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THE 1999 DEXTER AWARD ADDRESS

A PLACE IN HISTORY: WAS LINUS PAULING A REVOLUTIONARY CHEMIST?

Mary Jo Nye, Oregon State University

In 1998 the American Chemical Society published the 75th anniversary issue of Chemical and Engineering News (1). In preparation for the anniversary issue, the journal provided the opportunity for approximately 175,000 ACS members to nominate their choices for the "Top 75 Distinguished Contributors to the Chemical Enterprise" since 1923, using a ballot published in the magazine. Readers could nominate up to twenty people, living or dead, American or non-American.

The result was a list of more than 1,200 individuals, giving a top-75 group in which four chemists far outpolled the next 71. The top four were Linus Pauling, Robert B. Woodward, Glenn Seaborg, and Wallace Carothers (2). The contributions for which Linus Pauling was cited in the poll were the nature of the chemical bond; valence bond theory; concepts of electronegativity, resonance and hybridization; and the application of structural chemistry to biological molecules (3).

A different kind of poll was taken by the British journals New Scientist and New Society some twenty years earlier, using a questionnaire published in May 1975. That poll sought to assess readers' images and stereotypes of scientists by asking open-ended questions such as, "When I think of a scientist, I think of ... " The poll received approximately 1600 responses, of which 119 came from professional chemists. Of the scientists, past and present, who were most frequently mentioned in readers' responses, Pauling's name was the fifteenth most cited. Others included Darwin and Einstein, Galileo, Newton and Pasteur, and, among contemporary scientists, Jacob Bronowski, Fred Hoyle, and Peter Medawar (4).

In the New Scientist poll, professional and popular-science readers seem to have mentioned Pauling, like Bronowski and Medawar, on the basis of public image and public fame in the 1970s, whereas the Chem. Eng. News poll more clearly reflects judgments by Pauling's professional peers in the field of chemistry. Both polls point to a generalization that we hardly need to prove: that Linus Pauling is perceived both among chemists and among members of the general public as one of the most important figures in twentieth-century science.
Yet, we may ask, was Linus Pauling what may be called a revolutionary figure in the history of chemistry, and in the history of science more generally? Is his role in twentieth century science comparable to Galileo in the seventeenth century or Lavoisier in the eighteenth century or Pasteur in the nineteenth century? What makes a revolutionary reputation in science and who defines it: scientists, historians, or the wider public? The actors or the observers?

By way of addressing these questions, I will begin by describing some recent interpretations of the eighteenth-century Chemical Revolution and its embodiment in the historical figure of Antoine Lavoisier. I then will turn to a discussion of the aims and achievements of Linus Pauling, beginning with his earliest plans and ambitions in the 1920s. I shall conclude by re-opening the question of Pauling’s place in history, as defined by scientists, historians, and the public.

Revolutions, Revolutionaries, and Lavoisier

In Bernard Cohen's book Revolution in Science, Professor Cohen traces the changing meaning of the word “revolution,” from the sense of “turn” or “return,” as in “turn of the wheel” or “turn of Fortune,” to the implication of a historical break and transformation. In the political realm, eighteenth century writers used the new meaning of “revolution” in reinterpreting England’s rebellion or civil war of 1688 as a “Glorious Revolution,” and eighteenth-century Frenchmen soon applied the word “revolution” to political events of the 1790s in France (5).

In the realm of the sciences, Bernard Le Bovier de Fontenelle wrote in the early 1700s of the recent revolution in mathematics and mechanics associated with the name of Isaac Newton (6). More to our immediate concern, Antoine Baumé wrote in 1773 of a revolution in chemistry which had begun with the discovery of fixed air (7). That same year of Baumé’s printed remark, Antoine Lavoisier wrote privately in a laboratory notebook that his work on the fixation and release of airs seemed “destined to bring about a revolution in physics and in chemistry (8).” At that moment, as Larry Holmes has stressed, Lavoisier likely thought of himself as participating in a revolutionary movement begun by others, not of himself as initiating a revolution. We have evidence of Lavoisier’s view in a letter of 1774 that he sent to the Royal Society of Edinburgh, along with a gift of his Opuscules physiques et chymiques. In the letter, Lavoisier lauded the “illustrious savant” Joseph Black for Black’s theory of fixed air “that seems to prepare a revolution in physics and chemistry (9).”

The next generations of chemists after Lavoisier certainly thought of him as a founding father of a new chemistry. but the idea received a new twist from the French Alsatian chemist Adolphe Wurtz in 1869, on the eve of the Franco-Prussian War. In what became an understandably controversial statement, Wurtz wrote that “Chemistry is a French science. It was founded by Lavoisier, of immortal memory . . . . he was at once the author of a new theory and the creator of the true method in chemistry (10).”

As France’s Third Republic was established in the mid-1870s, Lavoisier was reclaimed by French scientists and politicians as a symbol explicitly of the modern, moderate, and scientific French Republic. Lavoisier had been a member of the liberal wing of civil servants and political activists in the ancien régime. Lavoisier had been a reformist member of Louis XVI’s tax-collecting agency, the Ferme Générale. He had been an innovative administrator in charge of the nation’s gunpowder Arsenal. He had been an alternate deputy to the States General when it convened in 1789 (11). Yet, as a former member of the Ferme Générale and a prominent member of the academic elite, Lavoisier had been personally disliked and under suspicion by some members of the Revolutionary Committee. Arrested in 1793, he was executed in 1794. Letters removed from his home included an unsigned letter to Mme. Lavoisier with the prescient and damning words, if evidence were needed of disloyalty: “This most beautiful revolution will make our streams run with blood and plunge us into total anarchy (12).”

By fortuitous coincidence, the 1889 centenary commemoration of the French Revolution was also the centenary of the publication of Lavoisier’s textbook, the Elements of Chemistry. Edouard Grimaux, a chemist at the Ecole Polytechnique, published a biography of Lavoisier (13), as did Marcellin Berthelot, chemist at the Collège de France and member of the French Senate. It was Berthelot who applied the phrase “chemical revolution” to Lavoisier’s achievements alone, attributing to one heroic figure what often had been described as a collective transformation of ideas (14).

By the end of the nineteenth century, then, Lavoisier’s image had become firmly an image of scientific hero and political martyr. The latter image only enhanced the former one. The iconography of Lavoisier’s memory clearly demonstrates this double image (15).
It includes sketches of Lavoisier in the laboratory and a magnificent portrait by Jacques-Louis David of Lavoisier and Mme. Lavoisier. There is also a contemporaneous sketch made of Lavoisier while in prison and a newer dramatic painting of 1876 by L. Langenmantel commemorating "The Arrest of Lavoisier (16)."

Further, the integration of the scientific and the political revolutions is absolutely faithful to the historical record, as registered in the well-known letter from Lavoisier to Benjamin Franklin in February of 1790. A "revolution... has taken place in... human knowledge since your departure from Europe," Lavoisier wrote to Franklin, describing opposing camps of phlogistonists and anti-phlogistonists, but "having brought you up to date on what is going on in chemistry, it would be well to speak to you about our political revolution (17)."

**Linus Pauling and the Remaking of Modern Chemistry**

I will return to Lavoisier and the eighteenth-century chemical revolution, but let me turn now to Linus Pauling, the son of a pharmacist, born in Portland, Oregon in 1901. In January 1917 he entered Oregon Agricultural College, where he quickly attracted the attention of his college instructors, who enlisted him to teach freshman- and sophomore-level chemistry courses while he was still a student (18).

While preparing his chemistry lectures in 1920, Pauling ran across Irving Langmuir’s papers of 1919 on the structure of atoms and the new electron theory of valence (19). Langmuir’s publications led Pauling back to the 1916 paper of G. N. Lewis, whose work and person he admired for the rest of his life (20). From then on, Pauling rarely had the chemical bond far from his mind. Nor did he relinquish the fascination with molecular form and structure that first engaged him in a course on the crystallography of metals with Samuel Graf. This focus on structure and on the chemical bond became permanent leitmotifs for Pauling’s chemical career.

During the summer of 1922 before entering graduate school at the California Institute of Technology, Pauling worked for the Oregon Highway Department near Astoria. By this time, he had proposed marriage to Ava Helen Miller, a student in his chemistry class of the previous spring. Pauling’s summer letters to Ava Helen give insights into the aims and ambitions of the young chemical engineering graduate. Not surprisingly, he was "anxious to get to California in order to find how long it will take me to get my Ph.D. and to see how well I’ll get along with really good men in the realm of science.” Indeed, he wondered whether he might be a "second A.A. Noyes (21)." (Noyes was director of Caltech’s chemistry division.) At summer’s end, Pauling wrote Ava Helen of his desire to live up to his ambitions and her expectations. He wrote that he aspired to the Nobel Prize, "something which connotes a lifetime of unselfish effort, as does the Perkin’s [sic] Medal (22).” In later years, a very elderly Pauling penned a note drawing attention to his youthful reference to the Nobel Prize. The Perkin Medal, in fact, eluded him (23).

After he arrived at Caltech in the fall of 1922, Pauling’s coursework included thermodynamic chemistry with Noyes; statistical mechanics and atomic structure with Richard Chace Tolman; kinetic theory with Robert Millikan; advanced dynamics with Arnold
Sommerfeld’s student Paul Epstein; and statistical mechanics and quantum theory with the visiting Austrian theoretical physicist Paul Ehrenfest (24).

Pauling wrote Ava Helen of his ambition to “lead my classes, except radiation” where he intended merely “to get along.” He was ecstatic following his first meeting with the Physics and Astronomy Club in October 1922. He wrote his fiancée that the clubroom had held a collection of physicists who are “the best in the country.” Even though he was a new graduate student, fresh from Corvallis, Pauling bragged to Ava Helen that he “argued a moment with Tolman and thus felt puffed up (25).” Ambitious and conscious of his ambition, Pauling moved ahead in his studies.

Pauling’s first paper with Roscoe Dickinson appeared in 1923, on the structure of the mineral molybdenite (MoS$_2$). In the next three years, Pauling authored or co-authored a dozen crystal-structure publications (26). His 1926 application for a Guggenheim Foundation Fellowship focused on something different, however. Pauling aimed to take up Professor Sommerfeld’s challenge for (27):

working out a complete topology of the interior of the atom and, beyond this, a system of mathematical chemistry, that is, one which will tell us the exact position of the electrons in the atomic envelope and how this qualifies the atom to form molecules and to enter into chemical compounds.

He wanted to take part in a new reductionist and mathematical program for chemistry.

Returning in late 1927 from eighteen months in Munich, Copenhagen, and Zurich, Pauling became an assistant professor in theoretical chemistry. He published an explanation in Chemical Reviews of Walter Heitler and Fritz London’s application of quantum mechanics to the hydrogen molecule, as well as treatments of the hydrogen molecular ion by Oyvind Burrau and Friedrich Hund (28). By 1928 Pauling had begun to sketch out his own novel ideas for theoretical treatment of the chemical bonds for methane. The notion was to do away with the distinction between 2$s$ and 2$p$ energy sublevels for the four shared electron-pair bonds in methane, in order to get the identical tetrahedral valences of the carbon atom (29).

Pauling lectured at Berkeley and Caltech during 1929 to 1934, developing for students and faculty the notion of “changed quantization” of electron energy levels in the carbon atom and setting up wave functions to represent classical valence, or electron-pair bonds, in compounds like carbon dioxide, benzene, and methane. He also began writing a series of papers on “The Chemical Bond,” published during 1931 to 1933, some of the papers being co-authored with Albert Sherman and George Wheland (30).

Pauling and his collaborators at Caltech were by no means the only ones working along these lines. Harvard University’s John Slater, whom Pauling first met in Cambridge in 1929, was using the same Heitler-London approach, while Robert Mulliken was taking up the strategy of Friedrich Hund and Erich Hückel for assuming that electrons of the outer shells of atoms can move in molecular orbitals spanning an array of atoms as a whole, rather than behaving as single electrons orbiting one atomic nucleus alone (31). They all were devising methods for creation of a new mathematical chemistry. But Pauling’s first paper in the “Chemical Bond” series was pathbreaking. William Lipscomb later said, simply, that this paper “changed chemistry (32).”

In July 1935 Pauling and E. Bright Wilson, Jr. completed the highly technical Introduction to Quantum Mechanics with Applications to Chemistry. The claims they make at the beginning of the rigorously mathematical book are modest, but profound (33):

The subject of quantum mechanics constitutes the most recent step in the very old search for the general laws governing the motion of matter. . . . it is now realized that the combining power of atoms and, in fact, all the chemical properties of atoms and molecules are explicable in terms of the laws governing the motions of the electrons and nuclei composing them.

While the Introduction to Quantum Mechanics is highly mathematical, Pauling’s Nature of the Chemical Bond and the Structure of Molecules and Crystals is not. This book is based on lectures he gave at Cornell University, and it first appeared in 1939. Here Pauling laid out in a largely nonmathematical way the theory of the electron valence-bond, including the concept of resonance in conjugated molecules, linking the theory of the chemical bond to explanations of molecular structure.

Like Lavoisier’s textbook on Elements of Chemistry, Pauling’s textbook on The Chemical Bond changed the way scientists thought about chemistry, presenting chemistry as a disciplinary field unified by an underlying theory. By demonstrating how the characteristics of the chemical bond determined the structure of molecules and how the structure of molecules determined their properties, Pauling showed for the first time, as Max Perutz said, “that chemistry could be understood
rather than being memorized (34).” In a fiftieth anniversary tribute to Pauling’s *Chemical Bond* in 1989, Eugene Garfield noted that this fifty-year old scientific book ranked in the top ten scientific publications cited in the ISI database since 1945, and that it ranked among the top five most cited books. Remarkably, in the year 1988 alone, *The Chemical Bond* received over 600 citations, while only around 30 publications received 60 or more citations (35). This is an extraordinary record for any scientific book.

Pauling pioneered the use of drawings and diagrams in chemical textbooks. His innovations can be seen in the first versions of a general chemistry textbook which Pauling began making available in 1941 to freshmen at Caltech as a lithographed volume. Pauling’s *General Chemistry*, finally published by William Freeman in 1947, included a profusion of illustrations ranging from X-ray and electron-diffraction photographs, to graphical constructions of atoms and molecules, to cartoon-like pictures of electron densities drawn as fuzzy orbital clouds around central atoms. The pictures were designed by the professional artist and licensed architect Roger Hayward, who began making illustrations for Pauling’s lectures as early as 1933 (36).

There is yet another way in which Pauling helped transform chemistry in the late 1930s and 1940s. In the fall of 1938 Pauling initiated correspondence with Joseph Hirschfelder about the usefulness of three-dimensional molecular models for teaching and research: the so-called “space-filling” models (37). As Eric Francoeur has noted, the German chemist H. A. Stuart had begun designing this new kind of molecular model in 1934 (38). Hirschfelder and Pauling corresponded about the diameters to be used for representation of the atoms, partly on the basis of Pauling’s work with Lawrence Brockway on covalent radii and bond-angle values from electron diffraction studies of carbon compounds (39). By 1939 the Fischer Scientific Company was selling kits of the models, with advertisements suggesting their use not only for studying spatial relationships and steric hindrance, but also for testing hypotheses about molecular structure (40).

By this time Pauling’s research was moving away from further technical development of quantum chemistry and toward the study of the structure and function of large, biologically significant molecules, by use of both physical methods of instrumentation and chemical methods of modeling (41). By the late 1940s Pauling’s chemistry laboratory was making space-filling models, as well as other molecular models, for the use of Pauling and his collaborators in studying the structures of polypeptides, proteins, and other molecules, including, by the early 1950s, DNA. The models were designed by Pauling, Robert Corey, Verner Schomaker, and J. H. Sturdivant (42).

As has often been recounted in histories of the DNA “double helix,” news circulated at Caltech in 1951 that Pauling’s team was constructing protein models precise to the finest details. There are several accounts of Pauling’s dramatic announcement of the protein struc-
He held up a child’s set of soft plastic pop-beads and snapped them together to show how amino acids connected. After a suitable introduction, he started moving toward the Model . . . . [and] unveiled it with a grand flourish: a beautiful, multicolored model of his right spiral, the alpha helix. It was the first time many in the audience had seen a space-filling molecule. . . . It looked ‘real,’ . . . it had depth and weight and density, a kind of visual impact that no other model had ever approached.

A September 1951 issue of *Life* magazine carried a large photograph of a grinning Pauling pointing to his space-filling model of the alpha helix, with the headline “Chemists Solve a Great Mystery”—presumably the mystery of life (45).

**Linus Pauling and Matters of Politics**

Although *Life* magazine had an idolizing attitude toward Pauling in 1951, this view would change in the course of the next decade. In 1951, *Life* praised the accomplishments of Pauling, who would receive the Nobel Prize in Chemistry in 1954. *Life*’s editors also expressed sympathy in 1951 with the chemist Pauling whose theory of chemical resonance was currently a subject of vilification from Soviet “officials” for its alleged bourgeois idealism (46). However, by 1962 it was *Life* editors themselves who were vilifying Linus Pauling. What happened? Pauling had become a political figure. Following World War II, Pauling, like many scientific colleagues, joined organizations concerned with atomic-science and atomic-bomb issues. He gave invited talks mostly to local California groups, including a left-wing organization of artists and intellectuals in Hollywood that became a target of the House un-American Activities Committee’s investigation of communism in the motion picture industry (47).

In late 1947 an anonymous member of the American Chemical Society contacted the Federal Bureau of Investigation (FBI) with concerns about the political views of the Society’s new president-elect. In 1948, while Pauling was on a visiting appointment in Oxford, FBI agents quizzed his co-workers, neighbors, and Caltech administrators, looking through his Caltech personnel file to detect any signs that Pauling was a communist sympathizer (48). The theoretical chemist whose resonance theory of chemical bonding was under attack by Soviet ideologists now found himself suspected of communist sympathies. Cleared of any wrongdoing by a Caltech committee in December 1950, Pauling was denied a US passport in 1952, preventing his attending a Royal Society discussion on proteins. His passport was restored, then denied again (49). When reports came out in the spring of 1954 of radiation poisoning of Japanese fishermen following the US explosion of a hydrogen bomb at Bikini Atoll, Pauling connected the problem of radiation poisoning and genetic damage from fallout to his own recent research interests in DNA and nucleic acids as carriers of inherited characteristics, including mutations in genes (50). Discussions with biologist Barry Commoner and physicist Edward Condon resulted in the idea of a written worldwide appeal for a ban on the testing of nuclear weapons. In early 1958, Linus and Ava Helen Pauling presented a petition with 9,006 signatures to Dag Hammarskjold at the United Nations. In response, *Life* magazine carried a negative story about Pauling, highlighting criticism from physicist Edward Teller and Rand analyst Albert Latter that “The worldwide fallout is as dangerous to human health as being one ounce overweight (51).” Teller and Pauling debated each other in live coverage on KQED television in San Francisco, with no clear resolution of technical issues for viewers (52). By 1960 the Senate Internal Security Committee, which had branded Pauling a fellow traveler in 1956, subpoenaed him to explain possible communist involvement in the nuclear-test ban movement (53).

In the fall of 1963, when it was announced that Linus Pauling would receive the 1962 Nobel Peace Prize, *Life* magazine, carrying the extraordinary headline “A Weird Insult from Norway,” stated that the limited test-ban treaty had nothing whatsoever to do
with Pauling or the 1958 petition to the UN (54). Caltech’s president, Lee Dubridge, praised Pauling’s efforts for peace but publicly noted that many people in Pasadena and the scientific community had disapproved of his methods. Pauling resigned from Caltech (55).

In the last decades of his life, Pauling’s concerns with genetics, molecular structure, and medical chemistry once again propelled him into the public limelight as he began to use his fame in a public campaign to establish Vitamin C as a cure for the common cold and, in huge doses, for cancer. Controversy over the merits of vitamins and other anti-oxidants in the treatment of cancer embroiled Pauling with members of the Mayo Clinic and the broader medical community (56). Pauling began to sound like a latter-day Anton Mesmer, fighting an entrenched medical and academic elite for the benefit of the public citizenry (57). His opponents, he charged, feared “monetary losses that would be inflicted on pharmaceutical manufacturers, professional journals, and doctors themselves” if the value of Vitamin C therapy were admitted (58). Pauling now spoke of a revolutionary age, saying that scientists should be radicals and not conservatives in their service to humanity (59).

Scientific Revolutions and Scientific Revolutionaries

As is well-known, Thomas Kuhn’s analysis of The Structure of Scientific Revolutions insists upon puzzle-solving as an ordinary activity among scientists. Anomaly and crisis, followed by invention of a new paradigm or a new textbook tradition, are essential features of scientific revolution. Not everyone has agreed with Kuhn. In fact, most everyone has disagreed with some aspect or another of Kuhn’s analysis, often by way of emphasizing histories of science as histories that are gradual transformations of ideas and disciplines rather than catastrophic ruptures with the past (60). Still there are markers of scientific change that seem to be a matter of common agreement among scientists and historians. New languages are invented, new textbooks are written, and new theories are superimposed on old theories, either ruling them out entirely, or limiting their applicability. New ways of seeing the world emerge. By and large, the terminology of “revolution”, like the terminology of “tradition,” is common and ubiquitous among scientists and historians.

What conclusions can be drawn in considering the legacies of Pauling and Lavoisier? In the case of Linus Pauling, as we have seen, Pauling did not set out to initiate a revolution in science, but he was eager to participate in the newest front of scientific advance. There was no crisis in chemistry in Pauling’s youth, but there were puzzles and anomalies to be solved, for example, in understanding the bond structure of methane and benzene, and the length and energy of aromatic and conjugated bonds. The application of quantum mechanics to chemical electron bonds was an exciting new frontier, and Pauling and others succeeded in constructing a mathematical quantum chemistry rather quickly from the late 1920s to the mid-1930s. Pauling, more than some of his colleagues, was concerned to integrate these results with both the theoretical assumptions of classical organic structure theory and the empirical applications of new physical instruments, like X-ray diffraction. Like Lavoisier, Pauling’s work ranged broadly across physics and chemistry, chemical and physical methods, mathematical and visual explanations, and biological and physical chemistry (61).

Like Lavoisier, too, Pauling saw clearly that the new chemistry he was helping to construct required a new language, new representations, and new textbooks. New principles had to be laid out at the beginning of chemical education, namely the principle of the electron-valence bond, including concepts of electronegativity, resonance and hybridization, and the principle of spatial architecture, with bonds, atoms, and molecules laid out precisely in three-dimensional space.

The General Chemistry, like The Chemical Bond, defined a new chemistry, just as assuredly as did the molecular models and model-building techniques associated with Pauling’s name. By the 1960s, the high school chemistry curriculum in the United States was based on the chemical bond approach (CBA) of the 1959 high-school textbook Chemical Systems (62). The CPK, or Corey-Pauling Space Filling Models with Improved Koltun Connectors, became as common in chemical classrooms and laboratories as the periodic table (63). As Hoffmann and Woodward wrote in Science in 1970, a “revolution” had occurred “in our image of what molecules really look like and what we can conceive of them doing or not doing in the course of a chemical reaction (64).”

An irony at the end of Pauling’s career, as at the end of Lavoisier’s career, was the way in which political events turned him into a public figure about whom very strong emotions and judgments were elicited from both scientific colleagues and members of the body poli-
tic. In each case, the man’s heroic status as scientist made him all the more controversial and, in the end, all the more visible as public figure and political victim. The political turns in Pauling’s life, like Lavoisier’s, were partly of his own making. The accusations of patriotic disloyalty were patently false, but allegations about intellectual arrogance and imprudent judgment were sometimes fair enough. With Pauling, as with Lavoisier, his long-term reputation as a revolutionary figure rests partly in the political dimensions of his life, which set him apart from many other scientists. Yet these political dimensions attract attention largely because his reputation as a great scientist had already been well established. Pauling’s place in history is firm. Whether he will be regarded as a revolutionary figure of twentieth-century chemistry at the end of the twenty-first century is a matter that future generations of scientists and historians will decide.

ACKNOWLEDGMENT

I am grateful to Clifford Mead, Head of Special Collections at Oregon State University Libraries, for permission to publish materials from the Ava Helen and Linus Pauling Papers. Thanks, too, to D. Erik Ellis and J. Christopher Jolly for research assistance and to Robert A. Nye for a critical reading of the preliminary draft of my Dexter Award Lecture.

REFERENCES AND NOTES

6. Ref. 5, pp 90, 161.
12. The events and the letters are discussed in Ref. 8, pp 376-415.
17. Ref. 5, p 230.


21. Letter from Linus Pauling (in Warrenton, Oregon) to Ava Helen Miller (in Corvallis), June 20, 1922. Courtesy of the Ava Helen and Linus Pauling Papers, Oregon State University Libraries (hereafter, Pauling Papers, OSU): LP Safe/1/1922x.06.20 LP.

22. Linus Pauling (Warrenton, Oregon) to Ava Helen Miller (Corvallis, Oregon), postmarked August 11, 1922, Pauling Papers, OSU: LP Safe/1/1922x.08.09 LP.

23. The Perkin Medal likely came to Pauling’s attention as a newly established award of the American Section of the Society of Chemical Industry / Société de Chimie Industrielle, founded in 1918 in New York.


25. Letters from Linus Pauling (Pasadena) to Ava Helen Miller (Corvallis), October 2 and 4 or 5, 1922, Pauling Papers, OSU: LP Safe/1/1922x.10.02 LP and LP Safe/1/1922x.10.04 LP.


27. Ref. 24: L. Pauling, Guggenheim Fellowship application for 1926, Pauling Papers, OSU.


34. Quoted in Hager, Ref. 18, p 217.


41. Linus Pauling, letter of application to the Carnegie Institution, February 9, 1932; Pauling Papers, OSU: LP


58. Hager, Ref. 18, pp 577-578.


61. In 1954, the year that Pauling received the Nobel Prize in Chemistry, Pauling wrote Dennis Flanagan, the editor of Scientific American, that he and Corey had taken “the most important step forward that has been made during the last 15 years or perhaps 50 years in this field.” Quoted in Hager, Ref. 18, p 377.

62. Raber, Ref. 36, pp 117-118.


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Introduction

It has been 200 years since Alessandro Volta invented his famous pile, the first electric battery, and thereby created an important starting point not only for the sciences of electricity and magnetism but also for the later electrical technology that so thoroughly has transformed society. The electric age in which we still live can reasonably be traced back to Volta’s discovery. His pile immediately became the subject of intense scientific investigation, which included theoretical ideas of the origin of the electrical tension that seemed to occur spontaneously if only two different metals were brought in contact. This question figured prominently in the science of the first half of the nineteenth century, and it occupied physicists and chemists alike. Indeed, at that time the separation between physics and chemistry had not yet become manifest.

In a letter of October 30, 1801 to the Dutch scientist Martinus van Marum, Volta referred to “a highly esteemed German scientist, a zealous cultivator of physics, natural history, and chemistry, and the author of works that are much to his honor (1).” The subject of Volta’s praise was Christoph Heinrich Pfaff, a 28-year-old German chemist and physicist with whom Volta had recently become acquainted. Pfaff was already an enthusiastic expert in galvanic science, a field of study he cultivated throughout his long career. His many contributions to animal electricity and, in particular, the understanding of Volta’s pile made him a key figure in Wilhelm Ostwald’s massive 1896 history of electrochemistry. According to Ostwald, Pfaff was a “painstaking historian of galvanism and zealous defender of voltaism” who “won special merit particularly in the propagation of the knowledge of galvanic phenomena in Germany (2).” In addition to his numerous works in electrochemistry and inorganic analysis, the versatile Pfaff published many papers and books on subjects of physics, medicine, meteorology, botany, and pharmacy. He seems to have known most scientists in Europe and corresponded or had personal relations with important scientists and scholars such as Cuvier, Gay-Lussac, Dumas, Lichtenberg, Gmelin, Ørsted, Volta, Berthollet, Thénard,
Lagrange, Berzelius, Liebig, Faraday, Mayer, and Goethe.

Although he was a central figure in the scientific life of his time, today Pfaff is largely forgotten or relegated to footnotes in works on the history of science. This is probably because he made no significant discoveries, but rather made an impact as a teacher and propagator of science and through his many books, reviews, and papers. There is indeed a Pfaff included in the Dictionary of Scientific Biography, but he is Johann Friedrich Pfaff, a mathematician and Christoph’s older brother. Curiously, when Chr. H. Pfaff does turn up in bibliographies and historical writings, his first name is often given as Christian rather than Christoph. For example, this is how he is named in the 1863 edition of Poggendorff’s authoritative bio-bibliography, in the British Museum General Catalogue of Printed Books (1963), and also in the classical historical works of Edmund Whittaker and James Partington. Yet his first name was Christoph, such as proved by his autobiography (3).

Life and Career

Born on March 2, 1773 in Stuttgart, young Pfaff entered in 1782 the nearby Karl Academy, named after Württemberg’s Duke Karl Eugen. He soon became fascinated by the scientific subjects that were taught at the Academy in addition to the classical languages. His early knowledge of chemistry mostly stemmed from Friedrich Gren’s Systematisches Handbuch der Gesammten Chemie (1787-1790), which he studied by himself. Among his fellow students was the Frenchman Georges Cuvier, four years older, who would later become such a famous pioneer of zoology and paleontology. The close and, in the spirit of the time, romantic friendship with Cuvier became a turning point in Pfaff’s life and reinforced his decision to devote his life to science. Cuvier became not only his friend but also his mentor and teacher. When Cuvier returned to Paris, he kept Pfaff regularly informed of Lavoisier’s latest works and the ongoing revolution in chemistry (4). As a result, Pfaff, who had originally accepted the phlogiston theory, converted to the antiphlogistic doctrines and became an advocate of the new chemistry and its transfer to German soil (5).

Pfaff completed his medical studies at the Karl Academy with a Latin dissertation on animal electricity (De Electricitate Sic Dicta Animali) which in 1795 appeared in an extended and revised German edition (6). It won him much praise and caught the attention of Volta, among others. After further studies in chemistry, physics and medicine he obtained in 1798 a chair at the Christian-Albrecht University in Kiel. He spent most of the year of 1801 in Paris, and it was here he met Volta and witnessed the Italian scientist’s famous demonstration of the pile in front of Napoleon and other luminaries. Pfaff was fascinated by Volta and his marvelous apparatus and immediately took up his own experiments (7). In 1802 the ambitious young scientist wrote to van Marum (8):

I am working at present on a complete treatise on galvanism, in which I shall assemble in systematic order all the really authentic facts, and in which I shall reduce them to the laws of electricity.

Volta knew about Pfaff’s project, of which he approved. On January 23, 1802, he wrote to Pfaff (9):

I am very much pleased with your idea of publishing a treatise which presents everything that has taken place concerning galvanism, and to put this matter in the clearest light; no one else can do it better than you. The works that you have done several years ago, [and] the order and method that govern them, prove it.

Although Pfaff’s “complete treatise” never materialized, his work earned him a reputation as one of Europe’s foremost specialists in electrochemistry and galvanism. Ludwig Gilbert, the German physicist and editor of Annalen der Physik, wrote that Pfaff (10):

...had worked meticulously in the new field of physics [and] with such excellent results that Volta, whom he met in Paris, entrusted him with advertising and cultivating his theory in Germany; ... [Pfaff’s] article in the tenth volume of my Annalen der Physik (the year 1802, pp 219 and 121) still belongs to the most instructive accounts of the theory.

From 1801 to the end of his life in 1852, Pfaff investigated the action of the pile, defended Volta’s notion of a metallic contact force, and wrote widely about voltaic phenomena. He was considered an international authority on the subject, which he surveyed in 622 pages for the new edition of Johann Gehler’s Physikalisches Wörterbuch. Ostwald later praised the survey for Pfaff’s “commendable care and thought (11).”

Yet galvanic and voltaic phenomena were only part of what Pfaff was concerned with during his busy scientific life. He was greatly interested in electromagnetism on which topic he wrote an early “history (12),” and in 1829 he learned from Faraday himself about the new way to produce electricity by means of induction.
Methodologically, Pfaff favored a positivistic view of science and never tired of emphasizing that chemistry and physics were solidly founded on experimentally established facts. He had no patience for the German Naturphilosophie and neither did he like Goethe’s revolt against Newtonian science. Having read Goethe’s Farbenlehre, he quickly responded with an anti-Goethe tract repudiating the views of the famous poet and heterodox amateur scientist (13). Much of Pfaff’s time was occupied with medicine and pharmacy, and he also contributed significantly to analytical chemistry. He developed analytical techniques and wrote in the early 1820s a practically oriented handbook of analytical chemistry (14), according to William Brock the “first major analytical textbook (15).” Among his few contributions to organic chemistry was an investigation, together with Liebig, of the chemical composition of caffeine (16). At the same time he did research in mineralogy, the composition of mineral waters, and technical chemistry (including the production of acetic acid and sulfuric acid) — to mention only some of his areas of work.

During the first half of the nineteenth century (until 1864) Kiel, the capital of Holstein, was part of the Danish Empire. Pfaff was often in Copenhagen and had close connections with H. C. Ørsted and other Danish chemists and pharmacists. In 1843, on the occasion of his 50-year’s doctoral jubilee, the Danish king conferred upon him the title of konferensraad (Conference Councilor), a great honor and a recognition of his services to Danish science and culture. During the last years of his life, Pfaff lost his eyesight and was unable to work in his laboratory. He died on April 23, 1852 in his beloved Kiel, where he is buried.

### Polemics I: Pfaff versus De la Rive

According to Volta, the action of the pile was due solely to a contact force (a forze motrice, or electromotive force) arising between two different metals, and not to chemical processes of any sort. This view was reflected in the title of Volta’s famous letter to Joseph Banks of March 20, 1800, namely, “On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds (17).” Other scientists, among them Giovanni Fabbroni, Davy, and Berzelius, questioned the contact theory and suggested that the pile was in reality a chemical machine. According to the chemical theory, chemical changes were necessary for the production in the pile of an electrical tension or, if the circuit was closed, a current. This was the beginning of an unusually long and complex controversy that lasted for more than half

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**Table I. Chronology of Chr. H. Pfaff**

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1773</td>
<td>Born in Stuttgart, Germany.</td>
</tr>
<tr>
<td>1782</td>
<td>Enters Karl Academy.</td>
</tr>
<tr>
<td>1793</td>
<td>Doctoral dissertation (M.D.) on animal electricity.</td>
</tr>
<tr>
<td>1798</td>
<td>Professor (extraordinarius) at Kiel University, Medical Faculty.</td>
</tr>
<tr>
<td>1802</td>
<td>Full Professor in chemistry and physics.</td>
</tr>
<tr>
<td>1804</td>
<td>Member of the Royal Danish Academy of Science.</td>
</tr>
<tr>
<td>1812</td>
<td>Corresponding member of the Berlin Academy of Sciences.</td>
</tr>
<tr>
<td>1828</td>
<td>Director of the Schleswig-Holstein Sanitation Board.</td>
</tr>
<tr>
<td>1829</td>
<td>Visit in Paris (J. B. Dumas) and London (W. Prout; M. Faraday).</td>
</tr>
<tr>
<td>1830</td>
<td>President of the physics-chemistry section of the (German) Society of Physicians and Natural Scientists.</td>
</tr>
<tr>
<td>1831</td>
<td>Chief editor of the Schleswig-Holstein pharmacopoeia.</td>
</tr>
<tr>
<td>1837</td>
<td>All-out rejection of chemical theory (Revision).</td>
</tr>
<tr>
<td>1838</td>
<td>Grand European tour.</td>
</tr>
<tr>
<td>1845</td>
<td>Last major work (Parallele). Resigns from Chair.</td>
</tr>
<tr>
<td>1852</td>
<td>Death.</td>
</tr>
<tr>
<td>1853</td>
<td>Publication of his autobiography (Lebenserinnerungen).</td>
</tr>
</tbody>
</table>
a century and involved many of Europe's finest chemists and physicists (18).

The voltaic pile was constructed from a large number of similar units connected in series, generally referred to as "galvanic" or "voltaic" elements. These much used and well known elements were composed of two dissimilar metals and a "moist conductor" that could be any kind of liquid or solution. Most of the numerous experiments conducted during the controversy were made with these galvanic elements rather than the voltaic pile, since one element conveniently constituted an adequate representation of the pile itself.

Pfaff was a self-proclaimed champion of the contact theory and considered himself a guardian of Volta's views. In 1814 he launched an attack on the chemical theories proposed by Davy, Berzelius and others; and fifteen years later he was again on the warpath against what he saw as chemical heresy. The principal reason was a series of papers written by the Geneva scientist Auguste De la Rive that amounted to a fully developed chemical alternative to the contact theory. Another advocate of the chemical theory, the Paris physicist Antoine-César Becquerel, was somewhat more cautious and admitted the existence of a metallic contact force, although he considered it to be of secondary importance only. Based on a large number of experiments, De la Rive argued from 1825 onward that chemical change was invariably a precondition for voltaic phenomena, whereas, in the absence of chemical action, "there is no development of electricity, at any rate not when thermal or mechanical action is absent (19)." To De la Rive, this proved that the contact theory was wrong. To Pfaff, it proved that De la Rive was wrong. Pfaff's campaign against Becquerel, De la Rive, and other adherents of the chemical alternative included a modified repetition of Volta's fundamental condenser experiment, performed in vacuum or in various dried gases. Since he obtained the same result as reported by Volta, an electrical tension, he concluded that "it is impossible to assign any external and foreign circumstance, other than the contact, as the cause for the electricity developed (20)." In order to demonstrate the production of electrical effects without chemical action, Pfaff also experimented with a zinc-copper galvanic element in which the metal pairs were separated by a saturated solution of zinc sulfate carefully freed from dissolved air. According to the chemical theory one would suspect the system to be electrically inactive because zinc sulfate exerts no chemical action on either zinc or copper. Yet Pfaff found that a strong electrical effect was produced, a result that left De la Rive puzzled. Pfaff measured the electrical effect both with a condenser and an electroscope (static or tension electricity), and with a galvanometer (dynamic or current electricity). Moreover, he challenged the "chemists" to explain why the tension of the pile increases with the number of couples.

Pfaff remained loyal to the contact cause, battling not only his chief opponent De la Rive but also other chemical theorists, including Becquerel in France, Michael Faraday in England, and Christian Schönbein and Friedrich Mohr in Germany. In 1837 he summarized his work on "galvano-voltaism" during more than two decades in a book that he believed would settle the matter in favor of Volta's theory (21). He was mistaken. On the contrary, he was wrong.

trary, at that time the chemical theory gained strength, in part because of Faraday's entrance in the debate. Becquerel and De la Rive continued to defend the chemical theory. Citing "thousands of experiments," Becquerel concluded in a textbook of 1842 that "the electricity released by the pile totally originates from the chemical action (22)."

It should be noted that although Pfaff was undoubtedly the most energetic and persistent advocate of the contact theory, he was far from alone in his criticism of the chemical alternative. In the 1830s he was followed by several other scientists, both chemists and physicists; and for a period the contact theory was generally believed to be a better explanation of the pile than the chemical theory. Among the German scientists who defended the contact theory were Georg S. Ohm, Johann C. Poggendorff, Gustav T. Fechner, and Georg F. Pohl.

Figure 4. An electromagnetic balance. The cells were connected to wires wound up around iron cores, in this way creating an electromagnet varying in strength according to the strength of the current. The electromagnet would attract the pans of the balance and thus enable a measurement of the current intensity in terms of weight. Illustration from A.-C. Becquerel and E. Becquerel, Traité d'Électricité et de Magnétisme, Libraire de Firmin Frères, Paris, 1855, vol. 1, 231.

An Indecisive Experiment: Grove's Cell

In 1839 William Grove, the British physicist and inventor of the fuel cell (also in 1839), constructed a cell of remarkable strength. His element consisted of a zinc electrode in a dilute solution of sulfuric acid and a plati-

num electrode immersed in nitric acid. The two liquids were separated by a porous wall. Together with his friend Schönbein, the famous discoverer of ozone and a long-time defender of the chemical theory, Grove performed in his London laboratory a number of experiments with the new galvanic element. The two scientists observed a considerable "chemical action" of the acid on the zinc plate, that is, the zinc corroded visibly because of the acid. Schönbein concluded that the powerful chemical action was connected with the equally powerful effects of the element, and that the cell was therefore a convincing argument in favor of the chemical theory (23). Pfaff, of course, disagreed. He decided to repeat the experiment and had his own design of Grove's cell made in Copenhagen. His version consisted of a central zinc rod within a porous clay cylinder surrounded by a platinumized porcelain cylinder (Fig. 3). With this cell Pfaff repeated the experiments made by Grove and Schönbein. He measured the power (Kraft) of the cell by means of an electromagnetic balance and found the very large carrying capacity of 40 pounds (Fig. 4). He then exchanged the sulfuric acid with an amount of zinc sulfate dissolved in water, that is, a solution incapable of exerting chemical action on zinc. The carrying capacity now measured 50 pounds.

The results made Pfaff note that (24):

To my great joy, though not surprise, for I firmly stand on voltaic ground, I found that the power was enhanced.

In a letter to his friend H. C. Ørsted, he wrote (25):

I hasten to inform you of an experiment entirely decisive for the theory of voltaism, definitively silencing the long fought struggle over the source of electricity in the closed [galvanic] chain, and completely ensuring the triumph of the contact theory.

The interpretation seemed obvious to Pfaff, who rhetorically asked his colleague in Copenhagen (25):

Could there be a more vindictive proof of the contact theory and against the chemical theory?

However, the experiments with the Grove cell were no more decisive than any other of the so-called crucial experiments that were so common in the controversy.

Polemics II: Pfaff versus Faraday

Michael Faraday's electrochemical works were another challenge to the contact theory. Even before 1834, the year when he announced his electrolytic laws, Faraday was predisposed toward the chemical theory; and his electrochemical discoveries strengthened him in his be-
An early version of the concept of energy conservation was "improbable" because it violated principles of natural philosophy. Faraday argued that the now considered the question in the light of general forceful attack on the contact theory. Apart from citing a wealth of experimental data (little of which were new), Faraday launched a new and defeat of the contact theory or to a conversion of Pfaff and his allies.

The chemical theorists eagerly welcomed this support from Faraday's Laws. For example, in 1836 De la Rive stated that (27):

The intensity of the currents developed in combinations and in decompositions is exactly proportional to the degree of affinity which subsists between the atoms whose combination or separation has given rise to these currents.

Friedrich Mohr believed, probably wrongly, that a large majority of Europe's scientists now followed Faraday in support of the chemical theory (28). Yet, although Faraday's Laws were welcome ammunition to the advocates of the chemical theory, they did not seriously change the situation. They certainly did not lead to a defeat of the contact theory or to a conversion of Pfaff and his allies.

With his seminal 1840 paper "On the Source of Power in the Voltaic Pile" Faraday launched a new and forceful attack on the contact theory. Apart from citing a wealth of experimental data (little of which were new), he now considered the question in the light of general principles of natural philosophy. Faraday argued that the contact theory was "improbable" because it violated what would soon be known as the conservation of force, an early version of the concept of energy conservation (29):

... the chemical theory sets out with a power the existence of which is pre-proved, and then follows its variations, rarely assuming anything which is not supported by some corresponding simple chemical fact. The contact theory sets out with an assumption, to which it adds others as the cases require, until at last the contact force, instead of being the firm unchangeable thing as first supposed by Volta, is as variable as chemical force itself. Were it otherwise than it is, and were the contact theory true, then, as it appears to me, the equality of cause and effect must be denied. Then would the perpetual motion also be true; and it would not be at all difficult, upon the first given case of an electric current by contact alone, to produce an electro-magnetic arrangement, which, as to its principle, would go on producing mechanical effects forever.

Faraday repeated his view in 1843, disturbed by "several attacks, from Germany, Italy and Belgium, upon the chemical theory of the voltaic battery, and some of them upon experiments of mine (30)." He undoubtedly referred to Pfaff, among others, who was unconvinced by Faraday's arguments and continued his life-long fight against the chemical theory. At the third meeting of Scandinavian Scientists in Stockholm in 1842, a young Danish scientist, Christian M. Poulsen, delivered a polemical anti-Faraday address that was based to a large extent on Pfaff's most recent experiments and arguments (31).

As late as 1845 the 72-year-old German scientist defended Volta's contact theory against the chemical challenge. His strategy was largely the same as in the controversy with De la Rive, namely to criticize Faraday's experiments and conclusions by his own counter-experiments. Pfaff suspected Faraday to be biased and his experimental results to be influenced by his wish to prove the chemical theory (32):

As a staunch defender of Volta's contact theory of the galvanic chain, I found myself doubly challenged ... to check with the utmost impartiality Faraday's reasons. ... I soon realized that Faraday, in his polemics against Volta's views, had not done the matter full justice, and that he maintained the chemical theory with a kind of passion and endeavored to secure its triumph; for this reason I became suspicious (and doubted) if all of the new experiments reported by Faraday were correct.

But Pfaff also addressed Faraday's more philosophical objections against the contact theory. He argued that the contact force, contrary to chemical forces, was a primitive power that was neither in need of explanation nor restricted by either Faraday's principle of inexhaustibility or Mayer's new principle of force conservation. According to Pfaff, the contact force belonged to the same category as gravity, "which indestructibly and inexhaustibly maintains the life of the large masses on whose motions the order of the universe depends, without its needing any nourishment from the outside that repeatedly rekindles its activity (33)."

Pfaff's 1845 book was primarily directed against Faraday, and secondarily against Schönbein and Gmelin; but it is also of interest because it included the first discussion ever of J. Robert Mayer's 1842 paper on the mechanical equivalent of heat (34). Mayer's publication, in which he introduced the idea of conservation of energy (or force), was later to be recognized as a landmark paper in the history of science; but initially it was ignored by almost all scientists. The exception was Pfaff,
who gave a detailed and critical account of Mayer’s view (35). Mayer acknowledged the discussion of the “very distinguished scientist” and in his autobiographical notes he referred gratefully to Pfaff.

One may think that Pfaff was just a stubborn and possibly smirking defender of orthodox voltaism, who failed to realize that with the principle of energy conservation “the contact theory had been dealt a mortal blow (36).” But this was not the case. The acceptance of the law of energy conservation did not imply that the chemical theory became universally accepted and the contact theory discarded. Although the chemical theory became much more popular in the 1840s, it was inadequate to replace completely the contact theory. At the time of Pfaff’s death the controversy was in decline, and most scientists had lost interest in what previously had been a hotly debated question. The reason was not that the question had been resolved, however, and for several more decades the chemical theory and the contact theory continued to coexist.

At last by 1850 it had become clear that the Volta problem could not be satisfactorily solved within the limits of contemporary science—and that a phenomenological approach was to be preferred. Such an approach invited compromises between the two camps. It was only in the 1880s, following progress in electrochemical theory, that the situation changed and it became possible to understand the pile in chemical terms, at least partially. “The chemical theory has fought its way back,” Ostwald asserted in 1896, adding that it had won “final victory (37).” Ostwald’s optimism was premature, however. The problem of the origin of the voltaic force was even more complicated than he imagined. It was only solved about 1940, when it turned out that both of the rival views, the chemical theory and the contact theory, were needed in order to account fully for voltaic effects (38). It was a conclusion that Pfaff would not have liked.

REFERENCES AND NOTES

5. For the dissemination of Lavoisier’s ideas to Germany, see K. Hufbauer, The Formation of the German Chemical Community (1720-1793), University of California Press, Berkeley, CA, 1982, which includes a section on Pfaff.
18. See Ref. 2 and, for recent surveys, H. Kragh, “Confu­sion and Controversy: Nineteenth-Century Theories of

19. A. De la Rive, “Recherches sur la Cause de l’Électricité Voltaïque,” Mémoires de la Société de Physique et d’Histoire Naturelle de Genève, Pt. 2, 1836, 7, 457-517, as quoted in Ref. 2, p 445. This was the third part of a series of papers, starting in 1828, all with the same title.


29. Ref. 26, par. 2071-2073.


33. Ref. 32, p 106.


37. Ref. 2, p 289.


ABOUT THE AUTHORS


HISTORY OF CHEMISTRY DIVISION
http://www.scs.uiuc.edu/~mainzvHIST/
GEORGE AUGUSTUS HULETT: FROM LIQUID CRYSTALS TO STANDARD CELL

John T. Stock, University of Connecticut

Born July 15, 1867 on a farm in DuPage Township in Will County, Illinois, George Hulett (Fig. 1) developed an aptitude for machinery repair in his boyhood. This aptitude served him well in later life, when he became one of the great experimentalists of his time (1). He entered Oberlin College in 1888, then in 1890 transferred to Princeton, from where he graduated in 1892. As an assistant in chemistry during the following four years, he wrote two articles, one on lecture apparatus and the other on the distillation of water. Hulett then traveled to Leipzig, to become one of the succession of American students and associates of Wilhelm Ostwald (1853-1932). Apart from their own later successful careers, these scientists were largely responsible for the growth of physical and analytical chemistry in America (2).

Hulett’s project at Leipzig was to study the continuity of phase transitions, especially of liquid crystals (3). In 1888, Friedrich Reinitzer (1857-1927) had found that cholesteryl benzoate melted to a turbid but fully fluid liquid which exhibited double refraction. On further heating, the liquid suddenly became transparent and no longer birefringent (4). In his studies of p-azoxyanisole and p-azoxyphenetole, which behaved similarly to cholesteryl benzoate, Otto Lehmann (1855-1922) termed such substances “fliessende Krystalle” (liquid crystals) (5).

The idea of a critical point for the transition of the turbid-transparent, or anisotropic-isotropic, liquid system arose from the known behavior of a typical liquid-vapor system such as that exhibited by CO₂. The transition of the liquid into its vapor under rising temperature and pressure is characterized by a continuously decreasing difference in the specific volumes of the two phases. Finally this difference vanishes at the critical point, where temperature, pressure and specific volume have fixed values for the system. Because the phases become identical at the critical point, the approach to this may be followed by observations of differences in any specific property, e.g., density, entropy, and heat of transition. Ostwald thought that the liquid crystal state had some connection with critical phenomena and that pressure studies might reveal this connection.

While Hulett’s work was in progress, Rudolf Schenck (1870-1906) published his studies of the two azoxy liquid crystals (6). Schenck found that the den-
Figure 2. Pressure-temperature curves of p-azoxyanisole (Ref. 3)

Figure 3. Hulett’s pressure-volume apparatus (Ref. 11)

due to some supersaturating effect, or to a real increase in the volume of water. Results obtained when the tube was filled under vacuum with air-free water showed that supersaturation was not involved. Even greater effects were obtained with liquids such as ethanol and ether.

Having dealt with liquid crystals, Hulett turned to the effect of pressure on the melting points of p-toluidine, camphor, and benzene (3). This followed a report that the temperature-pressure curve of p-toluidine exhibited a maximum at 180 atm. (9). Hulett obtained linear curves for the substances that he examined. A later paper described his determination of the compressibility of water at 9° C and 50° C, and of p-toluidine at 45° C (10).

Having obtained his Ph.D. in 1898, Hulett became an instructor at the University of Michigan, where he continued the study of negative pressure (11). He pointed out that, if the compressibility coefficient was the same for negative as for positive pressures, Berthelot’s experiments indicated negative pressures of approximately 52 kg.cm⁻² for water and 108 kg.cm⁻² for ether. Later workers, notably Osborne Reynolds (1842-1912), continued the study of negative pressure (12). Reynolds filled a 152-cm. barometer tube with water, then displaced the water by mercury; but this left a film of water on the tube walls. When the tube was turned upright, it remained full of mercury, although the column was twice the barometric height. In a device involving centrifugal force on water, Reynolds obtained a negative pressure of 5 atm. To relate volume change to negative pressure, Hulett devised the apparatus shown in Fig. 3, where T is the stout bulb of the mercury-containing manometer TG. The entire volume ABCDF was filled with the liquid to be examined. A platinum wire, fused in across the bore of the cali-
brated tube \( F \), was heated to collapse the negative pressure effect. Portion \( B \) of the apparatus was kept at constant temperature, while the temperature of portion \( CD \) could be varied. The heating of \( CD \) applied positive pressure to \( T \), causing the mercury thread in \( G \) to rise; the cooling of \( CD \) produced negative pressure, indicated by a fall in the thread. With ethanol, Hulett found that the pressure-volume curve was linear over the range +12 atm. pressure to -17 atm. Although these values are large, the actual tenacity, or tensile strength, of a liquid can be much greater. The values refer to the bulk of the liquid, not to the film that remains behind. Theoretical treatments by Josef Stefan (1835-1893) (13) and by Ottokar Tumlirz (1856-1928) (14) indicate that the values can be of the same order as the tensile strength of a metal such as silver.

When added to a solvent, a soluble substance (here regarded as nonvolatile and undissociated) dissolves and, under the influence of osmosis, diffuses to the boundaries of the solution. Here it exerts a force that tends to enlarge the volume of the solution, an effect opposed by the tensile strength of the liquid and by the vapor pressure of the solvent. Hulett regarded the osmotic effect as negative pressure; this causes the vapor pressure above the solution to be less than that above the pure solvent at the same temperature. He developed an isothermal cyclic process involving water and an aqueous solution, which led to the relationship:

\[
p_1 - p_2 = Dp = -\frac{Pj}{V} \tag{1}
\]

where \( j \) and \( V \) are the molecular volumes of water and of water vapor, respectively, at constant temperature \( T \) under vapor pressure \( p_1 \), while \( p_2 \) is the corresponding vapor pressure under osmotic pressure \( P \).

Hulett pointed out that Eq. 1 is analogous to that derived for the lowering of the vapor pressure of a liquid when it is compressed (15, 16):

\[
p - p = + P \phi j / V \tag{2}
\]

Here \( p \) is the vapor pressure of the uncompressed liquid and \( p \) that under (positive) pressure \( P \). Hulett examined corrections to Eq. 1, to allow for the difference in the densities of the solvent and of the solution. He then used known data of the freezing point of a 0.1 M aqueous solution and of the vapor pressure-temperature relationship of the ice-water system to calculate \( Dp \). The result agreed with that obtained from Eq. 1.

While at the University of Michigan, Hulett carried out various other investigations. These included the purification of mercury and a study of the electrical conductivity of saturated gypsum solution (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)). He found that, when finely divided gypsum was added to this solution, the conductivity first rose, then slowly declined. This is analogous to the "Ostwald ripening" of analytical precipitates, brought about because small particles have a greater solubility than larger ones. Returning to Princeton in 1905, Hulett became its first professor of physical chemistry in 1909. He was already involved in a lifelong interest, the study and development of standard potentiometric cells, work that required measurements of the highest precision and hence great skill and care.

In the decades that followed the invention of voltaic electricity in 1800, the need arose for a standard of electromotive force. The cell invented by John Frederic Daniell (1790-1845) in 1836 filled this need for over a quarter of a century (17). This \( \text{Cu} \text{CuSO}_4\text{(sald)} : Zn\text{SO}_4\text{(aq)} \) \( Zn \) cell was simple and had negligible temperature coefficient. However, because of the interdiffusion of the solutions, the cell lacked long-term stability (18). The single-solution cell \( \text{Hg} \text{Hg}_2\text{SO}_4\text{(s)} I Zn\text{SO}_4\text{(sald)} I Zn , \) introduced by Latimer Clark (1822-1898) in 1872, was much more satisfactory (19). Major improvements by Lord Rayleigh (1842-1919) and Eleanor Mildred (Mrs. Henry) Sidgwick in 1884 were replacement of zinc by zinc amalgam and an H-shaped container which kept the amalgam well away from the \( \text{Hg}_2\text{SO}_4 - \)covered mercury cathode (20). In 1892, Edward Weston (1850-1936) patented the cell that still bears his name (21). This cell, consisting of a cadmium amalgam anode and \( \text{CdSO}_4 \) solution as electrolyte, and the Clark cell were the subjects of Hulett’s extensive investigations.

Henry Smith Carhart (1844-1920) joined the faculty of the University of Michigan in 1886. His specialty was voltaic cells; in 1893 he described a modified Clark-type cell with an electromotive force (emf) of almost exactly 1 volt.

![Figure 4. The Carhart-Hulett H-form cell (Ref. 23)](image-url)
It is possible that association with Carhart triggered Hulett's interest in standard cells. In fact, Carhart and Hulett jointly authored a 1904 account of ongoing work in the preparation of standard cells. The purification of mercury and of the salt CdSO₄·8H₂O, as well as the preparation of cadmium amalgam and of the "depolarizer" Hg₂SO₄, was described. The H-form cell that they adopted (Fig. 4), with limbs shorter than those in the cell described by Rayleigh and Sidgwick, was sealed off at the necks after filling; it became generally adopted. The emfs of four sets of 6 to 10 cells maintained at 20°C were measured at intervals. Figure 5 shows the emf-time curve of cell D6, one of a set made with HgSO₄ precipitated from HgNO₃. A cell from a set made with electrolytically prepared Hg₂SO₄ behaved as indicated by curve D1. The immediate and continued stability of this type of cell was attributed to the use of nitrate-free Hg₂SO₄.

Hulett was the sole author of a second 1904 paper. This dealt with the purification of Hg₂SO₄, which can undergo hydrolysis, an effect minimized by addition of H₂SO₄. He next described a cadmium-cadmium amalgam cell with a stable emf close to 50 mV. A further study concerned amalgams and the purification of mercury.

At Princeton, Hulett compared the performances of the Clark and of the Weston cells. After gentle rotation, a Weston cell showed a long-term upward drift of emf, an effect attributed to nonequilibrium conditions at the cathode (Hg—Hg₂SO₄). After similar treatment, the emf of a Clark cell rapidly stabilized. At this stage, Hulett favored the Clark cell as a standard of emf, despite its much higher temperature coefficient. In fact, until 1908, this cell was generally accepted as the standard. Two papers of 1906 concerned materials for the construction of Weston cells and a further examination of the effects of cell rotation. That oxidation of Hg₂SO₄ by air was not the cause of emf drift was demonstrated by passage of hydrogen through the solution. Two opposing effects, hydrolysis of Hg₂SO₄ and a slow reaction of the products with the mercury surface, were suspected. In null-point potentiometry, the drift in emf of conventional working batteries necessitates frequent adjustment of the calibration resistor. Hulett developed the enlarged Weston cell shown in Fig. 6 to eliminate this nuisance. The paraffined cork of the 8-cm diameter bottle carries tubes for making contact with the mercury pool K and the contents of shallow dish A, which contains cadmium amalgam and mercury. Current from an external source was used to form Hg₂SO₄ on the surface of K. Discharging through a 10 KW resistor, the emf changed by only about 0.1 mV from the open-circuit value.

In 1908 Hulett reviewed the progress that he and others had made toward the establishment of a reliable standard of emf; the problem was an international one. He noted that solid cadmium amalgam was an isomorphous mixture of composition dependent on that of the liquid phase. Nevertheless, the emfs of cells made with amalgams of 10% and of 7% total cadmium differed by only 7 ppm. The
phase rule indicated that the potential of the anode (amalgam) system is invariant at fixed temperature. Hulett confirmed the indifference of the cathode system to dissolved oxygen and further examined the hydrolysis of $\text{Hg}_2\text{SO}_4$. He carefully analyzed the electrolyte solutions, to some of which $\text{H}_2\text{SO}_4$ had been added. Thus he was able to determine the solubility of $\text{Hg}_2\text{SO}_4$ at various acidities, both for the Weston (cadmium) and the Clark (zinc) systems (Fig. 7). In saturated CdSO$_4$ solution the rapid solubility decrease in the region up to 0.08 M $\text{H}_2\text{SO}_4$ is striking; such an effect is absent in ZnSO$_4$ solution. When cells were prepared with “neutral” CdSO$_4$ solution, efforts were made to remove all $\text{H}_2\text{SO}_4$ from the $\text{Hg}_2\text{SO}_4$, such as by washing with alcohol or CdSO$_4$ solution. However, the $\text{Hg}_2\text{SO}_4$ then undergoes hydrolysis, an effect accelerated by contact with mercury. Nevertheless, the emf of a cell with solution made 0.2 M in $\text{H}_2\text{SO}_4$ remained constant to within 0.03 mV over a three-year period. The only defect was very slow evolution of hydrogen.

To meet an objection to his assumption that the hydrolysis of $\text{Hg}_2\text{SO}_4$ was accelerated by mercury, Hulett rotated a tube containing $\text{Hg}_2\text{SO}_4$, CdSO$_4$, and the saturated solution (33). Portions of the liquid were withdrawn at intervals and tested on a clean mercury surface against a cadmium amalgam, thus forming a complete cell. The emf, 1.01800 V after one day, rose to 1.01870 V after 12 days, then remained unchanged. After addition of mercury, rotation of the tube was resumed. Cell measurements made after 18 days showed that the emf had risen to 1.01955 V, indicating an increase of dissolved mercury. Presumably the basic salt, $\text{Hg}_2(\text{OH})_2\text{Hg}_2\text{SO}_4$, formed by hydrolysis, first remains in solution and then begins to precipitate. Then the concentration of dissolved mercury, increasing up to this point, begins to fall. Equilibrium is not reached until the hydrolytically formed $\text{H}_2\text{SO}_4$ reaches a concentration of 0.08 M. Extreme precautions were taken in an experimental study of equilibrium in the mercury-cadmium sulfate-water system (34). The hydrogen-filled cell system (Fig. 8) contained CdSO$_4$ solution and five cadmium amalgams of accurately known composition. Platinum wires $a$ through $e$ led to the amalgams. With the saturated (5.902 % cadmium) liquid amalgam $a$ as reference, the potentials of amalgams $b$ through $e$ were measured, sometimes for 70 days. In the range 1% to $1 \times 10^{-6}$ % of cadmium, potentials agreed with the theoretical values.

In 1911, Hulett again reported on the construction of Weston cells (35). He described alternative electrolytic methods for the preparation of $\text{Hg}_2\text{SO}_4$ and its incorporation into a paste. Modified designs of the Clark cell and the construction of an electrically heated 100-L kerosene thermostatic bath were also described. Other 1911 papers dealt with the clarification of a misunderstanding of the hydrolysis of $\text{Hg}_2\text{SO}_4$ (36) and the carryover of metallic contaminants when mercury is distilled (37). Also included were methods for the purification of mercury and details of an electrically heated mercury still.

Several years elapsed before the appearance of other papers on standard cells. This is not surprising, for Hulett and his students were occupied with many other projects, such as the electrolytic determination of metals, silver coulometry, determination of the atomic weight of cadmium, and the use of cadmium amalgam for the reduction of iron (III). Eventually, however, a study on the use of the double salt $\text{K}_2\text{SO}_4\text{ZnSO}_4\cdot 6\text{H}_2\text{O}$ in the Clark cell appeared in 1916 (38). The addition of one or the other of the constituent single salts elucidated the conditions under which the double salt is the solid phase. The specific heats of the reacting substances are necessary for thermodynamic calculations on standard cells applicable to temperatures below the usual range (39). The specific heats of CdSO$_4$, 8/3 $\text{H}_2\text{O}$ and of CdCl$_2$, 5/2 $\text{H}_2\text{O}$ were determined as functions of temperature be-
tween the limits 87° K and 274° K. Along with available data on other cell constituents, the results provided a means for a test of the Nernst heat theorem. Calculations led to an estimate of 1.072 V for the emf of the Weston cell at 291 K, while the observed value was 1.071 V. The calculated and observed values for the chloride-salt cell were 0.7426 V and 0.7236 V, respectively.

More than a decade was to elapse before Hulett resumed work on standard cells. Hulett took a leave of absence to spend a year as chief chemist at the US Bureau of Mines and then returned to Princeton in the fall of 1913. He remained as consultant on the chemistry of coal and other carbonaceous materials. In 1917, when the US entered World War I, Hulett crossed the Atlantic, to provide service (later, highly commended) as consulting chemist to the US Army in Europe. After his return he organized a research unit at Princeton for the Chemical Warfare Service, which led to a continuation of studies on carbonaceous materials, especially charcoal. In 1920 a fall resulted in a crippling concussion that handicapped him as an experimentalist (40). Nevertheless, his research continued; and in 1929 he had returned to the study of standard cells.

Other workers had shown that Weston cells prepared by working in an atmosphere of hydrogen or nitrogen exhibited enhanced constancy, although no proof was offered that the presence of oxygen causes irregularities. Hulett decided to search for any effect of oxygen on cell emfs (41). He set up approximately 40 cells, using various preparations of the Hg2SO4 depolarizer. In some cases, oxygen was bubbled through the electrolyte solutions, and these were sometimes acidified with H2SO4. After observations of emf over a one-month period, Hulett concluded that the presence of atmospheric oxygen during the preparation of the cells had no noticeable effect. The abnormalities of the emfs of cells with oxygen-saturated solutions disappeared after about a month. Hulett believed that the hydrolysis of the depolarizer was more detrimental than any effect of atmospheric oxygen. The hydrolysis of Hg2SO4, evidence for which appeared in the early 1800s, had been examined by others, as well as by Hulett. He decided to examine the changes in the composition of the solid phase and in pH when a vessel that contained mercury, Hg2SO4, and saturated CdSO4 was rotated for extended periods (42). The experiments led to the conclusion that the washing of the Hg2SO4 with water previously equilibrated with this salt and mercury enhances the constancy of a Weston cell. If this liquid is used to make the saturated CdSO4 solution, it is slightly acidic and retards the hydrolysis of the depolarizer. In jointly authored papers, Hulett reported on polarization (43) and hysteresis (44) in standard cells. Overheating during cell construction may be the cause of emfs that are initially high but decrease during a month or so. In 1930 Hulett examined the Weston cells that he and Carhart had constructed in 1903-4 (23). The emfs dropped slightly in the few years up to 1906 but since then had remained constant (45).

Five short coauthored papers were Hulett’s final contributions to the study of standard cells. The preparation of crystalline Hg2SO4 by reduction of HgSO4 by SO2 was described (46). The hydrolysis of Hg2SO4 was further examined, with the conclusion that, to prepare the normal (i.e., unhydrolyzed) depolarizer, a concentration of at least 1 M of H2SO4 was necessary (47). In a Weston cell, dissolved mercury species slowly diffuse from cathode to anode (48). To examine this, typical cells were unsealed, so that a tiny amalgamated platinum probe could be inserted. This permitted the determination of mercury concentrations at various points in the solution. A distinct concentration gradient was found in a four-year old cell but none in a cell that had been aged for 18 years. Presumably a steady state had been reached in the older cell. On equilibrating electrolytically prepared Hg2SO4 with saturated CdSO4 solution and mercury in bulk, a mercury (I)/mercury (II) concentration ratio of 55.3 was found (49). If very finely divided mercury was used, the ratio was larger. Thus the emf of a cell made with “very black mercurous sulfate” (i.e., containing micron-range mercury particles)
should be initially abnormal. A cell thus constructed had an emf of 1.017366 V, but this had risen nearly to normal after 32 days. As previously mentioned, Hulett had found evidence for the enhanced solubility of tiny particles, which dissolve and then enhance the size of the larger particles. Presumably a similar effect was operating here. Hulett’s final work with the Weston cell was, in a sense, an update on the use of such a cell as the working source in potentiometry (31), in which he described a cell that contained 5.4 L of solution and 5 kg of mercury. Such a cell could supply a current of 1 mA with a voltage drop of only 0.5 mV (50).

Although Hulett retired in 1935, he continued to direct research until increasingly bad health curtailed his activities. He died on September 6, 1955. Apart from his superb experimental skill and great scientific ability, he was highly revered by colleagues and students.

ACKNOWLEDGMENT

This work was partially carried out under the Research Fellowship Program of the Science Museum, London.

REFERENCES AND NOTES

LETTER TO THE EDITOR

February 25, 2000

Louis Rosenfeld’s excellent article, “Otto Folin and Donald D. Van Slyke: Pioneers of Clinical Chemistry” [Bull. Hist. Chem. 1999, 24, 40-47], did not include any mention of the pioneering electrophoretic method used by Drs. Van Slyke and Dole to study blood during World War II. Vincent P. Dole was the first person noted among those who had worked with Van Slyke and who later had achieved prominence. During 1943-1944, I was Dr. Dole’s technical assistant at the Rockefeller Institute for Medical Research.

Using electrophoresis apparatus to analyze blood supplied by Van Slyke from malaria patients (mostly military personnel attacked by the disease in the Pacific theater of war), we attempted to find out whether the blood of those with relapsing malaria was different from “normal” blood. Separation of proteins in the blood was achieved because of their different mobilities in an electric field. In evaluating the results, we concluded that the severity of the disease in patients with relapsing malaria might be reflected in measurements of the total protein concentration and the albumin:globulin ratio. These and other studies were published in the Journal of Clinical Investigation.

The Nobel Prize in Chemistry was awarded to Arne Tiselius in 1948 for his contributions to the development of the electrophoresis apparatus and its applications. Developed by 1937, it was first used in 1939 in the study of diseases. The early versions of the apparatus were very large; I recall they were about 3 meters x 1.5 meters x 1 meter. Each analysis required a day for completion. Today, 12-cm glass tubes can produce separation in 1 – 2 hours; capillary tubes in 10 minutes. Esther B. Sparberg, Professor Emerita of Chemistry, Hofstra University, Hempstead, Long Island, NY 11550
The activities of Morris Loeb (1863-1912) (Fig. 1) had been of concern for some time, in terms of surveys of the students of Wilhelm Ostwald (1853-1932) at the University of Leipzig (1,2). Fortunately, the recent appearance of an account of Loeb's remarkable career (3) has allowed the present paper to be largely restricted to Loeb's major work at Leipzig.

Loeb was a student at Harvard from 1879 to 1883, where he was greatly influenced by Wolcott Gibbs (1822-1908), a major figure in the development of electrogravimetry (4). Loeb was almost certainly initiated into the field of electrochemistry by Gibbs. He never forgot his mentor, who probably advised him to undertake further studies in Germany. In Berlin, under the supervision of August Wilhelm Hofmann (1818-1892), Loeb investigated the reactions of phosgene with various amidines (5,6). Loeb submitted his dissertation in March, 1887 and, his Ph.D. secured, moved to Leipzig, where Ostwald had been appointed Professor of Physical Chemistry. Obstwald's growing reputation may have been the reason for Loeb's decision. However, a move away from organic chemistry was in line with Loeb's feelings after his tenure in Berlin (3). A few years later, Max Le Blanc (1865-1943) also went from Hofmann's laboratory to that of Ostwald. Le Blanc, who later clarified our understanding of decomposition voltages of solutions of acids, bases, and salts, nearly gave up chemistry after obtaining his Berlin Ph.D. (7). Fortunately, he changed his mind!

At Ostwald's suggestion, Loeb studied the apparent molecular weight of iodine in various solvents (8,9). He then began to work with Walther Nernst (1864-1941) (Fig. 2) on ionic velocities in solutions. Nernst, who received the Nobel Prize for Chemistry in 1920, was then beginning his highly successful career as Ostwald's first academic assistant. In fact, Nernst and Loeb both obtained their doctorates in 1887. Nernst's advisor was the Würzburg physicist Friedrich Kohlrausch (1840-1910). With such a mentor, Nernst was almost certainly the initiator of the joint project.
When a solution is electrolyzed, equivalent quantities of ions are discharged at the respective electrodes. This might seem to imply that the change in electrolyte concentration around the anode would be the same as around the cathode. In fact, the changes are usually dissimilar. In 1853, Johann Wilhelm Hittorf (1824–1914) (Fig. 3) had shown that, when a current is passed through a solution of an electrolyte, the anions and the cations migrate toward the respective electrodes with unequal velocities. In three papers, the last of which appeared in 1859, he described the measurement of the transference numbers (10). These are the fractions of the total amount of electricity carried by the anion and by the cation, respectively. In 1879 Kohlrausch, following up on Hittorf’s work, introduced the concept that the equivalent conductivity \( l \), of an electrolyte is the sum of the ionic conductivity of the cation, \( u \), and that of the anion, \( n \) (11). Thus:

\[
l = u + v. \tag{1}
\]

Because \( u \) and \( v \) are proportional to the mobilities of the respective ions, the transference number, \( n \), of the anion and that of the cation, \( 1-n \), can be expressed as:

\[
n = v/(u + v) \quad \text{and} \quad (1-n) = u/(u + v) \tag{2}
\]

With a minor exception, the symbols are those used by Loeb and Nernst (12, 13).

Transference numbers can be determined in various ways (10). In the Hittorf method, a chemical coulometer is connected in series with an electrolysis apparatus which, for example, contains \( \text{AgNO}_3 \) solution of known weight composition \( y_1 \). Appropriate electrodes, silver in this case, are located such that changes in the composition of the solution are confined to the regions around each electrode; the intermediate portion of the solution should remain unchanged.

Consider a hypothetical extreme case where \( n = 1 \); i.e., all of the current is carried by the anion. Then the concentration of \( \text{Ag}^+ \) in the anode region should rise to \( y_1 + y_2 \), where \( y_2 \) is the amount of \( \text{Ag}^+ \) formed by \( x \) coulombs of anodic dissolution. At the other extreme, when \( n = 0 \), the \( \text{Ag}^+ \) concentration in A should remain at \( y_1 \). In a real case, the final concentration will lie between the extreme limits, so that \( 1 > n > 0 \). The effect can be expressed in another way: The ratio of the weight of the metal deposited to the amount of metal lost by the fluid around the cathode (or its equivalent, the amount gained around the anode) represents the share of the negative ion, the anion, in the total movement (13).

Loeb and Nernst pointed out that Hittorf had needed fairly concentrated solutions to obtain sufficiently ac-
curate analyses. These workers used the apparatus shown in Fig. 4 for their projected study of dilute solutions of various silver salts. The design allowed the apparatus to be mounted in a thermostatic bath. The anode, near the bottom of compartment A (where the solution will become more dense), is the coiled end of a silver wire that is sealed into a thin glass tube. The free end of the wire passes through a short tube in the stopper and then through a piece of rubber tubing that is normally closed by a spring clip. A silver foil roll forms the cathode in compartment B, which has a similar spring clip closure. The bulb-like bottom of B traps particles of silver that may fall from the cathode. With the clip on A closed, gentle aspiration at the tube on B allows the apparatus to be filled through tube C to the level shown. After Tube C is capped, the apparatus is mounted in the bath and brought to the desired temperature. After the electrolysis, C is uncapped and, by gentle blowing at tube B, suitable portions of the solution are delivered into weighed vessels for subsequent titrimetric determination of silver. In some experiments the total electricity was small and would have deposited less than 20 mg of silver in the coulometer. In such cases, this total was obtained as the product of run time and the current, which was kept constant. This current was measured as the voltage drop across a standard resistor.

After making corrections for minor changes in the anolyte density and in the concentration of the intermediate portion of the solution, Loeb and Nernst found 0.524 as the transference number \( n \) of NO\(_3\)\(^-\) in approximately 0.1M AgNO\(_3\). They repeated the determination at various temperatures and dilutions. In agreement with Hittorf, they showed that considerable dilution did not change the value of the anion transference number. The numbers for various other silver salts were then determined in a similar manner. The demonstration that transference numbers could be determined at low concentrations was not the main aim of Loeb and Nernst's research. They were more interested in the validity of Kohlrausch's conductivity equation (Eq. 1), which was based on the total amount of electrolyte. The fact that some of Kohlrausch's results failed to support this relationship proved to be the impetus for the work undertaken.

The formulation of the ionic theory and Ostwald's studies on the conductivities of numerous electrolytes in dilute solutions (14) provided strong support for the view that only the ionized portion of a solution contributes to the conductivity. Thus Kohlrausch's concept is strictly true only when the electrolyte is completely dissociated, i.e., when the concentration approaches zero. The uni-univalent silver salts studied by Loeb and Nernst are strong electrolytes; and at very low concentrations their molecular conductivities, \( l \), are close to the maximum values, \( l_0 \), which apply to zero concentrations (15). Using the approach of Kohlrausch, Loeb and Nernst assumed that the \( l_0 \) value for a given salt could be estimated from the measured value of \( l \) at a concentration of 8 x 10\(^{-4}\) M, the lowest in their studies. A further assumption was that the transference numbers, which had been shown to be constant over the concentration range 0.025 to 0.01 M, would have the same values at zero concentration. Then the product of the transference number, \( (1 - n) \), of Ag\(^+\), the common ion in the series of salts, and the \( l_0 \) value of the corresponding salt, would be the ionic conductivity of this ion at 25\(^\circ\) C. The validity of this approach was upheld by the results of experiments with eight different silver salts, where values of this product ranged from 585 to 597 (average 591). The conductivities, which were actually measured...
by Nernst, were based on that of mercury, which was assigned unit value. Thus the given numbers do not agree with modern values. From data obtained at 25°C and 0°C, these workers calculated the temperature coefficients of the $\Delta$ values of their salts and of the ionic conductivities.

Although attainable with high accuracy, conductivity measurements indicate the molar or equivalent values, 1, for the electrolyte, and not the individual contributions of the anions and cations. However, knowledge of the relevant transference number allows calculation of the respective ionic conductivities from conductivity data, as was shown by Loeb and Nernst. Their work was a notable step in the then rapidly developing field of electrochemical phenomena and their interrelationships.

Loeb's activities after his return from Leipzig have been well documented (3). As professor at New York University, his publications, although not extensive, ranged widely. Examples are the use of aniline to absorb cyanogen in gas analysis, molecular weight determination, the ionic theory, the adducts of sodium iodide and various alcohols, and an attempt to find any effect of magnetism on chemical reactivity. He was devoted to the profession of chemistry and strove for its betterment. When he became Chairman of the New York Section of the American Chemical Society in 1909, his inaugural address naturally referred to the satisfactory growth of the section (16). He then turned to the lack of public recognition of the value of the industrial chemist, and how this situation might be improved. Noting that American chemists were often handicapped by lack of chemicals, many of which had to be imported, he suggested the establishment of a "museum," from which less common chemicals could be issued or loaned. His far-reaching idea was that the "museum" might even prepare official standards if given suitable staffing.

Loeb remained active nearly to the end of his life, so that his death, on October 8, 1912, came as a shock to those who knew him.

ACKNOWLEDGMENT

This work was partially carried out under the Research Fellowship Program of the Science Museum, London, and the research facilities of the Chemical Heritage Foundation, Philadelphia.

REFERENCES AND NOTES

In the scientific discovery process, one tends to focus on the "Great Name" and ignore the co-researcher who made the actual discovery or contributed significantly to the discovery. The first detection of pulsars was a classic example. The observation was made by a graduate student, Jocelyn Burnell, but it was her supervisor, Anthony Hewish, who received the Nobel Prize for the discovery (1). In the first decades of the 20th century, this lack of attribution to the lab-bench researcher has had a significant effect of hiding the contributions of women scientists, for few were able to break through the "glass ceiling" and attain recognition as prime researchers.

Atomic science was one area where women scientists played active though subordinate roles (2) (with the exceptions of Marie Curie and Lise Meitner). For example, Ernest Rutherford’s first research assistant was a woman—Harriet Brooks. We have reported elsewhere on her career, including the discovery of the recoil of the radioactive atom (3). In this paper, the focus will be on the contributions of three women to the early work on isotopes: Stefanie Horovitz, Ellen Gleditsch, and Ada Hitchins. But first, it is necessary to review the groundwork that made the discovery of the existence of isotopes possible.

**Background**

Present-day scientists tend to forget that, for the early history of chemistry, atomic weight was of supreme importance. For example, the value of the atomic weights of elements was the prime focus of the Karlsruhe Congress of 1860 (4). Thus chemists were inculcated with the view that the foundations of chemistry depended upon the unique value of the atomic weight of each element—and on the immutability of the elements themselves.

The first crack in the façade of traditional chemistry came with the discovery of radioactive transformations (5). The various species in the decay sequences were identified by names linked to that of the parent. For example, thorium decayed to mesothorium I, to mesothorium II, to radiothorium, to thorium X, and so on. At the time, each of these species was believed to be a new and unique element. It was McCoy and Ross in 1907 who provided the next piece in the puzzle with the statement that (6):

> Our experiments strongly indicate that radiothorium is entirely inseparable from thorium by chemical processes.

Examples of chemically nonseparable pairs (and groups) of radioactive elements began to accumulate very rapidly. Rather than use the cumbersome phrase ‘radio elements chemically nonseparable,’ Soddy suggested that the term ‘isotope’ be introduced (7).

> It was the Fajans-Soddy Group Displacement Law that provided the next step in the puzzle (8). In radioactive decay, loss of an α-particle resulted in a two-step shift to the left in the periodic table with an accompanying atomic weight loss of four units, while loss of a β-particle resulted in a one-step shift to the right with a negligible change in atomic weight. Starting with the atomic masses of uranium and thorium, Soddy calcu-
lated the expected atomic weights of the lead produced from their respective radioactive decay as very different from the 207.2 of ‘normal’ lead (9). To chemists, finding samples of lead that had ‘abnormal’ atomic weight would be a confirmation of the existence of isotopes and proof of the group displacement law. In particular, lead from the decay of uranium-238 was predicted to have an atomic weight of about 206 while that from the decay of thorium-232 was expected to have an atomic weight of about 208. It is the contributions of three women scientists to the discovery of lead with ‘abnormal’ atomic weights that will be the focus of this study (10).

To accomplish this task, researchers needed lead-containing samples from uranium or thorium ores. In addition, for the results to be accepted among the scientific community, the researchers themselves had to have credibility in the field of the determination of atomic weights to high precision. Although Soddy and his collaborator, Henry Hyman, and Maurice Curie, nephew of Marie Curie, both reported atomic weights of radioactive-origin lead that were significantly different from that of normal lead (11), neither of those reports was sufficiently reliable in the eyes of analytical chemists. As Badash has commented (12):

Fajans soon realized that the task [of precise atomic weight determination] required such accuracy that only the results of recognized experts would be widely accepted. Soddy persisted in his efforts, only to have his results viewed sceptically in some quarters.

The world’s leading expert on the measurement of atomic weights was Theodore William Richards of Harvard (13), but almost as high in estimation were his two former students, Gregory Paul Baxter, also of Harvard, and Otto Höngschmid at the Radium Institut in Vienna (14).

Stefanie Horovitz

Höngschmid had the talent and also the opportunity, for the major source of radioactive ores at the time was the mine at St. Joachimstal in Austria (15). Much of his work was accomplished with his research student, Stefanie Horovitz. Horovitz was born in Warsaw on April 17, 1887, her family moving to Vienna about 1890 (16). She graduated from the University of Vienna in 1914 with a doctorate in organic chemistry, although she seems to have started as a research worker at the Radium Institute of Vienna with Höngschmid in late 1913. Höngschmid was actually affiliated with the Technical University of Prague from 1911 to 1918, but he maintained research facilities in Vienna.

Horovitz’s initial task was the time-consuming separation of lead from the residues of the radioactive ores after the radium had been extracted. This was followed by the demanding gravimetric procedures to the nearest hundred thousandth of a gram. The first report by Höngschmid and Horovitz provided a value of 206.736 for the atomic weight of lead from the St. Joachimstal mine, compared to 207.190 for ‘normal’ lead (17). Such a significant difference from a respected analytical laboratory was the first definitive evidence that atomic weights were not necessarily invariant. As a result of its importance, this paper by Höngschmid and Horovitz was chosen by Henry Leicester as one of the crucial publications in chemistry in the first half of the twentieth century (18). The two researchers were dedicated to their work, as is apparent in a letter from Höngschmid to Lise Meitner (19):

... Miss Horovitz and I worked like coolies. On this beautiful Sunday we are still sitting in the laboratory at 6 o’clock.

Subsequently, Höngschmid and Horovitz analyzed new samples from St. Joachimstal as well as samples from two other mines: pitchblende from German East Africa; and bröggerite from Norway. These results were even
more convincing, giving values as low as 206.046 (20). A difference of over one mass unit could not be explained by experimental error. There clearly were significant differences in the atomic weight of lead, depending upon source.

Hönigschmid and Horovitz made a second contribution to the isotope story. Boltwood had claimed the discovery of another radioactive element, ionium (21). Most chemists accepted the existence of this element, it even being assigned a symbol, Io. However, it was the atomic weight and spectroscopic analyses performed by Hönigschmid and Horovitz that showed ionium to be no more than an isotope of thorium, making thorium only the second element for which isotopic behavior had been proven at that time (22). These were the last publications of Horovitz. Many years later, Horovitz's fate was discussed in an exchange of letters between Kasimir Fajans and Elizabeth Róna (23). In the last of the correspondence, Fajans commented (24):

You probably have not received any information from Vienna about the fate of Dr. Stephanie Horovitz. I learned about it from a mutual relative at Warzawa. Stephanie moved there after World War I and after her parents had died in Vienna to join her married sister. She was not active in chemistry and both were liquidated by the Nazis in 1940.

Ellen Gleditsch

Concurrently the master himself, T. W. Richards, had launched an investigation into what he called a subject of (25):

... peculiar and extraordinary interest, because it involves a readjustment and enlargement of many rather firmly fixed ideas concerning the chemical elements and their mutual relations, as well as the nature of atoms.

His first report described lead samples with abnormally low atomic weights, the lowest value of 206.40 coming from a sample of uraninite from North Carolina (26). This particular lead sample was noted in the data table as being provided by Gleditsch. This was Dr. Ellen Gleditsch, who at the time was working with Bertram Boltwood at Yale. In the paper, Richards stated that this "most valuable" of the samples had been supplied by Gleditsch as lead chloride; thus Gleditsch played an active role in the discovery process by performing the extraction of a pure lead salt from the uranium ore. In a subsequent paper (27) Richards reported atomic weights of 206.12 and 206.08 for lead from uranium ore samples obtained from Norway. He added that these two samples "of especial value and significance (27)" were both obtained from Ellen Gleditsch, who had returned, by then, to her native country of Norway. These values were so close to that predicted by Soddy for pure lead produced at the end of the uranium decay series that the group displacement law could no longer be in doubt.

Gleditsch was born on December 29, 1879 in Mandal, in southern Norway (28). After obtaining a pharmacological qualification, she became a research assistant at the University of Kristiania (now Oslo), being unable to afford to enroll as a university student. From 1907 to 1912, she worked with Marie Curie in Paris, where she received the qualification of Licenciée ès Sciences. In 1913, Gleditsch received a fellowship to work with Bertram Boltwood at Yale (29). Although he was opposed to women researchers, Gleditsch arrived before he had a chance to reject her application. Her
work on the half-life of radium (30) so impressed Boltwood that he became a warm friend. While at Yale, she received an invitation from Richards to visit him at Harvard, and it was possibly during the meeting that she agreed to supply the lead samples that proved most crucial. About this time, she was awarded an honorary Doctor of Science degree from Smith College, Northampton, Massachusetts.

Gleditsch was to have a very successful career at the University of Oslo, being hired initially as a docent and, by the time she retired, becoming a professor of chemistry. She spent most of her nonteaching time in Paris. For example, during World War I, Curie pleaded with Gleditsch to return to Paris to supervise the radium extraction facilities. This journey involved a dangerous voyage across the U-boat ridden North Sea; and Ernest Rutherford, a friend of Gleditsch, arranged for a security clearance for her stopover in England on the way. Her teaching demands at Oslo were very heavy, leaving little time for research. She did manage some, however, particularly during her many sojourns in Paris (31). Following Richards’ work, she reported on the atomic weight of lead in another mineral sample from Norway, this one giving a value of 206.17 (32). Then she commenced work on a study of the atomic weight of chlorine. Irène Curie had claimed to find a salt sample in which the atomic weight of chlorine was above the normal value (33). Gleditsch and coworker B. Samdahl showed that the value resulted from a contamination with bromide ion (34). Nevertheless, Gleditsch pursued a more thorough study of possible variations in the atomic weight of chlorine, some of the research being performed with her sister, Liv Gleditsch (35). The results showed that, unlike lead, the average atomic weight of chlorine was invariant with the mineral source. Gleditsch maintained an active life, becoming president of the International Federation of University Women, and during World War II, being an active member of the resistance. She died at the age of 89 on June 5, 1968.

Ada Hitchins

The search for the higher atomic weight value of lead derived from thorium-232 decay was pursued by Hönigschmid (36) and by Soddy. Soddy, in the report of his definitive result of 207.74, noted the contribution of his research student, Ada Hitchins, for the separation and analysis work (37). The sample used by Hönigschmid was provided by Soddy (37); thus both teams probably relied on Hitchins’ extractions. Born in Devon, England (38) in 1891, Hitchins graduated with a B.Sc. from the University of Glasgow in 1913. She commenced research with Soddy during her last undergraduate year; and when Soddy moved to the University of Aberdeen in 1915, Hitchins accompanied him, obtaining a position as Carnegie Research Scholar. It was during this period that Hitchins performed the extraction and analytical work on the lead samples from thorium ores. In addition, Hitchins took over the research on protactinium of Soddy’s other student, John Cranston, when the latter was drafted for World War I (39).

In 1916 Hitchins herself was drafted to work in the Admiralty Steel Analysis laboratories (40). She rejoined...
Soddy in 1921, by which time he had moved to Oxford University. Despite a Nobel Prize in Chemistry, Soddy had great difficulty in attracting graduate students to work with him (41); thus Hitchins played a crucial role in Soddy’s research program. Initially appointed as technical assistant, she was promoted to private research assistant in 1922. Soddy noted (42):

... she has also charge of my radioactive materials
... and has worked up considerable quantities of radioactive residues and other materials for general use.


**Commentary**

Scientific research in the early decades of the 20th century is commonly regarded as a male preserve, except for that of Marie Curie. Here, three women scientists have been identified who played significant roles in the discovery of the existence of isotopes, one of the most crucial scientific findings of the period. In an era when women scientists were largely confined to support roles (43), it is important to correct the historical record and acknowledge the contributions of Horovitz, Gleditsch, and Hitchins.

**REFERENCES AND NOTES**

2. It is noteworthy to recall that Marie Curie was a lecturer at the teaching college at Sèvres, her ability to do research being primarily a result of her egalitarian marriage to Pierre. She emerged from Pierre’s shadow only following Pierre’s untimely death, when she was judged to be his only suitable heir at the Sorbonne. See, for example: R. Pflaum, *Grand Obsession: Madame Curie and Her World*, Doubleday, New York, 1991 and S. Quinn, *Marie Curie: A Life*, Simon & Schuster, New York, 1995.
7. It is from the placement of different species in the same box in the periodic table that iso-topos — 'same place' — derives. The origin of the name is described by Alexander Fleck: “Up to 1913 we used the phrase ‘radio elements chemically non-separable’ and at that time the word isotope was suggested in a drawing-room discussion with Dr. Margaret Todd in the home of Soddy’s father-in-law, Sir George Beilby. Dr. Todd was an Edinburgh trained medical doctor and was a writer of some distinction under the name of Graham Travers. The readiness and etymological accuracy with which she produced isotopes is a standing testimony to her practical knowledge of the Greek tongue.” A. Fleck, “Frederick Soddy,” *Biogr. Mem. Fellows R. Soc.*, 1957, 3, 208.
9. ‘Natural’ lead has an isotopic composition of Pb-204 (1.5%), Pb-206 (23.6%), Pb-207 (22.6%), and Pb-208 (52.3%).
12. Ref. 8, p 251.


24. Kasimir Fajans to Elizabeth Rôna, August 31, 1963, Bentley Historical Library, University of Michigan, Ann Arbor, MI.


29. Gleditsch had probably developed a desire to work with Boltwood because of her earlier studies on the ratio of uranium and radium in ores in which Boltwood’s research is extensively cited. See: E. Gleditsch, “Sur le rapport entre l’uranium et le radium dans les minéraux actifs,” *Le Radium*, 1911, 8, 256-273.


31. On a visit to Paris in 1920, she was assigned the task of supervision of the Curie research group while Marie Curie was touring South America.


39. F. Soddy and J. A. Cranston, “The Parent of Actinium,” *Proc. R. Soc.*, Part A, 1918, 94, 385-405. The paper notes: “… the experiments were continued for a time by Miss Ada Hitchins ... Her valuable assistance has contributed very materially to the definiteness of the conclusions that it has been possible to arrive at.”


42. F. Soddy, undated reference for A. F. R. Hitchins, Oxford University Archives.


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ZOROASTER AND THE THEORY OF FOUR ELEMENTS

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Introduction

The concept of four elements: air, water, earth, and fire, thought to have its origin with the Greek philosopher Empedocles about 440 B.C., held sway for many centuries. Aristotle (384-322 B.C.) added to this concept that the properties of substances are the result of the simultaneous presence of certain fundamental properties. The Aristotelian doctrine was therefore concerned not with what modern chemists call elements but with an abstract conception of certain contrary properties or "qualities," especially coldness, hotness, dryness, and moistness, which may be united in four combinations: dryness and heat (fire), heat and moisture (air), moisture and cold (water), and cold and dryness (earth) (Fig. 1). Aristotle and his followers believed that all substances are composed of these four elemental states of matter and this is usually cited in history of chemistry books (1,2). Indeed there is no history of chemistry book comparable in depth and breadth to that of Partington (1), who devoted 370 pages to the early history, fully documented by thousands of references. He wrote about the Greek philosophers, about medicine, gnosticism, magic, astrology, and many other topics. However, he devoted only two pages to the earlier Persian philosopher Zoroaster and his religion. Not surprisingly, perhaps, the idea of four "sacred" elements is absent.

A typical argument is presented as follows (3). According to Aristotle, the basis of the material world was a prime matter, which had only a potential existence until impressed by "form." By form he did not mean shape only, but all that conferred upon a body its specific properties. In its simplest manifestation, form gave rise to the "four elements," air, water, earth, and fire which are distinguished from one another by their "qualities." In each element, one quality predominates over the other: in earth, dryness; in water, cold; in air, fluidity, and in fire, heat. None of the four elements is unchangeable. They may pass into one another through the medium of that quality which they possess in common. Thus fire can become air through the medium of heat; air can become water through the medium of fluidity, and so on. Another example often cited to show that matter is composed of these four elements is the following. If water in a container is sub-

![Figure 1. The four elements as represented in almost all chemistry and history of chemistry books.](image-url)
jected to fire, it becomes air (vapor) and earth (the dissolved residue remaining).

This legacy of Greek science held sway during the Medieval Renaissance and Early Modern eras in western Europe; but beginning in the seventeenth century, a number of natural philosophers began to challenge the Aristotelian view of matter. Johann Baptista van Helmont (1580-1644) argued that all substances, except air, were ultimately derived from water. To demonstrate this he made his quantitative experiment with a small willow tree, an experiment that took five years, and he concluded that the tree had grown entirely from the water that he had supplied to it during this long period. His theory had one great patron, Isaac Newton (1642-1727) who accepted it and referred to it in the Principia (London, 1687). Helmont’s most significant work was, however, his recognition of the material nature of what he called gas, a generic name that he used for those products of chemical reactions that had been previously regarded as merely spiritual and immaterial. He explained to chemists that the many familiar and destructive explosions that shattered their glass apparatus when they experimented on reactions in sealed or closed vessels were due to the release of “a wild spirit” or “gas.” In a simple way he observed differences between gas from various sources but, as he did not isolate any gas, his distinctions were not precise; and he sometimes confused one gas with another. He had, however, advanced the chemistry of his time by demonstrating that these substances were material.

In 1661 Robert Boyle (1627-1691) published The Sceptical Chymist, a book in which he discussed the criteria by which one can decide whether a substance is or is not a chemical element. He concluded that the Aristotelian elements and three principles commonly accepted in his time cannot be real chemical elements since they can neither compose nor be extracted from substances. The theory, however, was so influential that even Joseph Black (1728-1799) was still teaching his classes that water was transmutable into earth.

The works of Aristotle and the other Greek philosophers are numerous, and the books commenting on these works are extensive. Few of these commentary works, however, trace the influence of the oriental thought in general and the Persian in particular, on the philosophy of the Greeks. It also seems that the Theory of Four Elements is only a minor contribution by the Greeks as compared to their other philosophical concepts (4). Afnan (5, 6) for example, devotes only a few lines to fire. He mentions that Heraclitus considered fire to be the primary physical substance, from which other substances sprung, and into which they merged (5):

All things are an exchange for Fire, and Fire for all things, even as waves for gold and gold for waves.

The very exigence of Fire depends on this strife and tension.

Further, he mentions that Heraclitus regarded justice as the balance or equilibrium that prevailed between contending forces. It characterized the “ever living Fire, with measures of its kindling, and measures going out.” Justice, therefore, was maintained by identity in difference and unity in diversity, and in that respect was symbolised by Fire. Thus Fire became the crucible, or rather the principle of constant change, in which opposites meet and from which they emerge.

Origin

The origin of the Four Element theory, however, seems to be Persian and not Greek. It was the Persian prophet Zarathustra (600-583 B.C.) whose name was corrupted by Greek writers to Zoroaster about two centuries before Aristotle. This Zoroastrian concept of four elements has a different perspective which makes more sense than the Aristotalian. According to this prophet, air, water, earth, and fire are “sacred” elements (7-11). Humans and animals need air to breathe, water to drink, fire to cook food, and earth to grow plants for their survival. Earth, air, and water are to be kept free from defilement. To till the field and raise cattle are parts of one’s religious requirements. Rain water when it falls in abundance to irrigate the fields is a blessing from God. When it is scarce, famine may result. In a country like Iran (Persia) where earthquakes are frequent, their damage not only causes panic and loss of lives but it can be interpreted as a warning message from an angry God.

Fire, on the other hand, had a more complex significance. It is the symbol of divinity. It is not worshipped as thought by many writers who describe a Zoroastrian temple (Fig. 2). It is fed daily by the attendant priests with pieces of sandalwood. The worshipers come individually at any time they wish. Inside the entrance each follower washes the uncovered parts of his body, recites a prayer, and then, removing his shoes, proceeds barefooted through the inner hall to the threshold of the fire chamber, where he gives the priest his offering of sandalwood and money and receives in return a handful of ashes from the sacred urn, which he rubs on his forehead and eyelids. Bowing toward the fire, he offers
prayers and then retreats slowly backward to his shoes and returns home. These four elements, therefore, have nothing to do with the chemical elements.

According to Vuibert (12), Magism was the religion of the various Scythic tribes which inhabited the mountain range of Armenia, Azerbaijan, Kurdistan, and Luristan. Its chief objects of worship were air, water, earth, and fire. It was to these elements, to the actual material things themselves, that adoration was paid. Fire, as the most subtle and ethereal principle, was held in the highest reverence. On fire altars, erected in temples on top of lofty mountains, the sacred flame was ever kept burning. To a large degree, Magism supplanted the original creed of Zoroastrianism. The Magi religion was characterized by a belief in a divinely authorized priesthood. Its priests seem to have held their office by hereditary succession. They claimed not only a sacred and mediatorial character, but also supernatural prophetic powers. They explained omens, expounded dreams, and predicted future events. Their dress was imposing, their ceremonial magnificent, and their influence over people and kings unbound. They were not only the keepers of sacred things, the learned of the people, the philosophers and servants of God, but also astrologers. No transaction of importance took place without or against their advice. An unspecified number of these wise men came to Bethlehem to worship the newborn Jesus when they saw his star in the east. They offered him gold, frankincense, and myrrh, the most treasured commodities at that time. The Magi were also mentioned by Herodotus. Incidentally, the word "magic" is derived from the Magi and is related to superstition. The region where the Magi lived was an ancient metallurgical center, famous for using fire to melt rocks to produce copper, bronze, iron, and gold.

Pliny the Elder (23-79 A.D.) wrote the following statement about fire (13):

We cannot but marvel at the fact that fire is necessary for almost every operation. It takes the sands of the earth and melts them, now into glass, now into silver, or minium or one or other lead, or some substance useful to the painter or physician. By fire minerals are disintegrated and copper produced: in fire is iron born and by fire is it subdued: by fire gold is purified: by fire stones are burned for the binding together of the walls of houses ... Fire is the immeasurable, uncontrollable element, concerning which it is hard to say whether it consumes more or produces more.

Zoroastrianism

According to Zoroaster there is one god Ahura Mazda or the "Wise Spirit" and one evil (Ahriman). Fire had the "Wise Spirit." The result of this dualistic conception of the universe is a continuous warfare going on between the two hostile camps. All creatures, even vegetables, belong to one or another of these camps. All dangerous, noxious, poisonous animals and plants are evil by their very nature. This warfare will go on to the end of time when the Good triumphs and the Evil is annihilated. According to Zoroaster's teachings, a general resurrection will take place at the end of the present world. The good and evil will then be subjected to an ordeal of fire and molten metal. By this fiery test the evil will be made known by their terrible burning, but the righteous will find the fire kindly and the molten metal harmless. The world's history is therefore nothing but the story of the contest between good and evil which shall endure for 12,000 years, divided into four equal periods of 3,000 years. The final aim of Zoroaster's system is to assure world perfection by the individual's adoption of the right path.

A curious practice, however, arose in the disposal of the dead. No bodies could be burned, buried, or thrown into the water, as thereby defilement to the air, soil, and water would result. They were consigned to
high places called a "Tower of Silence" or "Dakhma." These are shallow pits in which the corpses are laid in the central enclosure, where they are devoured by vultures (Fig. 3). This results in the stripping of the corruptible flesh from the bones of the dead without contamination of the soil.

Zoroaster was highly venerated in antiquity. Darius the Great (549-485 B.C.), who reigned from 521 to 485 B.C., and his successors were loyal followers of the prophet. The Greeks and Romans were much impressed by what they heard of him and his religion. This is evidenced by the numerous references to him in the extant literature and by the fact that Plato was reportedly prevented, shortly after the death of Socrates, from going to Persia to study Zoroastrianism first hand by the outbreak of the War of Sparta with Persia in 396 B.C. Zoroaster was also mentioned by the Egyptian alchemist Zosimos (250-300 A.D.). While Zoroastrianism was the national religion of Persia, it spread to Armenia, Cappodocia, and the entire Near East. Cambyses first, then Darius, and later Xerxes, turned to world conquest. They marched into Egypt and then toward Europe. Xerxes invaded Greece, and perhaps only the disaster of Salamis prevented Zoroaster's faith from becoming a major religion of the Western World.

In 538 B.C. the Persian King Cyrus captured Babylonia. The Jews exiled in that land by Nebuchadnezzar came directly under the suzerainty of the Zoroastrians until the Persian empire fell under Alexander the Great in 330 B.C. The loss of the sacred books is attributed by the followers of Zoroaster to the invasion in 330 B.C. of Alexander, who burned the palace library at Persepolis. With the Sassanides the national religion was restored, and the priesthood became strongly organized with unlimited power. The head of the hierarchy was next in power to the king. When the Arabs conquered Persia in 636 A.D., they overthrew the religion of Zoroaster. Today only a few followers of the prophet are found in Iran, mainly in the ancient city of Yazed. Many followers escaped to Bombay, where they are known as the Parsees.

The first scholar to make the language and the contents of the sacred books of the Parsees known to Europe was a young Frenchman, Anquetil du Perron, who went to India in 1754 for this purpose. On his return in 1771 he was able to give to the world the first translation of the Avesta, the sacred book of the Zoroastrians. There are many striking resemblances between Zoroastrianism and Judaism and Christianity. Ahura Mazda, the Supreme Ruler with the attributes of omnipresence, eternity, and creative power which he employs through his "Holy Spirit" with the best of angels and archangels on his side, suggests the Old Testament Yahweh and his magnified manifestation in the Gospels. So Ahriman reminds one of Satan. There are also close parallel ideas as to the Messiah, the resurrection of the dead, and everlasting life. Zoroaster received his law on the "Mountain of the Two Holy Communing Ones," as did Moses on Sinai. There are six periods of creation in the Avesta like the six days in Genesis and a single human pair, Moshya and Moshyana, like Adam and Eve. The deluge of the Bible has its counterpart in the devastating winter. Shem, Ham, and Japhet are recalled by the three sons in the Avesta. Similarities in ritual details are many and have been studied at length. The larger number of
Figure 5. The four elements as illustrated in Mylius, *Philosophia Reformata*, Frankfurt 1622 (14)

Critics trace these analogies to the influence exerted on Judaism by Zoroastrianism during the period of exile, if not earlier. On the other hand, the contrary view is also advocated. Perhaps also fire in the form of a burning candle and water blessed by the Christian priest are two rituals in the church that may be traced back to the time of Zoroaster.

**The Four Elements in Art and Alchemy**

The concept of four elements survived for at least two thousand years. Seventeenth-century engravings attest to the influence of this theory. For example, the Flemish artist Crispijn van de Passe (1564-1637) depicts allegorical figures in decorative scenes symbolizing the four elements (Fig. 4). Fire (ignis) holds brands and a burning coal. Water (agua) wields a flowing pitcher while behind her a fisherman plies his trade; Earth (terra) carries a cornucopia of the Earth’s fruits while a hunter pursues its beasts. Air (aer) strides across the clouds, birds flying around him, the four winds blowing. Figure 5 shows the four elements as illustrated in a 1622 engraving (14). Each element was given a symbol based on a triangle; the alchemists used these symbols until the reform of Lavoisier and Berzelius. Figures 6 and 7 are representations of the elements from Michelspecher’s book dated 1654, while Figure 8 shows Roger Bacon pointing to a pair of scales in perfect equilibrium on which are being weighed water and fire, from a book published in 1617 (15). This may be an indirect reference to the Zoroastrian faith: the balance between the good and the evil.

**Epilogue**

The alchemists believed that water, on being heated, was converted at least in part into earth. This was the result of the observation that on boiling water some residue was always formed (from impurities in solution). This problem faced Lavoisier when he was asked to improve the supply of drinking water to Paris. At that time no chemical method for ascertaining the purity of water was available, and the only way was to determine the density of water by hydrometer. After studying all that had been published on the conversion of water into the earth Lavoisier concluded that it was not satisfactory and decided that further experiment was necessary. From October 24, 1768 to February 1, 1769 he heated a known mass of water, as pure as could be obtained by repeated distillation, in a weighed sealed glass vessel, the alchemist’s pelican, in which a liquid could be continuously distilled in itself. At the end of this 100-day experiment, the total weight of the unopened vessel and its contents was the same as it was at the beginning. He

Figure 6. Engraving dated 1654 from Cabala, *Speculum artis et matura in alchymica* by S. Michelspecher showing the seven steps leading to the Philosopher’s Stone, some alchemical symbols, and the four elements ignis, aeris, agua, and terra (15)
then weighed the pelican after opening it and pouring the contents into another vessel. Some earth had been formed. However, he found that the weight of the pelican had decreased by an amount nearly equal to the weight of the earth obtained. He therefore concluded that the earth had been produced by the erosive action of the water on the glass, not by the conversion of water into earth. This refuted the theory held for centuries and was accepted by many of his contemporaries.

The studies by van Helmont, John Mayow (c. 1641-1679), and Robert Hooke (1635-1703) suggested the existence of different kinds of air. Boyle’s studies that resulted in his famous law also undoubtedly convinced skeptics regarding the uniformity of air, since gases in general followed the inverse pressure volume relationship. The difficulty of collecting gases in a reasonably pure state discouraged studies of air. It was the English biologist Stephen Hales (1677-1761) who observed that plants absorb air through their leaves. He invented the pneumatic trough, a simple device for collecting gases over water, that allowed him to collect gases formed from different processes such as fermentation, calcination of limestone, heating of wood, etc. He was, however, interested in the quantity of air fixed in solid substances, not in possible differences in the air itself.

Fire remained a mystery for about two thousand years. The theory of phlogiston was introduced in the seventeenth century to explain its formation: a substance burns because it contains the combustible principle "phlogiston" which is liberated in the form of a flame. The theory was abandoned, however, a hundred years later when oxygen was discovered and the phenomenon of combustion was explained by Lavoisier in 1777 as an oxidation process, and with this began modern chemistry. However, an "earth" was still considered as an element that cannot be decomposed to simple components until Humphry Davy (1778-1829) in 1807 announced the discovery of the alcalis by electricity although...
he failed to decompose alumina, the earth obtained from clay. Charles Martin Hall (1863-1914) and Paul Héroult (1863-1914) finally decomposed this earth in 1886 by passing an electric current in a molten solution of alumina in cryolite.

The concept of four elements (air, water, earth, and fire) consistently mentioned in history of chemistry books as due to Greek philosophers, is shown to have a much older origin and a different meaning. About two centuries before Aristotle, the Persian philosopher Zoroaster described these four elements as “sacred,” i.e., essential for the survival of all living beings and therefore should be venerated and kept free from any contamination. As useful as the concept of the four elements was to the Ancients, these material entities have nothing to do with the modern concept of “chemical elements”. While lost in the mists of time, this theoretical construct remained central to our understanding of the material world and chemical change to the seventeenth century. It is recommended that authors of chemistry textbooks or history of chemistry books, when mentioning the Theory of Four Elements, should stress its Persian origin and should mention it as the “Theory of the Four Sacred Elements,” as it has nothing to do with chemical elements. This will eliminate confusion to the reader and also provide a philosophical concept that is related to our modern views regarding the environment.

REFERENCES AND NOTES


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IS SCIENCE A BROTHERHOOD? THE CASE OF SIEGFRIED RUEHMANN

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In 1946 Niels Bohr wrote: "Scientists have long considered themselves a brotherhood working in the service of common human ideas (1)." Such sentiments would be accepted today without question. Even during the height of the Cold War scientific exchanges occurred between the United States and the Soviet Union. However the life of Siegfried Ruhemann (1859-1943) offers an example of how this has not always been the case. Virtually unknown in the chemical community, Siegfried Ruhemann made a most important contribution in 1910 with the discovery of ninhydrin and its use as a reagent to characterize the presence of amino acids and peptides (2). Robert West has discussed the discovery of ninhydrin as an example of the adage of the well prepared mind (3).

Siegfried Ruhemann, the son of Abraham and Marriana (née Rosenberg), was born on January 4, 1859 in the East Prussian town of Johannesburg. Because Abraham Ruhemann, who was in the leather trade, died in 1866, when Siegfried was only seven, the family moved to Berlin. There Siegfried received his primary and secondary education and then enrolled at the Friedrich-Wilhelms-Universität in Berlin. The death of his father left the family in a precarious financial situation so Siegfried had to work to pay for his university fees. He obtained his Ph.D. under the direction of A.W. Hofmann for a dissertation entitled, "Contributions to the Knowledge of Di-and-Triamines of the Aromatic Series," which he defended on December 22, 1881. Ruhemann continued his association with Hofmann until 1885, when an opportunity was presented to him by Hofmann to move to Cambridge University as the assistant to the Jacksonian Professor of Natural Experimental Philosophy, James Dewar (1842-1923). At this time Cambridge was a scientific backwater still steeped in the tradition of the classical education, and Dewar also accepted the offer of the Fullerian Chair of Chemistry at the Royal Institution in London. This po-
sition did not require him to give up his Cambridge professorship; and, much to the dismay of Cambridge University, he held both positions until his death. Dewar was a brilliant researcher but had a very temperamental nature. One of his few friends, Henry Edward Armstrong, wrote of Dewar (4):

...men have sometimes said that he was cantankerous, contentious, quarrelsome, a man with whom it was impossible to work... choleric, irascible, he was certainly was at times... and a good hater."

Dewar had insisted that he should have an assistant (demonstrator) who would help prepare his lecture demonstrations. Dewar became disenchanted with Cambridge and spent more time in London, while his assistant took over more and more of the lecturing and supervision of research students. As Dewar came to realize the importance of organic chemistry, a field in which he himself had little interest or formal training, he decided the best way to improve this deficiency was to hire a German-trained Ph.D. to replace his first demonstrator who had resigned in 1884. The best possible person from whom to seek advice was A. W. Hofmann, who had been Professor of Chemistry at the Royal College of Chemistry and its successor institutions from 1845-1863. His laboratory in Berlin had become a mecca for many English students seeking to advance their education and careers by obtaining their Ph. D. in Germany. Who else was in a better position to suggest a person to fill Dewar's needs at Cambridge? Why Ruhemann was chosen is difficult to establish, but one can only speculate that Hofmann considered him a first-rate organic chemist. As a Jew, Ruhemann had a serious disadvantage to establish himself in German academia at that time. Young and single, he must have found the offer to go to England attractive. Upon his arrival in 1885 Ruhemann almost immediately took over the lectures in organic chemistry from Dewar, even though this was not part of his official duties. Space was available in the university laboratory, and within five years he had published six papers of his own work and seven in collaboration with students. These appeared in the Journal of the Chemical Society as well as in German journals such as Berichte. In his papers appearing in the Journal of the Chemical Society, Ruhemann identified himself as Jacksonian Demonstrator in the University of Cambridge. He proved to be an effective and popular lecturer and had a good command of English but with a distinct German accent. In his obituary notice in the Journal of the Chemical Society recollections of Ruhemann as a teacher by a Dr. J. T. Hewitt are quoted (5):

He always seemed to be as pleased in giving the lectures as the audience was in hearing them. Within a short time at the end of the lecture he came around the laboratory asking each individual who had been present, whether there was any further points that needed explanation. As a teacher of practical Organic Chemistry Ruhemann was even more in his element than in the lecture room.

In spite of his success, however, Dewar sought to dismiss Ruhemann after five years for reasons that are still not fully known. Dewar believed that he had the sole right to hire and dismiss his assistant and did not have to offer any reason. From a pamphlet Dewar had privately printed in 1891 (concerning the Ruhemann affair), one can speculate that Dewar felt Ruhemann had been a disloyal servant to his master (6). Given the heavy burden he was carrying in teaching and research, Ruhemann expected to be treated with the respect due a colleague, whereas Dewar treated him as a servant. Dewar requested that Ruhemann resign his position on December 7, 1890. Ruhemann tried to effect some kind of reconciliation with Dewar through the offices of George Liveing, the head of the University Chemistry Department. He asked to be given a suitable period of time to find a new position. Dewar would have nothing of it, writing Ruhemann that if the resignation was noted received by December 15, Dewar would assume that he had refused to resign. When the deadline passed, Dewar wrote the Vice-Chancellor of Cambridge University (the administrative head of the University) of his intention to appoint a new assistant. The Vice-Chancellor, the Rev. Dr. Montague Butler, Master of Trinity College, replied by noting the contributions that had been made by Ruhemann during his past five years (6):

It has become clear to me during the last ten days that not a few very distinguished members of the University have the strongest possible sense of the value of Mr. Ruhemann's service as a teacher, and that they regard his retirement from Cambridge, especially if it seemed to carry with it any stigma, as little short of a calamity. He is beloved and respected in no ordinary degree, and his dismissal would awaken very general and earnest sympathy.

The university committee charged with appointments, meeting on January 26, 1891, noted that Dewar was adamant in his right to do what he wanted in his capacity as Jacksonian Professor. A resolution to this situation was sought by appointing Ruhemann a University Lecturer in the chemistry department. However Liveing, who had been Dewar's research collaborator for many years, indicated that there was no room in the laboratory in which Ruhemann could continue his research.
Dewar ordered Ruhemann to vacate the laboratory space belonging to Dewar by June, 1891. In a paper published in 1890 Ruhemann identified himself as University Lecturer in Chemistry, but without laboratory space this would seem to have been a pyrrhic victory. Fortunately for Ruhemann, many of the constituent colleges of Cambridge University had their own laboratories at this time; and he was invited to use the facilities of Gonville and Caius College. From 1891-1909, when Ruhemann was readmitted into the university laboratory following Liveing's retirement, over 50 papers of his own work, as well as 35 papers involving student collaborators, were published, all marked as contributions from the Laboratories of Gonville and Caius College. Ruhemann published an additional 20 papers of his own experimental work and 5 in collaboration with students from 1909 until his resignation in 1915. In 1914 Ruhemann was elected a Fellow of the Royal Society, a mark of distinction conferred upon him by his peers for the contributions he had made to the advancement of chemical science.

On December 30, 1900 Ruhemann married Olga Liebermann (7) of Berlin. The birth of his son Martin, his only child, on January 17, 1903 prompted Ruhemann to become a naturalized British citizen. Life seemed to be very good for the family until that fatal day of June 28, 1914, when the Archduke Ferdinand was assassinated in Sarajevo. The beginning of World War I unleashed the pent-up forces of nationalism and was to claim Siegfried Ruhemann as one of its victims. The journal Nature offers a glimpse of the depth of feeling against Germany that the war generated. This inescapably led to the view that naturalized British citizens of German descent were not to be trusted. After the first battle of the Marne, September 6-12, 1914, it became evident that this was not going to be a short or glorious war. On Thursday, September 10, 1914 the Nature editorial ran as follows (8):

Many of us have been great admirers of Germany and German achievements along many lines, but we have now learned that her "culture" and admirable organization have not been acquired as we do not doubt was thought by the workers themselves, for the purpose of advancing knowledge and civilisation, but, in continuation of a settled policy, they have been fostered and used in order that a military caste in Germany, with the Kaiser at its head, shall ride roughshod over Europe, all treaties and national rights abrogated, all conventions set aside, all honour thrown to the winds, all laws of war and even of humanity disregarded. We are back in the days of the Huns.

In a letter to the editor appearing in the September 24, 1914 issue, the Secretary of the Dutch Society of Sciences, J.P. Lotsy, a neutral observer, succinctly summarized the scourge of nationalism for the scientific community. By this time the pattern of static trench warfare that would persist over the next four years had been established (9):

To my mind, worse than the young lives sacrificed, worse than the destruction of ancient monuments of arts and science, is the almost inevitable consequence of this terrible war: the sowing of hatred and distrust between different nations. Now it is my firm belief that it is the duty and the privilege of scientific men all the world over to do all in their power gradually to allay these feelings of hatred and distrust.
On October 8, 1914 Nature published the extremely virulent and inflammatory remarks of Sir William Ramsay titled Germany's Aims and Ambitions (10). The 1904 Nobel Prize winner in Chemistry for his discovery of the noble gases, Ramsay was one of the most vocal critics of Germany in the scientific community, especially in the early stages of the war. He began his remarks with a statement made in 1893 by Lord Rosebury: “We have to remember that it is part of our responsibility and heritage to take care that the world, so far as it can be molded by us, should receive the Anglo-Saxon, and not another character.” Ramsay then presented a racial argument for the aims of Germany in the war (10):

......and their ideal, with which they have infected practically all Germans, is to secure world supremacy for their race, in the conviction that the condition of humanity will thus be ameliorated. This is the aim which has permeated all classes of German society during the past generation, this is the cause of the present war. No means are to be neglected to secure this end; righteousness, truth, and justice are to be sacrificed in order that the German race may persist.

Further on Ramsay made the following statement (10):

The originality of the German race has never, in spite of certain brilliant exceptions, been their characteristic; their metier has been rather the exploitation of the inventions and discoveries of others.... The same obedience to command and the same attention to detail may be noticed in their industrial and scientific work as in their army... The conclusion is that this war is a war of humanity against inhumanity; principle against expediency; of right against wrong.

Ramsay argued for a victory that would lead to the destruction of the German nation as a threat to humanity in the future (10):

The motto of the Allies must be ‘Never Again.”... Will the progress of science be thereby retarded? I think not. The greatest advances in scientific thought have not been made by members of the German race; nor have the earlier applied sciences had Germany for their origin. So far as we can see at the present, the restriction of the Teutons will relieve the world from a deluge of mediocrity. Much of their previous reputation has been due to Hebrews resident among them; and we may safely trust that race to persist in vitality and intellectual activity.

This curious remark by Ramsay perhaps reveals his lack of understanding of the situation of the Jewish population in the Kaiser's Germany; or was it a very clever insult to the Germans in the sense that their great scientific prowess was the result of a people who were never really accepted as true Germans? In contrast to the millions of Jews in eastern Europe in 1914, the total Jewish population of Germany was approximately 570,000. More then 70% of that group lived in Prussia and Berlin in particular. Although Jewish emancipation had been realized by the time of the unification of Germany under Kaiser Wilhelm I in 1871, there was a persistent strain of anti-semitism in the population.

In theory all professions were open to Germans of Jewish background; but in practice, appointment to the faculties of universities especially in the humanities was almost impossible even for the most assimilated Jews. The law, civil service, and election to public office were also very restricted for Jews. The sciences as well as medicine were fields that were much more open, and the numbers of Jews in these fields vastly exceeded their proportion of the population. Although university professorships in the sciences were difficult for Jews to obtain, there were many opportunities in the expanding chemical industry.

The increasing prosperity of Germany after unification greatly reinforced the feeling of many Jews as being German first who happened to be of Jewish ancestry. Although strict religious observance was practiced by some German Jews, many of the highly assimilated Jews became members of the new reform movement which had begun early in 19th-century Germany. The precepts of the reform movement with its emphasis on adapting traditional Jewish beliefs, laws, and practices to the modern world were more in line with the growing sense of German identity. A portion of a letter from Chaim Weizmann to the British Foreign Secretary Arthur Balfour in 1914 succinctly summarizes the situation (11):

Those Jews who are giving their energies and their brains to the Germans are doing it in their capacity as Germans and are enriching Germany and not Jewry, which they are abandoning.

On November 12, 1914 in a commentary in Nature entitled “The Place of Science in Industry (12),” Ramsay disparaged the success of German industry by pointing out what he believed were deficiencies in industrial organization. Ironically, these deficiencies were the very reasons why the British chemical industry was not prepared in the least for a prolonged war. The editor of Nature on January 14, 1915 wrote with particular vehemence about the war. He pointed out that many German academics, such as Prof. Kuno Meyer, who had had long careers in Britain, now returned to Germany to act as agents of the German government. Meyer, who had been Professor of Celtic Studies for 30 years at
Liverpool University, was now trying to stir up feelings among the nationalist community in Ireland and of the American Irish in favor of Germany (13):

But the individual, in these days, must suffer ... Savages have a code that, after breaking bread in a man's house, it is treacherous to war against him; not so Prof. Kuno Meyer. It behooves us to treat with suspicion all naturalised aliens of Teutonic extraction; and yet we know, alas! that in doing this, we are acting unjustly in some cases for the crimes of his countrymen. It is such instances as these which make the Allies determined that such a race must be deprived of power to do mischief, whatever be the cost in life and money.

Ruhemann had stayed in his post in Cambridge through the 1914-1915 academic year with no thoughts of leaving. As a German, however, even though a naturalized British citizen and having lived in England for 30 years, he was viewed with suspicion in some quarters. The sinking of the Lusitania on May 7, 1915 (14) was to be the deciding factor that ended his Cambridge career.

The Cambridge Daily News of May 15, 1915 printed the following (15):

Many people are asking what the authorities intend to do about German members of the university-graduate and undergraduate. There is at least one German drawing a good salary from the University who has never made any pretense of concealing his anti-British sympathies. Incidentally, I notice that Cambridge University will probably receive a Government subsidy towards chemical research work. It is to be hoped that before parting with the taxpayers' money for this purpose the Government will see to it that the proposed researches are carried out by Britons...........

Was the last part of this statement a veiled reference to Ruhemann? Did Dewar, who was known to be a vindictive person, have some influence on having this appear in the newspaper?

Both Ruhemann and his family were harassed by the intense hostility felt after the sinking of the Lusitania. Martin Ruhemann was shunned by his schoolmates, and their family doctor refused to treat them any longer. Having received threatening letters, Ruhemann felt he must resign his lectureship for the sake of his family. Since it was impossible to return to Germany during the war, he lived quietly in Cambridge until 1919 when he returned to Berlin. As a testament to his belief in the international nature of science, however, he did not resign his fellowship in the Royal Society, where he continued on the rolls until 1924, when contact between the society and Ruhemann was severed.

Back in Berlin, Ruhemann first served as an assistant in Emil Fischer's laboratory and in 1921 was made head of an industrial research institute working on lignite and peat. These were happy and productive years in spite of the difficult times. His son Martin obtained his doctorate in physics in 1928 at the University of Berlin and later became an authority in the field of cryogenics, contributing pioneering applications to air separation and gas processing (16).

After Siegfried Ruhemann retired in 1930, he looked forward to a peaceful retirement in his native Germany. This was not to be, for within three years Nazism had swept Germany into a dark era that would only end in 1945. As a retiree he probably did not feel the full force of the Nazi racism directed against Germany's Jewish population. He belonged to that large group of assimilated Jews who thought of themselves as Germans first and Jews second. There was no thought of his leaving Berlin again, inasmuch as he was 74 years old when Hitler came to power. Where was he to go anyway? Even though still a British citizen, his experience in England had been in the end less than happy.

His son Martin had married a fellow physicist Barbara Zarnico in 1930. With no prospects of employment for either, they had gone in 1932 to work at the newly created Institute of Applied Physics at Kharkov in the Soviet Union. By 1937, Stalin's paranoia had led to the beginning of the purges, and foreigners were no longer welcome to work in the Soviet Union. Fortunately, Martin Ruhemann, who had established a reputation in low-temperature physics, was able to emigrate to Britain and obtain a research post at Imperial College. The events of 1938 culminating in the infamous Kristallnacht finally convinced Siegfried Ruhemann that he, too, should leave; and in 1939 he returned to Britain with his wife to spend his last four years living in North London near his son. He died of natural causes in August 1943 at the age of 84.

By no means was Siegfried Ruhemann the only innocent person who suffered at the hands of the rampant nationalism and xenophobia of the era. Many distinguished British scientists of German descent, such as the physicist Arthur Schuster (1851-1934), who was elected Secretary of the Royal Society in 1912, were questioned about their loyalty. Schuster, born in Frankfurt, had moved with his family to England in 1870. During the course of the war he was hounded by a small minority to resign an office to which he had been elected, merely because he was of German descent. Even after
the conclusion of hostilities, there was still a great deal
of enmity toward German science and scientists from
the British and American scientific communities. The
events discussed in this paper do not have a strict paral­
lel in World War II. The rise of fascism and the emigra­
tion of many prominent scientists from Germany and
Italy had an effect which moderated the extent of the
venomous exchanges of 1914-1918. Perhaps one of the
great ironies is that Churchill’s scientific advisor was
Frederick Lindemann, Lord Cherwell (1886-1957)—a
German-born British citizen.

ACKNOWLEDGMENT

For the help rendered in the preparation of this pa­
per I am indebted to Professor Brian Pippard, FRS (Cam­
bridge University), and Stephen Ruhemann (University
of Bradford), grandson of Siegfried.

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D. STANLEY TARBELL (1913-1999)

A Memorial Tribute

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Dean Stanley Tarbell, Distinguished Professor Emeritus of Chemistry at Vanderbilt University, authority on organic chemistry and the history of chemistry, and longtime HIST supporter, died on May 26, 1999 in Bolingbrook, Illinois. His wife Ann had predeceased him on August 6, 1998. Stan was born on October 19, 1913 in Hancock, New Hampshire and raised on a farm. In 1930 he entered Harvard College. He considered his first-year European history course the best course that he took there, but he majored in chemistry because he thought it “more promising as a profession.” He received his A.B. (1934), M.A. (1945), and Ph.D. (1937) degrees, becoming Paul D. Bartlett’s first Harvard doctoral student. While a teaching assistant under Louis F. Fieser in 1936-37 at Radcliffe College, he met senior chemistry major, Ann Hoar Tracy.

Stan spent the academic year 1937-38 as a postdoctoral fellow with Roger Adams at the University of Illinois. In Fall 1938 he became an instructor at the University of Rochester, where he developed a prolific research group and rose through the ranks, becoming professor (1948-62), Charles Frederick Houghton professor (1960-67), and department chair (1964-66).

On August 15, 1942 Stan and Ann Tracy were married in Concord, Massachusetts. During World War II he worked on the detection of mustard gas and the synthesis of antimalarial drugs. He spent sabbatical years at Oxford (1946-47) and Stanford Universities (1961-62). In 1967 he accepted an offer of a distinguished professorship at Vanderbilt University because his physicians recommended a warmer climate for his osteoarthritis and because he felt that “a prime need in the south was the emergence of some major universities.” Stan retired from Vanderbilt in 1981 but remained active in organic chemical research and in his second career in the history of chemistry, which he had begun in the 1970s, a time when many members in HIST became acquainted with him. He served as HIST chairman (1980-81).

Because there had not been a comprehensive account of the history of organic chemistry in the United States for many years, the Tarbells began work on this ambitious project. After they had prepared rough drafts of many chapters, they decided to undertake a biography of Roger Adams, complementary to, but separate from, their history. In 1986 the Tarbells’ book on the history of American organic chemistry appeared, and like the Adams biography, it received favorable reviews. In recognition of these two books and his 22 historical articles (16 of which were coauthored with Ann) Stan received the 1989 Dexter Award. His third book was an autobiography that contained as much about his mentors, students, and colleagues as it did about himself. Stan authored more than 200 articles on organic chemistry and was in demand as a consultant. A member of the US National Academy of Sciences and recipient of the Charles Holmes Herty Medal, he was a member of various scientific advisory boards and governmental agencies. By personality, training, and affection Stan and Ann formed an ideal research and writing team and spent many years of collaborative effort in various archives and libraries. They will both be sorely missed.

D. Stanley Tarbell’s Books on the History of Chemistry:


"WHAT’S IN A NAME?" FROM DESIGNATION TO DENUNCIATION — THE NONCLASSICAL CATION CONTROVERSY*

Stephen J. Weininger, Worcester Polytechnic Institute

In July, 1939 Christopher L. Wilson, a member of the Hughes-Ingold group at University College, London (UCL), published a paper on the rearrangement in chloroform of the terpene derivative, camphene hydrochloride (1). This reaction belongs to the class of so-called Wagner-Meerwein rearrangements, which are characterized by a change in the carbon-carbon bond skeleton as reactants are transformed into products. These rearrangements had long puzzled and fascinated organic chemists, since they represented a challenge to classical structural theory, which rested upon the postulate of skeletal invariance. For the UCL group, rearrangements provided a highly visible test of their electronic theories of organic chemistry. Twenty-six pages of Ingold’s classic *Structure and Mechanism in Organic Chemistry* are devoted to Wagner-Meerwein rearrangements (2). The title of Wilson’s paper announced it as Part I of a series on the “Use of Isotopes in Chemical Reactions.” The imminent outbreak of WW II seems to have precluded the appearance of further papers in the series.

From this seedling sprang a mighty cactus of contention; among its thorny spines were “some of the most powerful minds and personalities in organic chemistry (3, 4).” Whatever the status of the disputed ions, the invective they evoked was assuredly classical. The principal naysayer, H. C. Brown, seems to have been the main target of the more barbed comments. In one celebrated example he was accused by J. D. Roberts of preparing to “trample some wonderful and complex little flowers with his muddy boots (5, 6).” Lest one conclude that Brown was more sinned against than sinning, his antagonists claimed to have been provoked to these outbursts by Brown’s obduracy and duplicity (7)—all in all, not a pretty picture, one that the gentlemanly Paul Bartlett of Harvard took to be symptomatic of “abnormal psychology (8).” In their judicious review of the entire episode Arnett and co-workers even raised the question of whether it constituted an instance of “pathological science (3).” Furthermore, this topic seems to have limitless potential for generating contention. As recently as 1989 a paper on the archetypal nonclassical ion, norbornyl cation (9), ended with an editor’s note indicating profound disagreement among its referees. Two separate rebuttals and a counter-rebuttal appeared a year later (10).

Is there anything to be gained by an examination of this controversy, other than titillation from watching “some of the most powerful minds” (and largest egos) in organic chemistry fighting among themselves in fierce and often undignified fashion? The response is unquestionably yes. Writing in a 1965 collection of major contributions to the dispute, Bartlett praised the increased knowledge of valence theory and solvolysis mechanisms that the controversy had afforded (11). From the historical standpoint, I believe that an analysis of this episode can contribute to our understanding of many significant issues:

- the impact of new experimental techniques on the study of reaction mechanisms
- the shifting status among major subdisciplines within organic chemistry
- the role of Cold War funding in the evolution of post-World War II chemistry
the relationship of alternate theoretical formalisms to differing representations of molecules and the conflicts that arise when new forms of representation are introduced.

In this paper I concentrate on the last of these issues; I hope to treat others in subsequent publications.

Wilson’s results and his associated interpretation of them are as follows. Under the catalytic influence of hydrogen chloride, camphene hydrochloride ionizes with unexpected rapidity and also rearranges, producing only one of two possible isomeric rearrangement products (Fig. 1). The speed with which the starting material lost chloride ion suggested to Wilson that the organic cation, the camphenyl ion, must be unusually stable. It also seemed highly likely that the rearrangement took place following ionization, after which the rearranged cation re-captured chloride ion to give isobornyl chloride. The entire process was reversible, with equilibrium favoring isobornyl chloride. Wilson sought an explanatory mechanism that was in harmony with two signal findings: the ionization of camphene hydrochloride was much faster than anticipated (kinetic anomaly), and only isobornyl chloride was formed, although its isomer, bornyl chloride, was the more stable of the two (stereochemical anomaly). Figure 1 shows a “classical” mechanism for the rearrangement. However, this mechanism explains neither the kinetic nor the stereochemical anomaly. The first anomaly can be accounted for by assuming that chloride ion loss and carbon skeleton rearrangement are concerted; that is, the C-6/C-2 bond is formed simultaneously with cleavage of the C-2/Cl bond, thus bypassing free camphenyl ion altogether. Such an assisted ionization would indeed result in an accelerated rate of ionization (2). However, even this modified classical scheme cannot accommodate the stereochemical results.

Wilson’s ingenious but tentative solution to this dilemma was to propose that C-6 became only partly bonded to C-2, while remaining partly bonded to C-1 as well (Fig. 2a). In this bridged cation the positive charge would then be divided between C-1 and C-2. Moreover, the electron pair originally binding C-6 to C-1 would now be shared among or delocalized over three centers—C-1, C-2 and C-6. Wilson proposed this delocalized cation not as a fleeting transition state but rather as a reaction intermediate, long-lived on the molecular time scale. The partial bonding between C-6 and C-1 would preclude nucleophilic attack on C-1 from the endo direction, thus explaining the anomalous formation of only one product stereoisomer. The proposed intermediate would thus be neither a camphenyl nor an isobornyl ion but rather a mesomeric ion, i.e., a resonance hybrid of the two. Ever mindful of what we might call the Lavoisier gambit—seize the nomenclature and hearts and minds will follow—Ingold in 1951 named these species synartetic ions (12).

The novelty of Wilson’s explanation lay in the idea that the s electrons of the C-1/C-6 bond could be delocalized over more than two centers. The division of bonding electrons into two types, s and p, had been worked out several years earlier by the theoretician Erich Hückel (13). By treating the s electrons like the localized electron pairs of classical Lewis theory, while allowing the p electrons to be delocalized over more than two nuclei, the Hückel theory nicely rationalized the well established reactivity differences between single and
multiple bonds. The theoretically sophisticated knew that the s/p division was but one possible representation of multiple bonds, and that a strict boundary between localized and delocalized electrons was illusory. However, since the thesis of a qualitative difference between s and p electrons helped make sense of a raft of chemical and spectroscopic data, it came to be accepted as an accurate description of the actual state of affairs.

Incorporating the s/p dichotomy within the already very successful conventions for drawing molecular structures was not easy, and representing electron delocalization was particularly tricky. In the case of benzene it required at least two Lewis structures (resonance structures), both of which were fictional. The properties of the real benzene molecule are such that a single Lewis structure is inadequate to express them, and resonance theory is one way of dealing with that inadequacy without abandoning classical molecular representations (14, 15).

Wilson was proposing analogously that there was only one organic ion involved in the camphene hydrochloride rearrangement, that the ion was easily formed because it was resonance stabilized, and that this stabilization required the delocalization of a pair of s electrons (Fig. 2a). Wilson’s proposal occupied a mere line in his paper and was only put forward as a possibility, but its initial reception was apparently cool (16, 17). In addition to struggling with the correct structure of the ionic intermediate, Wilson also had to decide how to represent it. Literally pushed off to the side of the paragraph, the representation he chose was unusual (Fig. 2a). Double brackets were not very common and in this case rather unclear as well. This ambiguous representation, coupled with Wilson’s statement (1), that “it is possible that [the intermediate ion] is mesomeric between [the camphenyl] and the corresponding isobornyl structures,” (emphasis added) gives his presentation a very tentative air.

Subsequent to Wilson’s publication, a half dozen or more papers about bridged ions appeared that sought to extend the s delocalization concept to carbonium ions in general (18). Although the bridged ion thesis was gaining favor, the authors of these papers reported no new experimental work and many of them overlooked Wilson’s contribution. One might have concluded, a decade after its publication, that Wilson’s hypothesis had produced but a small ripple in the rising tide of physical organic research. In the mind of Saul Winstein, however, it had produced much more than a ripple. Both Winstein and the Wilson paper arrived at Harvard at about the same time in the fall of 1939. Winstein was taking up a National Research Council fellowship in Bartlett’s laboratory, fresh from doctoral and postdoctoral work with Howard Lucas at Caltech, where he studied metal ion-alkene complexes and neighboring group participation, both subjects with close affinities to the Wagner-Meerwein rearrangement (19, 20). Winstein apparently first read Wilson’s piece on September 22, 1939. In the course of the following three weeks he wrote out no fewer than 33 pages of notes on this paper and the antecedent literature, including derivations of the kinetic equations and verification of the calculations. He even went so far as to check the Eastman catalog for the prices of camphene, borneol, and other compounds necessary to continue the project (21). It seems fair to conclude that Winstein was not only deeply impressed by the Wilson paper but was making definite plans to pursue his own investigations in the area.

He did not act on this plan for almost a decade. However, starting in 1949 at UCLA, Winstein began publishing solvolytic studies of a simplified version of Wilson’s molecule that retained its most important structural feature, the strained bicyclic ring system (Fig. 2b) (22). He mustered an assortment of kinetic, stereochemical, and theoretical tools to establish the reality of cationic intermediates with delocalized s electrons. In concurrent investigations at MIT and then at Caltech, Roberts used 14C labeling to uncover the full complexity of the rearrangements taking place in norbornyl and other cations. Winstein thought the array of evidence strongly supported a delocalized structure for the norbornyl cation but, nonetheless, was cautious in terms of extending both the concept and the terminology. He observed that (22b):

> [t]he evidence for an unclassical (sic) structure for the norbornyl cation lends credence to the earlier suggestion of Christopher Wilson of a possible mesomeric cation from camphene hydrochloride. Such a formulation, while again not required by any one result, takes account the most simply of products and reactivities....The number of known cases of carbonium ions the stereochemistry of whose reactions is best accounted for, under some circumstances, by so-called non-classical structures, is still small....Thus it remains to be seen how general this situation may become.

It was Roberts, struggling with the “chimerical” cyclopropylmethyl cation, who had coined the term nonclassical (23) as a successful alternative to Ingold’s
It was not long before Brown and Ingold came into conflict over Brown's theory of steric strain (5). In essence, the theory holds that the course of a reaction can be profoundly affected by crowding in the reactants, products and/or intermediates. Camphene hydrochloride is just such a crowded reactant (Fig. 1), and the loss of chloride during ionization would partly relieve that crowding. Thus, the unusually high reactivity of camphene hydrochloride could be explained by the relief of ground state steric strain, without the invocation of any special electronic effect. By the time Brown publicly challenged the nonclassical ion hypothesis during a Chemical Society meeting in 1962 at Sheffield, England, the focus of the battle had become the norbornyl system (25). The two positional isomers of 2-norbornyl chloride, _exo_ and _endo_, differed in reactivity by a factor of several hundred. To Winstein this clearly signaled that loss of chloride from the _exo_ isomer led to a single organic ion stabilized by s-delocalization (22). Brown's counter-proposal was that the reactivity of the _exo_ isomer was normal and that of the _endo_ isomer retarded by steric effects. In Brown's model _endo_ ionization would lead to an increase in steric congestion, whereas _exo_ ionization would not. Furthermore, Brown insisted that the rearrangement could be accounted for by an equilibrium between two distinct, "classical" organic cations rather than requiring a single, delocalized cation (Fig. 2b)(26).

Brown's opposition to nonclassical ions puzzled as well as provoked many of his opponents. In the research that ultimately earned him the 1979 Nobel Prize, Brown explored the organic chemistry of diborane, B₂H₆. This
compound had long posed a structural conundrum, one that was finally solved by assigning it a pair of two-electron three-center B-H-B bonds. In other words, diborane exhibited just the kind of s-electron delocalization that Brown refused to recognize in nonclassical carbocations. In response to charges of inconsistency, Brown pointed out that diborane exhibited its delocalized structure only in the gas phase, while in solution where most nonclassical ion chemistry was being studied, diborane reverted to more “normal” modes of bonding (25). He also asserted that he was not opposed in principle to the concept of s-delocalization; the experimental data just did not support it. Brown likes to invoke Occam’s Razor and to claim that “Nature is simple (27).” One might, however, see the problem as not how simple nature is but how subtle.

Brown’s inability to accept the nonclassical ion hypothesis was rooted in the intertwined strands of his entire scientific career. In order to quantify steric effects, Brown studied a variety of equilibria among Lewis acids and bases. The results led him to the general conclusion that, while Lewis acids formed strong complexes with donors of the n-class and weaker complexes with members of the p-class, “donor-acceptor interaction has never been demonstrated for saturated alkanes or cycloalkanes, such as would be involved in the extension of participation to the proposed s-class (28).” In addition, Brown and his coworkers had formulated an important extension of the Hammett equation (29), itself based in “classical” resonance theory, which rested on a strict division between s- and p-electrons (30). Thus, one important issue at stake was the viability of the venerable and successful classical system of representing molecular structure. The system had managed to incorporate the Lewis electron pair bond and its numerous implications. It even accommodated resonance theory, although that development came perilously close to stretching the system to its limit. Further erosion of the distinction between s- and p-electrons could be seen as possibly undermining one of the most compact and powerful qualitative tools available to the organic chemist.

Brown was heavily outnumbered in this fight; several commentators likened him to “Horatio at the bridge (31).” Poised against him was an international coalition consisting of Hughes, Ingold, Dewar, Bartlett, Roberts, Cram, and Winstein, soon to be joined by a number of equal and lesser luminaries. But within the allied camp there were differences that were themselves of great significance. For if the physical organic “establishment” (32) shared ideas about structure and reactivity that were much more indebted to quantum mechanics than were Brown’s, there remained the troublesome fact that there was more than one way to harness quantum mechanics to chemical ends.

Nye has described in detail how two rival paths formed and diverged in the 1930s (15): valence bond (VB) theory, with which resonance theory is closely allied, and molecular orbital (MO) theory. While there was more than a little sniping between the principal players over which approach led to “true understanding,” for many chemists the crucial issues were more pragmatic: how well the methodology accorded with long established chemical concepts, and how effectively the calculations produced theoretical parameters of interest and reproduced important experimental measurements. The VB/resonance approach had a clear advantage with respect to the first criterion. Pauling insisted that resonance theory had purely chemical roots, and he was as well its very persuasive advocate. In that respect he far outshone Robert Mulliken, the champion of molecular orbital theory (33). When it came to the second consideration the outcome was considerably less clear and depended on the nature of the molecules under study, the properties being examined, and the skill and ingenuity of the theoretician.

Although hardly lacking in theoretical sophistication, the Hughes-Ingold group was quite committed to resonance terminology. Saltzman has described how Ingold’s development of mesomerism actually anticipated many resonance concepts (34). The smooth blending of Ingold mesomerism and the Pauling/Wheland resonance made that commitment perhaps inevitable (35):

The inception of the theory of mesomerism slightly preceded (1926) the discovery...of the fundamental significance of quantal resonance for the formation of covalent bonding (1927). However, during the following years, it became evident that quantal resonance has a closely similar significance for that modification of covalent bonds which is described in the theory of mesomerism.

At least one of Ingold’s admirers, the author of an influential textbook, seemed to harbor doubts about the utility of MO theory for most chemists (36).

It is certainly not the case that MO theory lacked adherents in the UK. The British theoreticians Christopher Longuet-Higgins and Charles Coulson (37) were pioneers in applying quantum mechanics to chemical problems. One of their younger colleagues who very
strongly believed in the power of MO methods in organic chemistry was Michael J. S. Dewar (38), but he was on the “wrong” (i.e., Robinson’s) side of the Robinson-Ingold dispute (39). As a result the relations between Dewar and Ingold were cool at best, and often worse (40). Dewar eventually migrated to the US, having already had a major impact on leading edge American physical organic chemists, who were chafing at the limitations of resonance theory.

Because of its qualitative aspect and its use of classical structural representations, resonance theory is very appealing. Once the rules for manipulating these formulas have been mastered, one is able to rationalize a large body of experimental data with amazing ease. Yet, as one presses the technique, it becomes necessary to keep adding ad hoc rules and hypotheses to explain, for example, why benzene is aromatic but cyclobutadiene is antiaromatic, or why cyclopropenyl cation is isolable but cyclopropenyl anion is not. MO theory can rationalize these differences without resorting to ad hoc hypotheses (41).

For Winstein and Roberts, then, as for Brown, the 2-norbornyl cation was a hook on which to hang a much larger agenda. The Californians were intent on alerting organic chemists to the benefits of abandoning resonance for molecular orbital theory. Roberts has described how difficult it actually was to use the seductively simple resonance approach (42):

> And there were others...who didn’t understand what Pauling was talking about, particularly with benzene. Pauling would say, ‘Well, you’ve got two resonance forms of benzene, and they’re nearly the same.’ And he said, ‘If they’re nearly the same, they’re both important, the molecules are a composite of the two forms, and will not be like either form.’ Nobody could understand the reality of the separate structures, and Pauling’s book wasn’t much help on this.

Thus, the nonclassical ion controversy was not only about the scope of electronic theories in organic chemistry; it also concerned the claimed superiority of one of the two prevailing theories. While resonance is a very useful tool for the explanation of experimental findings, MO theory is in many ways more effective for exploration of potentially new phenomena. After Andrew Streitwieser arrived in Roberts’ laboratory as a postdoctoral fellow concentrating on MO calculations, he and Roberts proceeded to have a “wild time...One or the other of us would draw some new structure. I remember doing things that hadn’t been contemplated before....Anything that we could do, we would do (33).”

Winstein’s conceptions of homoallylic resonance and homoaromaticity demonstrated the power of MO theory quite dramatically (43).

In the US enthusiasm for MO theory was an integral part of a general sense that American physical organic chemistry had come of age and was at least the equal of that of the English school. No one questioned Ingold’s singular role in bringing the field to center stage worldwide (44). At the same time, his often imperious manner did not sit too well with the ex-colonials (45). Ingold’s practice of aggressively coining and promoting his own systems of nomenclature was particularly effective at raising hackles on this side of the Atlantic (46):

> In the electronic interpretation of organic reactions certain English chemists have been pioneers. Their views might originally have been more cordially received in [the US] if presented inductively and in terms whose meanings are well known.

Beyond resenting Ingold’s linguistic hegemony, many Americans felt that his views had become dogmatic on some issues and impervious to revision (47). Within this context Roberts’ assessment of the significance of Ingold’s achievements is perhaps not quite so startling (48):

> The thing that depressed me about physical organic chemistry and the Ingold work was that it was terribly important in a way, and yet it really didn’t do much for organic chemistry.

The reasons for Roberts’ reservations become clearer when he lays out his vision of a characteristically American style of physical organic chemistry (49):

> Bartlett set a new style for physical organic chemists. Physical organic chemistry was going big in Britain...[b]ut they were working on compounds you could get off the shelf. They never made anything special; they did not utilize the special characteristic of organic chemistry, which allows you to tailor make molecules to prove particular kinds of concepts.

Of the many conclusions that might be gleaned from revisiting the nonclassical ion controversy, one is very familiar. Struggles among chemists over competing representations are often protracted and intense. Since at least the time of Lavoisier, chemists have known that symbols do not merely describe preexisting entities but rather help create and shape them. Ingold’s commanding position in physical organic chemistry is due in part to his astute recognition of that fact (50). The ways in which chemical bonds are represented are as much a matter of contention as theories that specify how they
are constituted (51). Thus, even when the protagonists agree on major conceptual issues, such as the superiority of MO over VB methods, there is ample room for dispute over representational issues. In this instance as well, nonclassical ions served as lightning rods. Dewar suggested in 1946 that carbonium ions undergoing rearrangement could be represented as p-complexes and further elaborated this proposal in his 1949 textbook (52). Thus, for Dewar, Winstein’s claims for the nonclassical nature of the norbornyl cation did not constitute “a major contribution to chemical theory;” Winstein was merely confirming Dewar’s prior proposals. According to Dewar, Winstein’s hostility toward p-complexes was not only ungenerous to a junior colleague (53):

[it] had unfortunate consequences for organic chemistry, because the large majority of ‘nonclassical carbocations’ are, in fact, p-complexes and their chemistry can be interpreted much more simply and effectively on this basis than it can in terms of the obscure ‘dotted line’ representation that Winstein introduced... (Fig. 2b).

Not surprisingly, Winstein had reservations about Dewar’s motives and methods. After praising Dewar’s “skillful qualitative discussion of the wave-mechanical basis of chemical bonding, especially from the molecular orbital viewpoint,” Winstein complained about the book’s “novel interpretations, novelty often being achieved by mere substitution of new language for existing explanations and employing a ‘p-complex’ interpretation for everything conceivable (54, 55).”

Arguments about the superiority of one notational convention over another are often motivated by personal pique and priority claims. Nonetheless, different conventions can lead to different outcomes. A graduate student attending a seminar on the nonclassical ion problem was inspired to conceive a very important experimental approach to the problem because he had seen Streitwieser’s then recently published three-dimensional MO structure for the 2-norbornyl cation (56).

Introducing a planned series of articles on “The Nonclassical Ion Problem,” the editor of Chemical and Engineering News wrote (57):

[t]o someone not expert in carbonium ion chemistry, the nonclassical ion problem may seem largely one of notation... But the root of the problem goes much deeper than notation and nomenclature, or the topic could surely not have absorbed so much of the energies of some of the leading physical organic chemists for more than 15 years.

Precisely so. Speaking of his student Robert Mazur’s work on the “chimerical” cyclopropylmethyl cation, Roberts put his finger on one of those deep problems (58):

It was especially important as the opening of the Pandora’s box of an extraordinarily difficult and subtle problem—a problem concerned in an important way with what we mean when we write chemical structures on paper.

ACKNOWLEDGMENTS

Much of the research for this paper was carried out while the author enjoyed the hospitality of the Beckman Institute and Division of Social Sciences and Humanities during a sabbatical leave at California Institute of Technology. The author thanks Professor Mary Jo Nye for inviting him to present this material at the Dexter Award Symposium. Professor Leon Gortler generously shared a number of his interviews with me, and he together with Professor Martin Saltzman offered helpful critiques of the original draft. I thank the Caltech Archives and the Department of Special Collections, University Research Library, UCLA, for permission to quote from their holdings. Finally, I express my gratitude to Professors Herbert C. Brown, George A. Olah, and John D. Roberts for generously sharing their opinions and recollections with me.

REFERENCES AND NOTES

*An earlier version of this paper was presented at the Dexter Award Symposium at the American Chemical Society meeting in Dallas, March 31, 1998.


4. A trenchant overview may be found in W. H. Brock, The Norton History of Chemistry, Norton, New York, NY, 1993, 558-569. (Note that on p. 567 norbornane should be norbornene.)


6. A letter from Brown’s wife, Sarah, charges that at an Organic Symposium, Saul Winstein had said that Brown “was arguing like a shyster lawyer” (Chem. Intell., 1999, 5 (1), 4; Brown himself made the same claim to me on August 20, 1998). In the same letter George Olah is accused of calling Brown “senile;” in conversation with me (May 28, 1998) Olah admitted to making a comment he later regretted but one not nearly so derogatory. It would seem that even recollections of the controversy have the potential to be controversial.


17. In a letter to Derek Davenport, Wilson claimed that Ingold had not initially supported the mesomeric ion hypothesis. This statement is challenged by K. T. Leffek, who asserts that Wilson was “not a man to allow a punch line to a story to be diminished by a strict adherence to the truth” (Sir Christopher Ingold: A Major Prophet of Organic Chemistry, Nova Lion, Victoria, BC, 1996, 149-150). Martin Saltzman, who interviewed Wilson at length in the 1980s, believes that Wilson’s claim was not made in jest (private communication).


21. Winston Papers, Department of Special Collections, University Research Library, UCLA, Collection 1290, Box 18.


24. Ref. 11, p 65.


27. That these themes constitute a leitmotif for Brown is attested to by numbers of his graduate students and postdoctoral fellows: Remembering HCB: A Collection of Memoirs by Colleagues and Former Students of Herbert C. Brown, Dept. of Chemistry, Purdue University, 1978.


31. That precise characterization is used by both Roberts (Ref. 7, p 89) and Brock (Ref. 4).

32. Both Brown and others have referred to Brown’s feeling of exclusion from the bicoastal American physical organic network: H. C. Brown, interview with L. Gortler, June 7, 1982; Ref. 7, p 250.

33. According to Roberts, “...if Pauling had really pushed the molecular orbital theory, and Mulliken had pushed resonance, I just sort of have the feeling that we may never have heard much about resonance” J. D. Roberts.
35. Ref. 2, p 82.
36. "Both the electron pair method and the molecular orbital method are approximations, and the exact truth probably lies intermediate between them. The latter cannot be described as a wave-mechanical theory of valency, however, and the conception of the 2-electron bond as originally put forward by G. N. Lewis still provides the most useful picture of the molecule for the purpose of interpreting chemical phenomena" (H. B. Watson, Modern Theories of Organic Chemistry, Oxford University Press, Oxford, 1937, 14; emphasis added). In the second edition (1941) the underlined phrase was replaced by a more neutral one.
42. J. D. Roberts, interview with Rachel Prud'honne, 1987, Caltech Archives, Pasadena, CA, 47. See related comments in Ref. 38, p 15.
44. Weinstein expressed great pride in "join[ing] Ingold and Hammett on the list of recipients of the American Chemical Society Norris Award (letter to C. R. Hauser, April 13, 1967, Weinstein Collection, UCLA, Box 2).
47. Hearing that Ingold had been ignoring one of his important discoveries, the special salt effect, Weinstein observed that "a good many Americans think he has been an ass in his recent papers on ion pairs and solvolysis. In fact, I'm building up to murder him" (letter to E. F. Jenny, January 13, 1958, Weinstein Collection, UCLA, Box 2).
48. Ref. 33, p 94.
49. Ref. 42, p 32.
50. Ref. 15, pp 269-271.
52. Ref. 38, pp 211-213.
56. This intriguing story and much else relating to the non­classical ion controversy may be found in B. P. Coppola, "Deeper Beneath the Surface of the Chemical Article: Richard G. Lawton and the Norbornyl Cation Problem," Chem. Intell., 1998, 4 (2), 40-49.
57. Ref. 28, p 87.
58. Ref. 7, p 64.

ABOUT THE AUTHOR

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Where and who were the female scientific role models for the women of the late 20th Century? This question has been asked for the last twenty-five years, and it has not been an easy task to identify them. Additionally, while most can identify in general some of the hardships that the women scientists faced in the 1800s and early 1900s, the specific challenges and hurdles faced by these pioneering women and contributions to their chosen field of endeavor are harder to identify. Who where they? Where did they get their education? Who were the trailblazers? What were their lives like?

Mary Creese has put together a splendid survey of those pioneering scientific women that helps to match names and lives with those women who faced the challenges of society. The women who because of their drive, love of science, and love of learning faced the hardship of obtaining a scientific education, publishing, and making notable contributions to their chosen field of study. The survey focuses on American and British women who published between 1800 and 1900—but does not stop there. As one might anticipate many of these women published in the later 1800s and, thus, continued to work through the first half of the 1900s and some beyond. Creese, following the careers, lives, and contributions of many of these women throughout their entire life, gives a wonderful picture of the scientific world from the perspective of these women during the later part of the 19th century and gives names and life to those women who paved the way for today’s female scientific leaders.

The survey is based on a bibliography of scientific journal articles extracted from the London Royal Society’s monumental Catalogue of Scientific Papers, 1800-1900. The preface provides a statistical breakdown of the number of female authors by country and discipline; and each chapter provides additional information on the number of papers presented by decade. This allows the reader to put the women into context, i.e., when and where. Thus, Creese provides a foundation for why she chose to focus on American and British women.

The survey itself is broken up into three parts: life sciences; mathematical, physical and earth sciences; and social sciences. Chapters are focused on particular disciplines such as “Largely Lepidopterists,” “Ripple-Marks in the Sand, Images on the Screen, Unit Standardization,” and “Geographers, Explorers, Travelers, and a Himalayan Climber.” As one can see from the choice of titles, this is not a dry approach to the chronicling of these women’s lives and contributions. Each chapter is a set of life stories—the struggle to be educated, to publish, and to continue the scientific enterprise. And each story provides a glimpse into the culture that shaped the road that each of these women had to travel. Thus, the reader also gets a tremendous sense of the strength of character that each of these women must have had in order to make the contributions listed here.

To get a flavor of how Creese brings these women to life while at the same time chronicling the publications and providing biographical and bibliographical information, here are two brief excerpts of stories that show this strength of science and character. The first is from the life of Florence Stoney, who became known for her X-ray work in army hospitals. The story recounts an episode during World War I:
By 8 November the unit was reestablished at Cherbourg, ... and Stoney and her staff of seven women doctors and twelve nurses served there until 24 March 1915. This time they were quartered in the sixteenth-century Chateau Tournalvillle, picturesque but hardly ideal for their purposes ... Sanitation was primitive, a bucket system being necessary and no running water except on the ground floor. Water for surgical use had to be carried up two flights and sterilized by boiling over oil stoves. Within a week of their arrival the French had filled the seventy-two beds with critically wounded men... The less seriously ill were sent south directly. Most of Stoney’s cases were compound fractures, and her X-ray work was invaluable in determining the precise locations of shell fragments in the exceptionally septic wounds. With constant practice she also became skilled at distinguishing dead bone from living and found that removal of the former speeded recovery. Of the 120 patents the women’s team treated during their four and half months only ten died.

The second relates to the life of chemist Ellen Swallow Richards. She was recognized as a prominent chemist and was the first woman student at MIT and its first woman instructor:

However, as early as the 1880s Richards was well aware that, despite her extensive involvement in the Massachusetts water survey and other projects, her opportunities for professional development and advancement in chemistry were limited. So she gradually turned to other areas where she felt she had something to offer. Her public health work had made her increasingly conscious of the then barely recognized dangers from air and water pollution and adulterated foodstuffs in a society rapidly becoming more and more urban and overcrowded. Nutrition research and the setting up of dietary standards became special concerns, and from there she was drawn into the tasks organizing the field of home economics.

Both excerpts reflect how the times and the conditions had a tremendous effect on the women involved. The survey is filled with these stories—some tragic, some heroic, and some frustrating. The survey also includes the impact on these scientific women of mentors, the schools, and the trends in scientific institutions such as the Academy of Science and the formation of the American Association of University Women. Creese treats us to the nonscientific accomplishments of these women as well. Because of the drive and strength of character, many of these women were active in social endeavors as reflected in the excerpt on Ellen Richards.

The survey that Creese has put together is extremely comprehensive. It includes a wealth of biographical and bibliographic information that makes it an essential reference for anyone who is interested in the history of women in science. Mary Creese has achieved success in a most difficult task: bringing the lives and accomplishments of women scientists into the open while at the same time not rewriting history. She has put a face to the challenges and has described how the women coped within the confines of the social framework of the time. Thus, the role models and the change agents have come to life for all to see. These women truly were trailblazers in the world of science. Frankie K. Wood-Black, Phillips Petroleum, Borger Refinery and NGL Center, Borger, TX 79008


Greenberg, who is Chair of the Chemistry Department at the University of North Carolina-Charlotte, provides what he calls a “light-hearted tour through selected highlights of chemical history.” He is writing for chemists, chemistry teachers, and interested lay readers, not professional historians of chemistry. Although he has aimed at producing “light reading,” filled with intriguing illustrations and richly peppered with humorous episodes, ironic anecdotes, and jokes, he also wished to create an effective adjunct for teachers and a book that might lead the general reader toward a greater appreciation for the chemical arts. He succeeded.

This is, indeed, a delightful book, filled with curious lore and wry observations. Greenberg states in the front matter that “I am not a chemical historian,” and at times this is noticeable (a minor point in illustration: George Starkey and James R. Partington both acquire here the first name “John”). But Greenberg never intended to write a contribution to scholarship in history of chemistry. Instead, regarding alchemy, we read a section on “Rats a Rizzo and the Poet Virgil as Transmuting Agents;” regarding Van Helmont, “A Tree
Grows in Brussels;" regarding Starkey, "A Harvard-Trained Alchymist;" regarding Priestley, "Making Soda Pop;" regarding a famous Edinburgh professor, "Black's Magic;" and regarding Cannizzaro, "My Parents Went to Karlsruhe and All I Got Was This Lousy Tee-Shirt!"

It is a measure of Greenberg's success that even professional historians of chemistry will find this book filled with clever—and sometimes even profound—observations, and many arresting illustrations. "And if a few students are caught snickering over a page of Rabelaisian chemical lore or some bad puns," Greenberg remarks, "would that be such a bad thing?" This reader does not think so. Alan J. Rocke, History of Technology & Science, Case Western Reserve University, Cleveland, OH 44106.


These books comprise volumes 17 and 16, respectively, of Chemists and Chemistry, a series by Kluwer Academic Publishers "devoted to the examination of the history and development of chemistry from its early emergence as a separate discipline to the present day." Previous topics in the series have been biography, chemical concepts, nomenclature, scientists' attitudes, polyolefins, lactic acid, rare earths, instruments, chemistry in America, and the development of chemical engineering.

The volumes reviewed here augment and expand on the meager amount of work published in book form in English on the history of chemical technology and manufacturing in Europe, particularly that of Haber (1, 2) and to some extent that of Hohenberg (3), Aftalion (4), and Arora, Landau, and Rosenberg (5). They grew out of two workshops sponsored by the European Science Foundation during 1995 and 1996 on the Evolution of Chemistry in Europe. Twenty-nine authors, mostly academics from fourteen countries, bring expertise and insight from such diverse fields of learning as history, chemistry, chemical engineering, economics, control engineering, general science, and technology. Longer than usual "Notes on Contributors," including their addresses, bolster the academic worth of the books.

All essays in both books are well researched, well documented, well indexed and will be of lasting value. Issues they raise will provide grist for the mills of future research. As might be expected of the output from a cadre of authors, some chapters are more interestingly written than others, and some contain more meat than others. Because the essays as collections tend to be disjointed, and fail to present a "big picture," namely, a coherent unified history, they are far more likely to be consulted for the important details, insights, and perspective they can bring to the standard works. I found less of an overarching commonality among the essays within a theme of Volume 16 than those of Volume 17. For that reason, I reviewed each essay of Volume 16 separately.

Obscure words and complex sentence structures in a few essays in both books often caused me to reread for meaning. The lack of thorough copy editing and proofreading is apparent in both. Missing punctuation, missing words, misspellings, and inconsistencies in format and layout, although stumbling blocks to the perfectionist, are not sufficient in number to mar the value of the contents. The print in Volume 16 was more difficult to read than that of Volume 17. Prices of both volumes, at about $0.45 per page, although steep for the average reader, are in keeping with those of other works of limited distribution.

The 17 chapters of Volume 17 are published in three themes: Patterns of Industrialization, Pollution, and Chemists and Companies.

In the first theme, Patterns of Industrialization, five chapters cover the formation and growth of chemi-
The histories trace the rise of major chemical companies and their products with emphasis on the cultural, economic, and political climates that engendered them and hastened their growth: a need, know-how, access to capital, available factory sites and labor, supplies of raw materials, and, in time, expanding markets. Over time, the national industries moved from reliance on craft or "recipe based" knowledge to academic knowledge based on theory. Intertwined with the growth of national industries was the inevitable growth in chemical education, journal publication, and the formation of chemical societies. Decline of the industry in Britain and its corresponding ascendancy in Germany are attributed to matters of 1) vision both by the state (subsidized higher education) and within industry (innovation, diversification, managerial techniques, etc.) and 2) cooperation by the state, academia, and industry at all levels.

"How to Tell the Tale," the final section in the essay on Switzerland, is particularly noteworthy. It contends that in writing chemical industry history, it is no longer appropriate simply to chronicle those events, statistics, and bold strategies by principals, which culminate in success. The history must also grapple with the effects of social and cultural issues, such as labor disputes, catastrophes, and the life cycle of products. The history must also remember those companies that failed. I would add only that the shortcomings of an industry of 25, 50, or 100 years ago must be judged within its context, not by modern-day values.

The four chapters on Pollution, which to me are the most important in the book, contain far more material on the subject than all the histories cited above. Three chapters focus on rising public concern and governmental action in the latter half of the 19th century to curb pollution in Britain (HCl gas from alkali works), the Netherlands (acid wastes in streams from dye works), and Germany (arsenic wastes in streams from dye works). The presentation is objective. Pollution is treated as an issue to be dealt with rather than, as is often the case, a mere nuisance foisted on industry by malcontents. The historical material strongly reinforces the contention by some that industry, even today, when faced with environmental complaints, is likely to stonewall by pointing a finger at others or by contending that reducing pollution is not economically feasible. When, however, industry is forced to clean up its act, it often finds ways to make a profit. The essay on Robert Angus Smith (1817-1884), chief enforcer of Britain’s Alkali Act of 1863, also provides a lesson for today. Once pollution laws are enacted and government has the upper hand, it can accomplish far more by working with industry than by arrogant penalization.

My only criticism of this section is that so much of pollution’s toll is documented in economic terms: for example, the effect of HCl gas on crops and landscape, which were important to the landed gentry, while so little is said about its toll on humanity. In fairness, though, the authors reflect their sources. It was the gentry who complained and whose records were preserved. Chemists and physicians were of little help. Chemists tended to be tools of industry. Blinded by mindset and lack of knowledge, physicians often dismissed the poor health of workers as a result of intangible miasmas. Desperate to put bread on his table, the affected worker had little choice but to tolerate even the vilest working conditions. Towns and cities whose economic viability depended on the giant industries could easily look the other way.

Of the seven chapters in Chemists and Companies, six deal directly with the work of chemists and one is an outlier. Using Britain’s alkali trade as a model, one chapter examines the general processes that led to the employment of trained chemists in laboratories and shows how the functions of laboratories evolved from simple control tools to include research and innovation. Another chapter contrasts how three companies—Hoechst, Bayer, and Schering—organized for innovation and discovery in the pharmaceutical industry.

Four chapters deal specifically with the work of four chemists. Principal among them is Heinrich Caro (1834-1910) in his role as head of the Central Research Laboratory at BASF and as an outstanding mediator between academia and industry. Another chapter explores Caro’s close friendship with Ivan Levinstein (1845-1916), owner of a family dye works in Britain, and their collaboration in business. The other two chapters are devoted to Paul Schützenberger (1829-1897) and Daniel-August Rosenstiehl (1839–1916), obscure Alsatian dye chemists who, like Caro, fostered close collaboration between academia and industry. The outlier chapter in this section shows the impact of the development of measuring instruments and process control on the chemical industry, its products and labor force, a subject not covered at all that I can find in any of the standard histories.

Part 1, A New Technology for the 20th Century, consists of a single masterfully written, concise, fact-filled chapter, "High Pressure Industrial Chemistry: The First Steps, 1909-1913." It hails high pressure industrial chemistry as "nothing less than the paradigm shift that thrust the chemical industry into the 20th century." This thrust was initiated in 1903 with the pioneering academic work of Fritz Haber (1868-1934), later sponsored by BASF, who by 1907 had synthesized ammonia directly from nitrogen and hydrogen in a catalyzed system, operating continuously at 250 atm. and 600° C. In 1909, Carl Bosch (1874-1940) of BASF took on the task of scaling up Haber's bench-top process. It required mostly new technology from start to finish. Problems of scale abounded, such as finding a cheaper catalyst, hydrogen embrittlement of steel reaction vessels, catalyst poisoning, and inefficient gas compressors. Yet, by 1912, a commercial plant had been brought on-line, and by 1915, converters 12 meters high and weighing 75 tons had begun to supply ammonia for conversion to nitric acid for German munitions during World War I.

The chapter then outlines the postwar development of competitive ammonia processes necessitated by BASF's reluctance to license the Haber-Bosch process to others. The momentum created provided worldwide incentive for academic and industrial research of the reactions of all types of gases under high pressure. By the mid 1920s high-pressure chemistry had become the fastest growing sector of the industry. Notable industrial outcomes were coal-to-oil processes, polyethylene, and the remarkable acetylene chemistry developed by BASF's J. Walter Reppe (1892-1969) to make a variety of organic chemicals.

Part 2, The Impact and Burden of World War I, in two closely related chapters, lays bare both the human and economic tolls of war.

"Chemistry for Kaiser and King: Revisiting Chemical Enterprise and the European War" fully catches the war mentality to win at any cost, which led to the use of poisonous gases. After failing German tactics bogged down what both sides thought would be a short war, and after a British blockade reduced by half Germany's supply of nitrates, German forces were soon faced with a shortage of munitions. To stall for time until nitric acid production could be increased, Germany, in April 1915, resorted to the most dreaded of weapons—toxic gases. The Allies retaliated, and as the attacks escalated, the talents of the chemical community were increasingly enlisted to develop new gases (lachrymotors, skin blisters, lung injurants), gas delivery systems (portable generators, exploitive shells), and personal defenses (impervious masks, clothing). By 1916 evenly matched armies of the chemically trained numbering in the thousands were serving on both sides. By the end of the war in 1918, it is estimated that Germany had delivered 66,400 tons of toxic gases and the Allies, mostly Britain, 57,800 tons. Perhaps the most constructive outcome of this particular type of carnage was the forced engagement and cooperation among the chemical interests—government, academia, and industry—in Britain, France, and the United States.

"Productive Collateral or Economic Sense: BASF Under French Occupation, 1919-1923" examines the war's aftermath which vindictive victors wrought on Germany's chemical industry. Although the war left Germany's chemical plants largely intact, its toll on the industry was very heavy. What happened to BASF at the hands of the French is typical. After the fighting stopped in November 1918, French forces occupied BASF plants in December, and over the next year assigned teams, including an array of chemists, to search out systematically BASF secrets. Under the Versailles treaty BASF was required to hand over 50 percent of its stockpiles of dyes, chemicals and pharmaceuticals, to supply 30,000 tons of ammonia per year and, for the next three years, allocate 25 percent of its total production for export at pre-war prices. Furthermore, BASF, in exchange for France not destroying its giant Oppau chemical plant, consented to give France know-how for the Haber-Bosch ammonia process. Other countries that had been at war with Germany were also free to exploit BASF patents and trademarks. When, by May 1923, reparations had fallen behind schedule, French troops once again occupied BASF plants and between then and October confiscated 500 railway cars of dyes and 60,000 tons of fertilizer, goods valued at 49 million RM. France also tried and sentenced the entire board of directors to at least eight years in prison for lack of cooperation. The long-term result of the war on the hobbled German chemical industry was that, in order to survive, eight of the largest companies came together in 1925 to form IG Farbenindustrie AG, the largest chemical company in the world.
Part 3, Science in Industry, consists of four essays that provide excellent insight into today’s ongoing debates over the relative merits of theoretical vs. practical work and how resources should be allocated to each.

“Basic Research in Industry: Two Case Studies at I. G. Farben AG in the 1920s and 1930s” starts at the right place with an evaluation of definitions of research related terms. Basic science, basic research, pure research, fundamental research, and pioneering research can all be taken to mean acquisition of knowledge for knowledge’s sake. A science-based industry is one that is reliant on basic research supplied primarily by academia. By contrast, applied science, applied research, and industrial research are the practical application of basic research to manufacturing and production. Technology and development are not applied research but disciplines in their own right.

Then, in the economic and political context of the 1920s-1930s the chapter examines research at BASF’s Central Research Laboratory in Ludwigshaven and at its Ammonia Laboratory in Oppau as to types of projects undertaken, number of personnel, and management outlook. In doing so, the author builds a case for the presupposition, “It is difficult and in many cases even pointless to distinguish between applied and basic research.” He then redefines basic research as “work toward deeper understanding of corporate-related science and technology....” As I interpret the findings, the types of projects undertaken depend on at least three factors: the corporate definition of research, the research director’s personal philosophy of research, and the funds available to do research.

Although this essay is enlightening, in my opinion, there is still enough confusion over the use of research-related terms to warrant some authoritative body such as the IUPAC to build a consensus of meanings within academia and industry through the use of well established terminological principles and procedures.

“Ambros, Reppe and the Emergence of Heavy Organic Chemicals in Germany, 1925-1945” delineates the intertwined careers of two Munich trained organic chemists: Otto Ambros (1901-1990) and J. Walter Reppe (1892-1969). Ambros, a highly personable, persuasive authority on synthetic rubber manufacture, rose quickly through I. G. Farben ranks to become, at age 40, the youngest member of its board of directors. Reppe was the brilliant innovator in acetylene chemistry who provided the scientific breakthrough that led to the synthesis of butadiene and the I. G.’s commercial process for making synthetic rubber. Unlike Ambros, Reppe was hot tempered, easily provoked, and lacking in social skills. Although his one ambition was to be recognized through his work as the chemical leader of Germany, he advanced slowly in the company and became bitter over this failure. When BASF was revived after the war, Reppe was made research director and served until his retirement in 1957.

After World War II, Ambros was tried as a war criminal and sentenced to eight years in prison. Though not mentioned in this essay, the charges against Ambros related to his use of forced labor in building the synthetic rubber plant at Auschwitz. He was convicted of slavery and mass murder.

This story is very readable. It is jargon-free and has lots of contextual material, interesting pictures, and explanatory charts of research organizations and chemical reactions. It concludes that the joint R&D efforts of Ambros and Reppe paved the way for the West German chemical industry to switch from coal-based to petroleum-based chemicals in the 1950s and early 1960s.

“The Development of Chemical Industries in Sweden and the Contribution of Academic Chemistry after 1900” primarily examines the role of laboratory research in three industries: superphosphate fertilizer, pulp and paper, and sodium perchlorate made by the electrolysis of sodium chlorate. It shows that although the pulp and paper industries maintained laboratories, the labs were small, poorly equipped, staffed by nonchemists, and used primarily for control purposes. What the industries needed primarily was practical knowledge and adequate financing. However, because the labs presented an image of science to outsiders, they were useful in advertising. Industry in general saw science as unprofitable, and government was reluctant to support applied science except in industries critical to the economy. Academic chemists had little interest in fertilizer and paper from which research results and patents were likely retained by the companies. However, science-based chlorate electrolysis attracted a large number of dedicated researchers.

Though slow in arriving, science and applied research came to Swedish chemical industry by two avenues: 1) professional consultants who brought an outlook to the plant totally different from that of the practitioner; 2) contacts with technical and scientific institutions in which industrial work was part of the responsibility of the professional chair holder. These people, however, were troubleshooters who improved existing
processes rather than develop new ones. Applied research and its attendant laboratories came ultimately with the hiring of chemically trained staff.

"Selling Science: Dutch Debates on the Industrial Significance of University Chemistry, 1903-1932" shifts the emphasis from the consumers of research to the producers of research by focusing on the efforts of university chemists to create jobs for their graduates. In 1876, the Dutch Parliament had overhauled the nation's university system and, in doing so, had turned Utrecht University into a research based institution where a degree required seven or more years for completion. At the same time, the Polytechnic Institute at Delft was turning out chemical technologists in four years. Because industry gave Polytechnic graduates a decided edge in hiring, the University had to convince industry of the value of its graduates and the kind of work they were trained to do.

A government proposal in 1903 to raise the status of the Polytechnic to that of the University sparked a two-decade-long debate over the type of education best suited to industry and the compatibility of academic knowledge with practical experience. Opinions ranged from an "unbridgeable gap" to "closely related activities." As proposed terms and definitions were revised and repeatedly modified, a compromise slowly emerged: pure research was driven by curiosity, and applied scientific research was necessary for plant and production problems.

During World War I the need to reduce imports of food, fertilizer, and all kinds of chemicals forced industries into research. For example, Phillips Electrical had to build its own plant to make argon for filling light bulbs. Capitalizing on this turn of events, university chemists began to emphasize the social aspects of being a researcher and of building a strong nonelitist sense of the chemist's functions in society not above society.

Part 4, Different Routes to Competitive Advantage, contains five essays which describe how the chemical industries in Britain, Norway, and Switzerland used science, technology, education, advertising, shrewd marketing, and astute management to gain market footholds.

"Modernizing Industrial Organic Chemistry: Great Britain Between Two World Wars" begins with the struggles of the British chemical industry during World War I to recover know-how for making products it had once mastered but then lost to German competition. When the war brought explosives, drugs, dyes, and toxic gases under government strategic planning, it also forced interaction and cooperation within the chemical industry. The postwar result was an industrial reassessment of available raw materials, new technology, particularly high-pressure processes, and new products, such as plastics, resins, and adhesives. To position itself in world markets and to offset foreign competition, industry sought new directions. The government brokered mergers of small companies and created new ones. Among new industrial and governmental organizations growing out of this forced cooperation were The Association of British Chemical Manufacturers, The Department of Scientific and Industrial Research, and the National Research Laboratory.

The story is told with particular emphasis on ICI, formed in 1926 to compete with DuPont, Dow, and I. G. Farben, and the development of its processes for synthetic fibers, phthalocyanine dyes, polyvinyl chloride, methyl methacrylate, polyethylene, sulphonamides, and coal-to-oil fuels.

"Scaling Up: The Evolution of Intellectual Apparatus Associated with the Manufacture of Heavy Chemicals in Britain, 1900-1939" would have been better titled "Scaling Up: Britain's Role in the Early Development of Chemical Engineering." Although the term "chemical engineering" seems to have been coined in Britain in the 1880s; and without doubt, George Davis (1850-1906) of Manchester Technical School published the first book on the subject in 1901, the concept of unit operations, as proposed by Arthur D. Little in the US in 1915, is generally recognized as the intellectual basis of the profession of chemical engineering.

This essay compares the development of the profession in the United States and in Britain. John W. Henchley (1871-1931), who followed George Davis at Manchester, introduced the concepts of material and energy balances to arrive at the most economical way to produce a given chemical, namely through "process design." Likewise, he was the first to draw on students' training in civil, electrical, and mechanical engineering to educate them in "plant design."

Much of the history of chemical engineering hinges on how terms have been defined. Britain's Institute of Chemical Engineers (I Chem E) made the "capacity to design manufacturing plants on a commercial basis" central to its definition, as distinct from the American concept of unit operations. While it is stated here that the I Chem E, as early as 1925, "pioneered reaction treatments of materials" or what would become known as
unit processes, I was unable to find supporting data. The concept of unit processes is usually attributed to a paper in 1928 by P. H. Groggins (b. 1888), of the United States Department of Agriculture, followed by his text, *Unit Processes in Organic Synthesis*, published in 1935.

“The Use of Measuring and Controlling Instruments in the Chemical Industry in Great Britain and the USA during the Period 1900-1939” is an attempt to show that instruments were introduced into the chemical industry to reduce waste and labor costs and to improve product quality. It is based on limited data mainly from three sources: trade literature, instrument sales data for the US and Britain, and technical articles published in the 1920s and 1930s. Three reasons are given for the more rapid acceptance of instruments in the US than in Britain: development of mass production processes, standardization of products, and acceptance of the principles of scientific management with “one best way” for doing everything. In Britain, by contrast, the chemical industry was based on small production units, a flexible approach to production, and greater reliance on the skills of craft based labor.

In my opinion, this essay overly emphasizes the role of instruments in labor cost reduction at the expense of their role in product quality improvements. I also question the validity of comparative data on worker productivity in the US and Britain without such knowledge as respective union and/or governmental work rules, hourly lengths of work weeks, and the contributions of labor saving machinery.

“Norwegian Capitalists and the Fertilizer Business: The Case of Hafslund and the Odda Process” tells a fascinating, almost mystery-like tale of the development in 1928 of the now virtually unknown Odda process for making a highly concentrated, nonmixed, three-component (N, K, Ca) fertilizer to compete with I. G. Farben’s Nitrophoska. The chemistry given for the process is very sketchy but appears to have consisted of treating phosphate rock with excess nitric acid and then neutralizing with ammonia; but the chemistry involved is not the point of the story. Rather, it is about why the company Odda Smelteverk came to develop the Odda process and why neither it nor its parent company, the Hafslund group, ever used the process, but licensed it to I. G. Farben. In particular, the essay provides a close-up of the inner workings of the companies, the personalities of their principals, their dealings with banks, their gamble on the research and development of innovative products, and how the company’s desire for short term profits governed its policies. In short, it is the story of an industry’s intricate strategies to survive during the difficult period between the wars.

“The Swiss Pharmaceutical Industry: The Impact of Industrial Property Rights and Trust in the Laboratory, 1907-1939” is true in content to its well worded title. The modern pharmaceutical industry based on laboratory research dates from the 1880s, when Swiss firms began to concentrate on name-brand specialized products of high profitability. They also brought the principles of scientific management to production and established effective international marketing and advertising for prescription drugs supplied through physicians. Although well established companies such as CIBA and Sandoz took the lead, a number of smaller companies manufactured patent medicines. In the 19th century, Swiss firms had not recognized foreign patents so specialized in imitation rather than innovation. After a trade agreement against such “piracy” became fully effective in 1907, the number of Swiss patents doubled over the next six years.

Diversification of product lines resulted in specialized research in pharmacology, bacteriology, and physiology; and advertising aimed at convincing the public of the effectiveness and supremacy of name-brand remedies. The result was that by the 1930s the large corporations based in Basel represented 90% of the Swiss pharmaceutical business, and Swiss drug exports increased from 4.6% in 1911 to 19.7% in 1939. This growth was also due in part to a worldwide decline in patent medicines after they came under increasing governmental regulation starting in the 1920s.

Part 5, *State Intervention and Industrial Autarky*, in four essays considers the role of government regulation in the development, or lack thereof, of the chemical industry in Italy, Spain, Denmark, and Finland.

“Technical Change in the Italian Chemical Industry: Markets, Firms, and State Intervention” is crammed with facts on firms, patents, products, markets, and sales that are bolstered by examples from Montecatini, Italy’s leading chemical firm. Prior to 1930, chemical production in Italy was based on the needs of agriculture and traditional manufacturing. However, government efforts in the 1930s to accelerate R&D and to buy foreign technology advanced the industry by providing the technical skills, scientific know-how, and practical experience needed for extraordinary growth after World War II. The impact is summarized for five industries: aluminum, dyes, pharmaceuticals, oil refining, and polymers.
Governmental autarky policies instituted in 1934, namely those designed to establish a self-sufficient national economy, generally worked well; and there was a high degree of convergence between the strategic purposes of the chemical industry, the ideas of the technocrat managers of state-owned industries, and Mussolini’s fascist ministers. The balance of power was such that no one segment could dominate, and conflicts such as the allocation of scarce resources required compromise. The working rationale, still valid, was this: to improve long-term economic prospects and to gain status in world markets, a nation must not slavishly adhere to competitive costs and short-term advantages, but must invest in those industries, technologies, and human resources which improve overall productivity.

“The Frustrated Rise of Spanish Chemical Industry Between the Wars,” starts with the premise that World War I was beneficial to the chemical industry in Spain. As a neutral country, it could readily attract investment capital to enlarge existing facilities such as explosives, sulfuric acid, and alcohol. When, after the war, it faced strong competition from recovering nations in Northern Europe, the industry declined in spite of protectionist laws and tariffs. The reasons cited for Spain’s industrial backwardness, which lasted until the 1960s, include: lack of vital resources (raw materials, cheap power, investment capital, modern transportation, and scientific and commercial know-how), stagnant markets, and a short-sighted management that lacked self-confidence. Added to these were the lack of theory-oriented technical schools and research institutions, lack of industrial R&D, and the perverse effects of over regulation by government.

Between World Wars I and II, progress in addressing these conditions within and among competing interests resulted in modest gains on all fronts. The underlying factors leading to growth in five industries — sulfuric acid and soda, explosives, dyes, fertilizers, and alcohol—are examined in detail.

“The Take-Off Phase of Danish Chemical Industry, ca 1910-1940” gives an overview of those events that gave the industry its impetus to grow. Denmark, a largely agricultural country, had few of those natural resources—minerals, oil, coal, forests—needed to establish a heavy chemical industry. What chemical industry it had at the turn of the century was dominated by small, geographically isolated, technically backward firms that mainly produced goods associated with agriculture. At the outbreak of World War I, 60% of the industry’s gross income derived from sugar refineries, margarine factories, breweries, distilleries, and oil mills. Some highly successful ventures developed between the wars included cryolite mining for aluminum smelting, beet sugar refining, hydrogenated coconut oil for margarine, and the production of insulin. Contributing to the take-off was a tradition dating from 1832 at the Polytechnical College in Copenhagen of training engineers highly qualified in chemical process technologies. Although a modern patent law was passed in 1894, few Danish companies filed patent applications; and few of those were developed. Two prime examples were the quinhydrone electrode [1920] for measuring pH and discovery of the element hafnium [1923], which became important in the Dutch electrical industry.

Plans in 1918 to build a Haber-Bosch ammonia plant failed to materialize as did one based on an electric arc process in 1933. One reason was that the government was eager to maintain friendly trade relations with Norway, to which it sold agricultural products and from which it bought fertilizer.

“Neglected Potential? The Emergence of the Finnish Chemical Industry, 1900-1939” focuses on the question of “why Finland’s chemical industry developed so slowly and so late and achieved so little considering its potential.” The answer in short is that, before World War II, industries of all types competed for the same resources: waterpower, timber, funding, technical expertise, and management skills. The government did not attempt to attract large transnational companies by offering economic incentives. Efforts to buy foreign know-how could easily get mired in bureaucracy. Although higher education could offer a few outstanding chemists, it was not organized to do research that would foster industry. Furthermore, Finland’s industries hired few chemists and did little or no research on their own. Through the mid-19th century, Finland had exported pine tar, pitch, potash, and saltpeter; but as technology changed, shipbuilding in particular, the markets for these craft-based industries slowly collapsed. A new beginning came in the 1890s-1900s, with the building of plants for carbide, dynamite, potassium chlorate, and consumer rubber goods; but by the time of World War I, these had largely withered and died.

After the nation gained its independence from Russia in 1917, it began to develop its mineral and copper resources, further develop its hydroelectric power, establish fertilizer works, and manufacture caustic soda, sodium sulfite, Glauber’s salt, and calcium hypochlorite for its flourishing pulp and paper industry. One very bright spot was government-built plants (17 in
all) to convert spent sulfite pulp waste to fuel alcohol. During 1941, the peak production year, these plants produced 31,000 tons of alcohol. Herbert T. Pratt, 23 Colesbery Dr., New Castle, DE 19720-3201.

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**SIXTH HISTORY OF CHEMISTRY SYMPOSIUM**

at

**SACRED HEART UNIVERSITY**

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on

Saturday, November 11, 2000

8:45 A.M. – 4:15 P.M.

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Purdue University, IN

Dr. Peter Childs
University of Limerick, Ireland

Dr. Kathryn Steen
Drexel University, Philadelphia, PA

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**Topic**

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The Royal Institution of Great Britain from 1800-2000

History of Chemicals from Seaweed: from Alkali to Iodine to Alginates

U.S. Synthetic Organic Chemicals Industry in World War I and the 1920’s

History of Catalysis

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