydroxide. As such, this led to the conclusion that this material was a copper compound of some form. Combustion analysis then led to the formula of $C_{44}H_{64}Cu_3$ (22, 48). These collected analyses led to the conclusion (48):

> There have been analyses of different preparations, which give such well-matched values that we should not hesitate to address these light brown copper acetylene compounds as a single, albeit very complex composite compound.

This study was then followed by a related conference report in May of the following year by Paul Sabatier (1854-1941) and Jean Senderens (1856-1937) (50).

Sabatier and Cuprene

Paul Sabatier (Figure 7) was born at Carcassonne, France on November 5, 1854 (51-53). He received his primary education at a lyceum in Carcassonne, followed by a move to a lyceum in Toulouse in 1868 (52, 53). He graduated first in his class at the Ecole Normale Supérieure in 1877 (52,53), after which he taught for a year at the Lycée of Nîmes (52). He then became an assistant to Marcellin Berthelot at the Collège de France in 1878 and presented a thesis on the thermochemistry of sulfur and the metallic sulfides in 1880, for which he received the degree of Doctor of Science (51-53).

After a year spent in the Faculty of Sciences at Bordeaux, he took charge of a course in physics at the University of Toulouse in January 1882 (51, 52). A year later, he took charge of an additional course in chemistry before becoming Professor of Chemistry in November 1884 (52, 53). In 1908, Sabatier was invited to fill the position of Henri Moissan (1852-1907) at the Sorbonne, as well as Berthelot's position at the Collége de France, but he declined both to remain in Toulouse (53).

Sabatier was awarded the Lacaze prize of the Academy of Science of Paris in 1897 (51, 52) and was then elected a corresponding member of the Academy in 1901

Figure 7. *Paul Sabatier (1854-1941) (right) with Edgar Fahs Smith [Edgar Fahs Smith Collection, University of Pennsylvania Libraries]*

(52, 53). In 1905, he was awarded the Jecker prize by the Academy (51, 52) and also became Dean of the Faculty of Sciences at the Collége de France (51, 53). For his contributions to the hydrogenation of organic compounds via heterogeneous catalysis, he was awarded the 1912 Nobel Prize in chemistry, which he shared with Victor Grignard (1871-1935) (51-53). The following year, he was made a full member of the Paris Academy of Sciences (52, 53). He then received the Davy Medal from the Royal Society in 1915, to which he was elected as foreign member in 1918 (51, 52). Sabatier finally retired from his professorship in 1930 (52, 53). Although retired, Sabatier had special authorization to continue lecturing, which he did almost to the end (52, 53). He died at Toulouse on August 14, 1941, at the age of 86 years (51-53).

At the May 12, 1899, meeting of the Chemical Society of Paris, Sabatier presented initial results obtained with his collaborator Jean P. Senderens, in which they found that heating acetylene with copper at ca. 180°C produced a yellow-brown material (50). This material, which they described as a complex hydrocarbon, was very light and voluminous with small traces of dispersed copper. This was then followed up with a report published in *Comptes Rendus* the following year (54). Here, they describe the thermal reaction of acetylene with copper in significantly more detail. When a stream of acetylene was passed through a tube containing copper at low temperature, no reaction was observed. When the temperature was raised to 180°C, however, the copper turned brown and the pressure decreased due to condensation of acetylene. As the process continued, the copper would gradually take on a darker hue and the mass swelled to fill the tube, completely closing off the passage of gas. It was found that if a small amount of brown substance was smeared into a fresh tube and heated to 180-250°C in a stream of acetylene, expansion would begin again, with the material swelling once again to fill the entire tube. This process could be repeated three to four times before no additional reaction was observed (54).

The material prepared in this manner was described as a dark yellow solid, which appears to be composed of a thin twisted filament assembly when viewed under a microscope (54). The material was described as soft and lightweight, yet a slight compression can give it the consistency and look of wood. No solvents were found that could dissolve the material, but the material burned to give off an aromatic odor and smoky flame, leaving a black residue of cupric oxide. It was concluded that the material was a hydrocarbon in which small amounts of copper (1.7-3%) were distributed. Multiple analyses led to an empirical formula of C_7H_6. Due to the origin of the material, they proposed to name it *cuprene* (54).

They admitted that they rushed the publication of the study due to a similar report by Hans Alexander (55), which they became aware of after Alexander's paper was highlighted in the *Bulletin de la Soci*été *Chimique de Paris* in late January 1900 (56). However, as their initial Chemical Society of Paris presentation (50) predated Alexander's publication, they maintained their priority of the discovery (54). Of course, it is interesting to note that they do not recognize the very similar previous report by Erdmann and Köthner (48) and it is unknown if they were aware of it or not.

Alexander and Continued Studies of Acetylene over Copper

Little is known about Hans Alexander, other than that he worked in the electrochemical laboratory of the Royal Technical University of Berlin and published a handful of papers over the timespan of 1898-1910. Only one of these papers is pertinent to the current discussion, which he published in August of 1899 (55), three months after Sabatier presented his initial findings on cuprene at the meeting of the Chemical Society of Paris (50). He begins the paper by pointing out its relationship to the previous work of Erdmann and Köthner (48), as well as some related work by Sabatier and Senderens on the hydrogenation of acetylene over nickel. He does not seem to be aware of the report of Sabatier at the Chemical Society.

Using very similar methods to Sabatier and Senderens (54), Alexander passed acetylene through a tube containing evenly distributed copper. At ordinary temperatures, no visible reaction was observed. However, when the acetylene-filled tube was slowly heated, a change was seen at 225°C, in which the copper began to swell, the gas flow slowed, and greenish, strong smelling droplets of hydrocarbons condensed on the colder part of the tube. If the temperature was allowed to reach 260°C, black shiny carbon crystals began to deposit on the walls of the tube. However, if the temperature was held between 240 and 250°C, the reaction proceeded smoothly to fill the whole tube with a light brown mass (55).

The material produced exhibited a non-uniform composition. The material at the entry point of the gas was found to be comprised of lightweight, odorless, dark colored flakes. The material at the other end of the tube, however, contained a strong hydrocarbon smell and a slightly darker color, but the main content of the tube consisted of a uniform, light brown mass. Analysis of the copper content of the material revealed greater copper content in the material located near the entry point of the gas, but that the bulk of the material was found to contain 2% copper (55).

Alexander reports that no solvent was found that could dissolve the material, but that some copper was removed by treating the material with dilute HCl. However, the material could not be made completely copper-free by such treatment, even after boiling the material for several hours. However, it was found that the copper could be completely removed by boiling the material in HCl containing some ferric chloride. The material treated in this way now contained trace amounts of iron, even after boiling with fresh HCl, with a final iron content of 0.2%. This nearly metal-free material looked a little brighter than the original copper-containing material, but otherwise exhibited no measurable difference (55).

As a result of these observations, Alexander disputed the previous claim by Erdmann and Köthner (31) that this material was a copper compound and believed that the copper was only mechanically mixed throughout this material. He ultimately concluded (55):

> In my view, the copper serves only as a contact substance, under the influence of which a polymerization of the acetylene takes place. Here, a small amount of aromatic hydrocarbons form, which distill out, while mainly a very high molecular weight hydrocarbon of cork-like nature arises.

Following Alexander's report, but still before Sabatier's full publication, yet another related study appeared in November of 1899 (57). This study was the first report on the subject from outside Europe, coming from Frank Gooch (1852-1929) and De Forest Baldwin at Yale University in the United States.

Gooch and Further Studies of Acetylene over Copper Oxide

Frank Austin Gooch was born on May 2, 1852, in Watertown, Massachusetts (58, 59). His formal schooling also began there, but he transferred to Mr. Atkinson's school in Cambridge (later known as the Kendall School) when he was 12 (58). He entered Harvard College in 1868, at the age of 16 (58, 59). There, he devoted himself to physics and chemistry, graduating in 1872 (39, 40) with the degree of A. B. *cum laude*, with "*summos in Physicis et Chemia honores*" (58).

Following graduation, Gooch began graduate work at Harvard, studying chemistry, physics, and mineralogy. He became an assistant to Josiah P. Cooke (1827-1894) in his second year (58,5 9), while also serving as assistant in the quantitative analysis laboratory for the 1874-1875 school year (58). His training under Cooke furthered his interest in chemistry, but he was also greatly interested in the physics of crystals, and thus he spend the following year abroad in Straßburg and Vienna studying such subjects (58, 59).

He resumed his studies at Harvard in the autumn of 1876. Having completed work for his A.M. and Ph.D. degrees in early June 1877, he left again to pursue the possibility to work with Julius Thomsen (1826-1909) in Copenhagen. His time abroad, however, was short lived and he returned to Harvard to work with Wolcott Gibbs (1822-1908), which lasted for two years (58). Following this, he held a number of positions performing analytical work with the United States Tenth Census (1879-1881), the North Transcontinental Survey (1881-1884), and the United States Geological Survey (1884-1886) (59). Gooch then moved to New Haven, Connecticut, in 1886, to become Professor of Chemistry in Yale College, where he spent the rest of his career. Although his published work covered a wide range, it focused chiefly in the field of analytical chemistry. He died on August 12, 1929, in New Haven (58).

On November 4th, 1899, Gooch and his coauthor De Forest Baldwin reported (57) a continuation of the previous study by Erdmann and Köthner (48). After a brief summary of the results of Erdmann and Köthner, they pointed out that careful examination of the analysis data revealed an error in the calculations (57). Thus, while Erdmann and Köthner had reported a formula of $C_{44}H_{64}Cu_3$, Gooch and Baldwin stated that the correct carbon to hydrogen ratio should be 6.45:5.70, i.e., less hydrogen than carbon rather than the inverted relationship initially published. They also expressed doubts about the copper percentages, but could not give more correct values without more detailed information (57).

In order to provide more accurate data, the authors then proceeded to perform their own study of acetylene over copper oxide under various conditions in order to determine any effects on the chemical composition of the products. As Erdmann and Köthner had observed faster reaction rates when using copper oxide compared to copper (48), Gooch was especially interested in any possible role of oxygen in the observed reactions. Depending on the conditions, copper content was found to range from 1.54-24.21% and it was found that the use of cuprous or cupric oxide gave nearly identical results.

Similar to observations reported by Sabatier (54), it was found that samples could be further heated with acetylene to restart the reaction, thus giving products with lower percentages of copper. To further study the effect of copper versus copper oxide, one end of a copper coil was oxidized in a flame. The full coil was then subjected to acetylene under heat, resulting in the formation of product only at the oxidized end while the other end simply changed color (57).

These studies revealed that the material produced in all cases was not uniform, with the bulk of the material a spongy mass of light brown color, while that material closer to the original copper source was darker in color. The material of "the brightest color" ("der hellsten Farbe") was found to contain very little copper and no oxygen, while the darkest product contained higher copper and oxygen content, with the oxygen believed to originate in the copper oxide reagent. As such, it was ultimately concluded that the product was not a copper compound and that the copper and/or copper oxide was mechanically entrapped in the hydrocarbon produced. Under the assumption that the product consisted of only carbon and hydrogen, the data was fit to give formulas ranging from $C_{12}H_{10}$ to $C_{16}H_{10}$, with an average empirical formula of $C_{14}H_{10}$ (57). Recalculating the data of Erdmann and Köthner under these same assumptions gave a formula consistent with the low end of this range, which is also consistent with the empirical formula of Sabatier and Senderens.

Not only did Gooch and Baldwin directly connect their work to that of Erdmann and Köthner (48), but they seem to be the first of those discussed so far to also connect these reactions over copper to the previous thermal polymerizations of Berthelot (18, 19). As no mention is made of either Sabatier or Alexander, it is unclear if they were aware of these additional studies. After this second flurry of studies on acetylene-based materials from 1898 to 1900, no further reports appeared until that of Sima Lozanić (1847-1935) in 1907 (60).

Sima Lozanić and a Return to Polymerization via Electric Discharge

Sima M. Lozanić (Losanitsch) was born on February 24, 1847, in Belgrade, Serbia (61). He studied law at Belgrade College, after which he spent four years in Zürich and Berlin. There, he studied chemistry under Johannes Wislicenus (1835-1902) and August Wilhelm von Hofmann (1818-1892). In 1872, he joined the Department of Chemistry at Belgrade College, which became the University of Belgrade in 1905. With the transition from College to University, Lozanić was appointed the chairman of the University Board and later became the first University president (61).

The Serbian Academy of Sciences was founded in 1883 and Lozanić became a corresponding member two years later (61). He became a full member in 1890 and was twice elected the Academy's president (in 1899 and 1903). Lozanić was awarded an honorary doctorate by the University of Belgrade in 1922 and he retired in 1924, although he continued to work until 1929. He died July 7, 1935 in Belgrade, at the age of 88 (61).

In the fall of 1907, Lozanić reported a series of experiments on electrosynthesis in which various gases or gaseous mixtures were subjected to electric discharge (60). These efforts used a discharge device originally designed by Berthelot, although with a couple personal modifications. These modifications allowed him to hermetically enclose the gases in the apparatus, as well as measure the gas pressure during the experiment. Although much of the report details experiments of bimolecular mixtures of acetylene with other species (O_2, CH_4, ethylene, H_2S, CO, and SO_2), he started his study of acetylene with the pure gas (60).

As with previous studies, Lozanić's efforts resulted in the generation of two products, one described as a viscous mass soluble in alcohol or ether, and the other an insoluble, strong smelling solid (60). The greater of these two was the solid product, described as yellow-brown in reflected light and yellow-red in transmitted light. As previously reported by Berthelot (42), both products were found to decompose rapidly at temperatures over 100°C to give carbon. Otherwise, however, the products were found to be very stable, with no reaction observed upon treatment with hot, fuming nitric acid (60).

Lozanić was troubled by the results of analysis of the products, which revealed content beyond carbon and hydrogen (60). He initially assumed that this was due to an impurity in the acetylene used, but carefully purified acetylene gave similar results. He then noticed that the solid material stored in a desiccator gained mass, with this gain saturated after 26 days at ca. 10%. After eliminating nitrogen as a possibility, he concluded that this must be due to oxygen absorption (60).

Although Lozanić appeared to be familiar with the previous reports of Berthelot, he did not mention any of the other previous studies on the effects of electric discharge on acetylene, nor did he connect the products of electric discharge to those produced via thermal polymerization. Although he stated that he planned to follow up the oxygen absorption at a later date, he did not seem to do so and no further reports appeared until that of Daniel Berthelot (1865-1927) three years later in 1910 (62).

Daniel Berthelot and UV Polymerization

Daniel Paul Alfred Berthelot was born on November 8, 1865, in Paris (63). His father was Marcellin Berthelot (63, 64), with whom the whole current account began. The younger Berthelot was educated at the Sorbonne and in the Museum at the Collège de France, his teachers including Paul-Quentin Desains (1817-1885), Henri Becquerel (1852-1908), and Gabriel Lippmann (1845-1921) (64). He was then appointed professor of physics at the École de Pharmacie of the Université de Paris (63, 64).

At the École de Pharmacie and in his laboratory of plant physics at Meudon (64), he became known for his work in physical chemistry, including contributions in pyrometry, the electrolytic nature of acids, and the physical characterization of gases. He was perhaps best known, however, for his contributions in photochemistry (63, 64). For his accomplishments, Berthelot was awarded the Jecker Prize by the Académie des Sciences in 1898 and Hughes Prize in 1906. On February 24, 1919, he was elected a member of the Académie. Berthelot died March 8, 1927, at the age of 62 (63).

In collaboration with Henri Gaudechon, Berthelot reported the photochemical polymerization of acetylene in 1910 (62). Using a quartz mercury vapor lamp (110 volts, 2.5 amps), acetylene gas was irradiated with UV light to generate a yellow solid which was reported to have the characteristic odor of acetylene polymers. No benzene was produced in the process and no other gaseous products were detected. Irradiation of mixtures of acetylene with either hydrogen or nitrogen resulted in more efficient generation of the yellow solid, with H_2 or N_2 appearing to act only as inert buffer gases and no reaction of these gases was observed (62). Finally, mixtures of acetylene and ethylene were irradiated to again give the yellow solid identical in appearance to the previous acetylene polymers, along with a greasy coating stated to be consistent with condensed ethylene.

Unfortunately, no further study of the yellow solid was reported, nor was any connection made to the many previous studies discussed above. Following the independent studies of Lozanić and Daniel Berthelot, there was another sizeable gap in related studies. Efforts ramped up again in the 1920s and 30s, however, beginning with the work of H. P. Kaufmann (1889-1971) in 1918 (65).

Kaufmann and Comparative Studies of Electric Discharge vs. Thermal Polymerization

Hans Paul Kaufmann was born October 20, 1889, in Frankfurt, Germany (66). Starting in 1908, he studied chemistry in Jena, Heidelberg, and Berlin (66, 67), obtaining his Ph.D. under Ludwig Knorr (1859-1921) at Jena in January 1912 (66). He worked as a research assistant at Jena's Chemical Institute from 1911 to 1914, before joining the German army with the outbreak of World War I. After the delay caused by the war, he finally obtained his habilitation on May 17, 1916, while on leave from military duty (66, 67). He was seriously wounded shortly thereafter and was assigned to war-related scientific work following his recuperation (66). He became auβerordentlicher Professor (Professor extraordinarius) and Director of the Analytical Division of Jena's Chemistry Institute in 1919 (66, 67).

After the early death of his mentor Knorr, he moved to Jena's Pharmaceutical Institute (66), where he began teaching in 1922 (66) after finishing the pharmaceutical state examination (67). He then moved to Münster as Professor of Pharmacy in 1931 (66, 67) and remained there until he moved to Berlin as Professor of Pharmaceutical Chemistry in 1943 (66). He returned to Münster in 1946 to become Professor of Pharmacy and Chemical Technology. He became Professor Emeritus in 1958, although he continued as the director of the Pharmacy and Food Chemistry Institute until April 1959. After an extended illness, Kaufmann died October 2, 1971 (66).

Although best known for his work on fats and oils, he did not publish in this area until 1925 and his habilitation thesis was concerned with the polymerization of acetylene (65, 66). His habilitation research, in which he attempted to provide some clarity concerning the composition of the products generated by subjecting acetylene to electric discharge, was then published in 1918 (65). These efforts began with optimizing the reaction conditions in order to produce the products in higher yield, such that a suitable amount of material could be obtained for further study. He found that if the discharge apparatus was suitably cooled, only the liquid product was produced. Alternately, if the apparatus was poorly cooled, the solid product was favored (65, 68).

As found previously by the Thenards (31) and others, the solid product adhered rather firmly to the apparatus walls. Kaufmann, however, found that the addition of ice water caused the product to loosen from the walls as a brown, brittle mass (65). Even better, he found that if the initial oil was subjected to discharge as a heated solution, a fine, light yellow powder was produced, which exhibited all of the properties of the previous solid mass, but was more suitable for further analysis. Kaufmann then proceeded to study the treatment of this product with various reagents (65).

These efforts began with the study of oxygen absorption, originally observed by Berthelot. Kaufmann stated that although Lozanić had previously proposed that the amount of oxygen absorbed should allow calculation of the number of double bonds contained in the product (60), he disagreed as only non-cyclic double bonds would be expected to react with oxygen. He thus stated that this reactivity did not allow one to draw any conclusions about the material at present (65).

He then continued his study by treating the solid product with various reducing and oxidizing agents. Although no reactions were observed with reducing agents, heating the solid material in dilute nitric acid for prolonged periods did result in some nitrated products. Treating the solid with alkaline potassium permanganate was more successful, however, ultimately giving low amounts of benzoic, isophthalic, and terephthalic acids. He thus concluded that much of the structure consisted of unsaturated chains, which generated carbon dioxide upon permanganate oxidation (65).

Kaufmann then followed this with two additional papers in which he compared acetylene polymerization via electric discharge to its catalyzed and non-catalyzed thermal polymerization (68) and studied the copper-catalyzed process in more detail (69). As previously noted by others, he reports that the nature of the catalyst plays a significant role, with copper bronze and copper oxides working much better than pure copper (68, 69). He then went on to show that cuprene could be successfully produced via the use of catalytic cupriferrocyanide ($CuFe(CN)_6^{2-}$) (68), but ultimately concluded that the presence of oxygen in the process was required (69).

As previously shown by Alexander (55), the copper content could not be removed by treatment with HCl. However, he found that several hours of boiling with aqua regia did result in a material with only trace copper content (68). He then went on to analyze these products via reduction or oxidation. As with his previous study of the electric discharge products (65), reduction was unsuccessful. However, treatment of the copper-catalyzed products with 80% HNO_3 gave mellitic acid (benzenehexacarboxylic acid), benzoic acid, and a naphthalene derivative as oxidation products (68). Lastly, he found that cuprene could be brominated via treatment with Br_2 in the presence of iron halides, although he noted that different brominated products formed according to the exact experimental conditions (68).

These collective results led to the conclusion that cuprene is not a uniform substance, and that the term must be understood to mean a mixture of acetylenic condensation products, the composition of which was variable (69). In addition, cuprene must contain benzene units, as well as attached carbon chains that were not completely aliphatic, but yet likely not fully unsaturated either (68). It was thus felt that the unsaturation was primarily included as aromatic units (69). Within a couple years of Kaufmann's work, the Belgian Walter Mund (1892-1956) showed that acetylene could also be polymerized via the application of alpha rays (70).

Mund and Polymerization via Alpha Particles

Walter Emile Marie Mund was born in Antwerp on January 22, 1892 (71). After attending the Jesuit College in his hometown, he enrolled as a candidate in the natural sciences at Leuven (Louvain) in October of 1910. He then received a doctorate in natural sciences on July 24, 1914, with a dissertation entitled "On the Vapor Pressures of Sulfur Dioxide," under the direction of Pierre Bruylants (1885-1950) (71).

Unfortunately, World War I broke out only days after he completed his doctorate, thus interrupting what should have been the start of a promising academic career. In August of 1914, Louvain fell to the German First Army and was the subject of mass destruction shortly thereafter. Mund and his family were evacuated to Manchester, England, where he joined an oil company as a chemist. It is unclear whether Mund left Louvain before or after the German occupation. He left his laboratory in 1916, however, to join the Battle of the Yser first as a mere rifleman, and later a corporal. His bravery and his leadership earned him the Cross of Fire and the Medal of Victory (71).

After the war, Bruylants succeeded to the chair of general chemistry and Mund was called to lead the Physical Chemistry Laboratory at Leuven. For more than thirty years he taught physical chemistry there and distinguished himself by his researches in what would now be described as radiation chemistry, with particular emphasis on the study of chemical reactions that can be triggered by α particles. He published more than 100 papers in the *Bulletin des Sociétés Chimique Belges* and his work was recognized by the government's Decennial Award of Chemistry. He died on August 15, 1956, at the age of 64 (71).

In 1925, Mund and W. Koch began studying the effect of radiation on various hydrocarbon gases, including methane, ethane, ethylene, and acetylene (70). Using radium, they treated a 40 cm^3 bulb of acetylene with 58 millicuries of emanation and monitored the reaction for 8 days. Within the first day, a dense fog filled the bulb with a fine yellow-brown powder depositing on the walls. Collecting the greater part of this yellow powder, they found it to be odorless, light as pollen, and with no obvious crystalline structure when examined under a microscope. In addition, the powder exhibited low solubility and no trace of fusion in sulfuric acid up to 300°C. Ultimately, it was determined that the product was a hydrocarbon with a formula that approximates that of acetylene (70) and proposed that it was identical to the material previously reported by Alexander (55).

Later that same year, they studied the effect of α particles on acetylene in more detail, this time using radon as the source (72). It was determined that each α particle caused the condensation of 4.38×10^6 molecules of acetylene, but it was admitted that not all molecules may have undergone polymerization and some molecules could have been absorbed by the resulting product. In terms of mechanism or structure, they admitted that it was not easy to establish either, but they were convinced that the material was identical to cuprene (72).

The following year, these studies were continued with a focus on the effect of oxygen, pressure, and temperature (73). However, it was determined that none of these variables had any effect on the previously determined values. Mund returned to the study of acetylene with two later papers in the 1930s (74, 75), but by then the primary study of acetylene polymerization had been continued by Samuel Lind (1879-1965) (76).

Lind and the Continued Study of Acetylene Polymerization under Various Conditions

Samuel Lind was born in McMinnville, Tennessee, on June 15, 1879 (77). He was educated in the public schools there, before enrolling at Washington and Lee University in 1895. He spent most of his first three years studying French, Latin, Greek, German, and Anglo-Saxon. Entering his senior year, he still needed six credits in science, and was persuaded to take chemistry. Although he had little previous chemistry knowledge, he became captivated by the subject due to the influence of Jas Lewis Howe, who taught all the chemistry courses. Receiving his B.A. in 1899, Lind returned to Washington and Lee for additional chemistry courses, as well as courses in geology and mineralogy (77).

In the fall of 1902, he entered the Massachusetts Institute of Technology (MIT). Although MIT did not give graduate degrees at the time, he carried out research under the direction of Arthur Amos Noyes (1866-1936). Awarded a Dalton traveling fellowship in 1903, he decided to go to the Institut für Physikalische Chemie in Leipzig, where he began research under Max Bodenstein (1871-1942) on the kinetics of the reaction between H_2 and Br_2. After Lind received his Ph.D. in August 1905, Bodenstein offered him an assistantship, but he decided to return to the United States where he accepted a teaching position at the University of Michigan (77).

In 1910, he spent time in the Paris laboratories of Marie Curie (1867-1934), where he gained proficiency in the handling of radioactive species. He then moved to the newly formed Institut für Radiumforschung in Vienna in 1911 to study the action of alpha particles on oxygen molecules. Such study of chemical reactions induced by ionizing radiation was then to be his main field of research for the remainder of his career (77).

Lind accepted an appointment with the U.S. Bureau of Mines in 1913, where he worked on the extraction of radium from carnotite. He remained there until 1925, when he became assistant director of the Fixed Nitrogen Research Laboratory of the U.S. Department of Agriculture. He did not stay long, however, and became the head of the University of Minnesota's School of Chemistry in 1926, where he remained until his retirement in 1947. He became a consultant to the Union Carbide Corporation in 1948 and then served as acting director of Oak Ridge National Laboratory's chemistry division for several years. He died on February 12, 1965, while fishing below Norris Dam in Tennessee (77).

Lind began studying the effect of ionizing radiation on ethane in 1924, before extending this to additional organic gases the following year (76). In his late 1925 paper, Lind confirmed the previous report of Mund and Koch (70) as well as expanding the study to additional gases. The following year, Lind focused these studies on the more complex unsaturated gases acetylene, cyanogen, HCN, and ethylene (78). Here, he again confirmed that the treatment of acetylene with α radiation resulted in a light yellow powder, which he stated was similar to cuprene via copper-catalyzed reactions or related materials produced via UV light or electric discharge (78). For the most part, his acetylene results were very similar to that of Mund and Koch (70).

To compare the polymerization of acetylene via α particles to that of UV light, Lind then carried out detailed studies of the parameters of UV-induced polymerization in a 1930 communication (79). He found that wavelengths shorter than 253.7 nm were required to induce polymerization, most likely due to the transparency of acetylene at longer wavelengths. After studying the rate under various conditions, he proposed that the polymerization rate was proportional to the intensity of absorbed light but is otherwise independent of the acetylene pressure. Lastly, he determined a quantum yield of 7.4 ± 2.5 for the photo-induced reaction (79). He then followed this with a full paper in 1932 (80), which provided more details, but came to all of the same conclusions. This second report did provide a more accurate determination of the quantum yield, however, with a value of 9.2 ± 1.5.

Lind returned to the photochemical polymerization one last time in 1934 (81), primarily to further refine the quantum yield to account for the additional generation of ethylene and ethane as byproducts. Thus, the total quantum yield for all photochemical processes was estimated to be 9.7. More importantly, however, he also proposed the following radical mechanism for the reaction:

$$C_2H_2 + h\nu \rightarrow C_2H_2{}^* \rightarrow {}^{\cdot}C_2H + {}^{\cdot}H$$

$${}^{\cdot}C_2H + C_2H_2 \rightarrow {}^{\cdot}C_4H_3$$

$${}^{\cdot}C_4H_3 + C_2H_2 \rightarrow {}^{\cdot}C_6H_5 \text{ (etc.)}$$

$${}^{\cdot}C_nH_{n-1} + {}^{\cdot}C_mH_{m-1} \rightarrow \text{solid}$$

Lind also attempted to study the polymerization of acetylene by electric discharge in 1931, with emphasis on the reaction rate and potential insight into the reaction mechanism (82). However, no firm conclusions could be made and it was determined that further analytical data were required. Lind's final paper on acetylene polymers was a 1937 study of the oxygen-induced oxidation of cuprene samples generated via α radiation (83).

What Exactly Is Cuprene?

By the early 1920s, it was clear that cuprene was not a copper-based species. As noted by Kaufmann, however, the name cuprene was to be retained even though it had been shown to be a hydrocarbon (68). In addition, it was now being recognized that all of the various polymerization methods described above were producing either the same or nearly the same material, with an empirical formula very close to that of acetylene (42, 54, 57). Still, the structure of this material was unknown.

Following the mechanism proposed by Lind (81), the product should essentially be what we now recognize as polyacetylene, $(HC{=}CH)_n$. In fact, this was believed to be the structure at some point, with even such polymer luminaries as Paul Flory (1910-1985) reporting its structure as such (84). However, such a structure is not consistent with the results of Kaufmann (65, 68, 69), nor was the color of cuprene consistent with polyenes longer than 4-9 repeat units (13, 17). Yet, Lind believed cuprene to exist in repeat lengths of ca. 20 (81). Of course, the report of substantiated polyacetylene by Natta in 1958 (11, 12) then finally confirmed that this was most certainly not the structure of cuprene.

A solution was then proposed in 1964, with a report that polyacetylene could be converted to a cuprene-like material by heating under O_2 at temperatures above 200°C (85). Thus it was proposed that cuprene is formed via the initial polymerization of acetylene into linear polyenes, which were then converted to the final product by the action of residual O_2. This was then further reinforced by an additional 1971 report (86) that supported a mechanism in which acetylene underwent primary polymerization to give linear polyenes, followed by a rapid secondary polymerization of these polyenes, and ultimately condensation and crosslinking to lead to the final intractable solid cuprene. A simplified representation of this process is illustrated in Figure 8. However, it should be stressed that cuprene's intractability, coupled with its potential structural complexity, has made a detailed determination of this structure difficult. As such, there is still much that is unknown about both its true structure and the full mechanistic details of its formation.

A product resulting from the currently accepted mechanism given above would then consist of both saturated and unsaturated sections, with the unsaturated sections consisting of relatively low conjugation length to give the material its yellow color. This species could then be viewed as a heavily crosslinked polyacetylene. However, as the crosslinking removes points of unsaturation, this perhaps more closely resembles a crosslinked polyethylene with some added points of unsaturation. This latter view is of some historical interest as crosslinked polyethylene was not reported until 1953 (87).

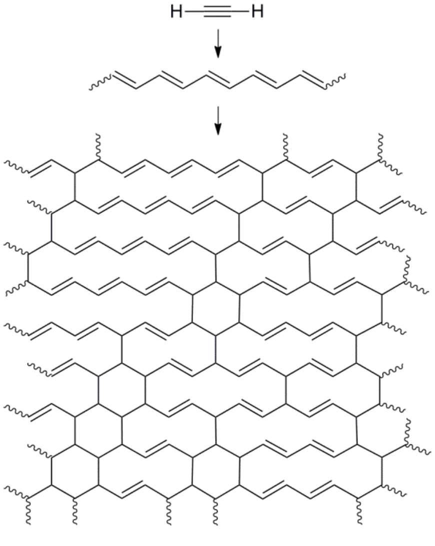

Figure 8. *Simplified representation of the proposed formation of cuprene.*

Conclusion

The polymerization of acetylene to generate a light yellow, intractable material that later came to be known as cuprene dates back to 1866. Following the initial non-catalyzed thermal polymerization in 1866, it was shown that this material could be generated from acetylene by electric discharge, copper-catalyzed thermal polymerization, UV photopolymerization, and ionizing radiation (α particles) from radium or radon. These polymerization studies consisted of a large number of reports over the time span of 1866-1937, after which the number and frequency of papers rapidly declined. To date, however, the detailed history of cuprene has been limited due to the disconnected nature of many of the studies of this material. At least some of this was due to the fact that prior to the work of Kaufmann in the 1920s, it was not generally recognized that these various methods were generating the same material. As a result, this produced multiple intertwined historic paths rather than a single linear narrative.

The initial interest in this material was largely due to the fact that acetylene was one of the more reactive gases known at the time and one of the only such gases that could generate a solid material other than simple carbon, which was quite remarkable in the formative period before the introduction of the modern macromolecule. The unknown nature of this solid product then continued to generate interest from continuing generations of researchers who attempted to reveal its ultimate nature. Although cuprene never developed into a commercially useful polymer, it is clearly a well-studied, early example of a synthetic polymeric material that deserves to be included in the history of polymer science along with contemporary synthetic materials such as polystyrene and polyethylene.

Acknowledgements

I would like to thank Vera V. Mainz (University of Illinois) and Elsa B. Atson (Chemical Heritage Foundation) for assistance with tracking down sources on Paul and Arnould Thenard, as well as my brother, Kent A. Rasmussen, for continued assistance with translations. Lastly, 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.

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COMMENTARY

Moving Past a Seminal Generation in the History of Chemistry: A Moment to Reflect

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The recent deaths of John D. Roberts (June 8, 1918-October 29, 2016), Jerome A. Berson (May 10, 1924-January 13, 2017), and George Olah (May 22, 1927-March 8, 2017) took my breath away. They were all of a venerable age—Jack was mighty close to 100, Jerry was 92, George was almost 90—and they had lived long, successful, well-appreciated, and honored lives. But they were also my friends and my heroes, and I miss them.

Jerry was still enjoying life when he died. Shortly before his death, he wrote to me:

> Considering my age, I am not in bad shape. I go to the gym 3 times a week and it does me good. My piano studies have developed into a fierce contest between me and Chopin. He is winning, but it's fun.

For Jerry—for anyone—that's an excellent way to go.

The deaths of these giants call to mind the many giants from what is often called the Golden Age of Chemistry. There are too many to name here, but we especially salute those whose lives were cut far too short: Saul Winstein at just 57, R. B. Woodward at 62, and especially Rosalind Franklin at 37.

Thankfully, numerous others, like Berson, Roberts and Olah, lived long and full lives. Paul Bartlett and Georg Wittig, 90; Carl Djerassi, Gene Garfield, Vladimir Prelog and Günther Wilke, 91; H. C. Brown, 92; William Doering, Carl "Speed" Marvel, Tetsuo Nozoe, and Linus Pauling, 93; Frank Westheimer, 95; Sir John Cornforth and Herman Mark, 96; Helmut Zahn, 100; and Wilson Baker, 102, to name a few.

Many more of their generation, happily, are still living, and several are still publishing. E. J. Corey, now 88, published four state-of-the-art papers in the *Journal of the American Chemical Society* and two in *Organic Letters* in 2016. Albert Eschenmoser, now 91, published seven papers on corrin syntheses leading to the total synthesis of vitamin B_{12} in 2015. These papers spanned almost 600 pages in one issue of *Helvetica Chimica Acta.*

Also still with us in their late 80s and 90s are synthetic chemists (Alan Battersby, Teruaki Mukaiyama, Gilbert Stork, E. C. Taylor, Zen'ichi Yoshida), natural products chemists (Duilio Arigoni, Madeleine Joullié, Jerry Meinwald, Koji Nakanishi,), and physical organic chemists (Norman "Lou" Allinger, Ned Arnett, Marjorie Caserio, Rolf Huisgen, Andy Streitwieser, Ken Wiberg).

Because I am an organic chemist by education and research experience, my examples are primarily from organic chemistry. But clearly chemists from the other subdisciplines who still live should be cited—crystallographer Jack Dunitz, 93; inorganic chemist John Goodenough, 95; and physical chemist Sir John Rowlinson, 91, among others. And "Queen of Carbon Science" Mildred Dresselhaus who just died at 86.

Let us pause to reflect on the wonderful achievements of these and many other icons of chemistry and on the times in which they, and we, have lived.

I ask: Is there something fundamentally special about THIS generation of chemists that distinguishes them from the greatest chemists of earlier generations? I believe so. There certainly is a natural tendency for each of us to look upon the leading figures of our own era, when we "came of age" in chemistry, and conclude that this was truly THE Golden Age of Chemistry. But our giants—and there surely were a large number of them—appeared larger than life. They lived and worked through a major explosion in chemical knowledge and a concomitant expansion in the entire academic and commercial chemical enterprises. The reach of chemistry in our lives also has expanded along with scientific prestige. Indeed, their research had much to do with unprecedented advances in chemistry.

Consider how far we—they—have come in the last 50 years. These pioneers began their careers in near technological darkness and yet uncovered many wonders of our science. Most of them began their research lives before routine NMR, gas chromatography, or mass spectrometry. Certainly they had no HPLC or FT-NMR. Their early days were those of mimeograph machines, typewriters, and plastic molecular models—unless one could afford to own or could borrow Dreiding models. There was no ChemDraw; there were only India ink and Fieser chemist's triangles, stencils and rub-off letters and chemical symbols. Thin-layer chromatography was just becoming routine.

It may be easy to take our heroes for granted, an example of Robert K. Merton's concept of Obliteration by Incorporation. Our heroes are so well known to us that we tend to consider their existence, their names and their legacies as common knowledge. Sadly, many of our youngest contemporaries know little of their own profession's history, let alone the accomplishments of their chemical ancestors. Many chemists have little idea about how we got to where we are today. It's like being partially colorblind or deaf to half of the audio spectrum. I posit, and I am surely not the first, that a scientist's professional experience will be enriched mentally and tangibly with an appreciation of the history of their field. A knowledge of one's own professional underpinnings can have leveraged effects. I ask: What can we, as chemist-historians, do for our discipline, for the communities in which we live and work, and for our colleagues?

We and the chemical enterprise stand on the shoulders of these giants. We should be proud of our history. Our pride stems from roots in a history that is vast, wonderful, and deep—extending beyond Mendeleev, Lavoisier, and Boyle; beyond medieval alchemy; all the way back to man's ancient history.

Those of us who are chemist-historians can take proactive steps to revitalize the pride chemists have in their profession, to bring history of chemistry back into the educational agenda, and to encourage interdisciplinary interactions involving the history of chemistry.

We can bridge the gap by incorporating history into our professional activities. When we teach, prepare grant proposals, or write research results, it would be germane to provide a concise but relevant discussion of the historical roots of our subject. We can insert a paragraph or two on the relevant history of chemistry into our lectures and our writings. We can also make it known to our colleagues that we can provide a history of chemistry "insert" into one of their classes. The Chemical Heritage Foundation, with help from the Division of History of Chemistry of the ACS and historians of chemistry, can provide pedagogical resources that are easy for educators and researchers to access and use. We can invite colleagues to participate in the Division of History of Chemistry's programming (or other history of chemistry groups), even to write an article for the *Bulletin for the History of Chemistry* or for the *Journal of Chemical Education.* We can visit the Chemical Heritage Foundation in Philadelphia and participate in some of its activities.

We can also do something very personal. For those of us fortunate to have teachers and mentors who are still alive, the time to connect with them is now, while they are still around. A call, a postcard, a letter, or a visit would bring them great pleasure. You may be surprised by the joy and enrichment—intellectual and emotional—such a gesture also would bring to you. Because after all, learning begins with human connection, which is the underpinning of our profession.

About the Author

Jeffrey I. Seeman was Chair of HIST in 2005-2006. He served on the Board of Directors of the Chemical Heritage Foundation from 2008-2014 and was Chair of CHF's Heritage Council during the same six years. He is currently on the advisory board of the journal *Accountability in Research*.

BOOK REVIEW

The Chemists' War, 1914-1918, Michael Freemantle, Royal Society of Chemistry, London, 2015, 342+xvi pp, ISBN 987-1-84973-989-4, $45.88.

In September 2013, the Government of Syria launched a chlorine gas attack on its own population, killing 1429, including 426 children. Since then, the humanitarian tragedy in the Middle East has reached epic proportions. Almost three hundred thousand have died, and the conflict looks likely to worsen. Reports come in of the use of a variety of chemical weapons. For over three years, the United States has led in helping dispose of Syria's declared CW stockpile, 1300 metric tons, and dismantling its 23 CW production facilities, and has overseen the neutralization of 600 metric tons of sarin, VX, and mustard gas. We have reports that as of October 2015, about 90% of the world's declared stockpile of chemical weapons had been destroyed. But the world remains unsure about the future use of what the US Senate Armed Services Committee has called "the world's worst weapons," and the April 2017 attack in Syria has demonstrated that stocks remain in active use.

What has become, we may ask, of modern society, of the legacy of the Geneva Protocol of 1925 and its successor, the Chemical Weapons Convention, to which 190 states—including Syria—have given their assent? More generally, what has happened to the international prohibition of chemical weapons, the odium that surrounds their use, and the norms that this has inspired?

These norms were born from the use of chemical weapons in the Great War and the appalling legacy left to generations on both sides.

This is the legacy that formed the subject of Michael Freemantle's earlier book, *Gas! Gas! Quick Boys!: How Chemistry Changed the First World Wa*r (Spellmount: The History Press, 2012)—his title drawn from Wilfred Owen's famous poem, and his subtitle perceptively suggesting "How Chemistry Changed the First World War." The present book returns to the subject, and re-captures the Great War in popular memory as "the chemists' war"—a sobriquet attributed to Richard Pilger, Registrar of the Institute of Chemistry in London.

Whilst historians now share chemistry's infamous fame with all the other sciences that contributed to the war effort, it is clear that chemical weapons, even more than the damaging effects of aerial bombardments, artillery barrages, submarine attacks, and the ravages of hunger and disease, have left an indelible impression on modern memory. In its narration, science lost its moral status, and was reduced to such memories that such author-soldiers as Siegfried Sassoon and Wilfred Owen could parse and summon. But with Freemantle's earlier book, this book is not only about chemical warfare, but also about the war of applied chemistry and chemical industry. Behind the Front lay the mobilization of a vast international chemical industry, prominent in Germany, but soon dramatically impressive across France and Britain as well, and with everlasting consequences for the United States.

In twenty chapters, Freemantle builds upon his earlier work, and familiarizes the reader with the making of shells and explosives, and with the leading men and women chemists who shaped this aspect of modern warfare. In so doing, he does not fail to do justice to the increasing uses of chemistry in caring for the starving, sick and wounded, in fighting infection, and in killing pain. As such, the Great War (as other wars before and since) graphically stimulated the "dual uses" of science—a phenomenon well illustrated by a Gordon Cain Symposium held at the CHF in 2008, and attended by representatives of the State Department and policy studies institutes in the US and the UK.

As Freemantle writes, America's principal contribution to the *materia chemica* of gas warfare was chlorovinyldichloroarisine, better known as Lewisite, and subsequently dubbed by the US Chemical Warfare Service "the dew of Death." But, as always, there was another side. The "double-edged sword," with which Freemantle ends his story, sees chemistry in wartime use in protecting health and preventing disease. We know that chlorine, released to purify drinking water and sterilize swimming pools, has found appalling applications in barrel bombs. But we cannot mistake the value of life-saving antiseptics and disinfectants.

Like Freemantle's earlier book, this is a highly professional account—like many, especially in Britain and Australia, deriving from family experience of the War. His professionalism as a science writer (of journalism and textbooks) shines through his prose as he explains—in approachable, layman's terms—the basic ingredients of wartime gas chemistry. Inevitably, the story focuses on organic chemistry, and on features that are—like the manufacture of acetone— comparatively well known. Readers will also recognize at least some of the many "fractured friendships," in Freemantle's phrase, which first soured, then destroyed long-standing relationships between British and American chemists and their German teachers and colleagues. At the end, whether by accident or design, the book ends poignantly with two chapters, one commemorating the sacrifice of the fifty-five British chemists memorialized in marble at the Royal Chemical Society in London; and the other, listing the leading "Fifty Chemicals of the Great War" that many of them helped produce.

Perhaps the book's most original contribution lies in drawing attention to the "metals of war," such as nickel, tin, tungsten, chromium, manganese, and zinc. In the emerging materials science of industrial war, such metals took a "starring role" on the battlefield—as did aluminum in the making of Zeppelins, and phosphorus in making the Pomeroy bullets that brought them down. The celebrated use of platinum as a catalyst—key to making sulfuric acid, thence nitric acid, ammonium nitrate, and high explosive—joins a story ennobled by the applications of silver, essential to photography, and of calcium and tungsten in medical X-rays. And so the chemical catalogue continues, through the history of the tank—made of iron, copper, nickel and zinc—with pistons of aluminum, machine guns housed in phosphor-bronze mountings, and shell cases packed with amatol. The lesson is clear—warfare had become a case of chemistry and industry compounded.

Like its predecessor, *The Chemist's War* is a good introduction to the subject in its widest dimensions. Just a few shortcomings might be mentioned. First, surprisingly little attention is given to the vast chemical-industrial corporations that contributed to the war, whether in Germany, Britain, France, or America. Just as the Great War was the making of modern chemistry, so did modern chemical industry emerge in its wake. Second, the structure of the book tends to recall a sequence of articles rather than an unfolding narrative. Some chronologies are reversed, and some topics are duplicated. But readers can easily take such matters into account. Both these books are well worth including in any working library on "The Chemists' War."

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The BULLETIN FOR THE HISTORY OF CHEMISTRY (ISSN 1053-4385) is published biannually by the History of Chemistry Division of the American Chemical Society. All matters relating to manuscripts, book reviews, and letters should be sent to Dr. Carmen J. Giunta, Editor. Subscription changes, changes of address, and claims for missing issues, as well as new memberships, are handled by the Sec./Treas.

BULLETIN FOR THE HISTORY OF CHEMISTRY
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