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Division of the History of Chemistry of the American Chemical Society

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Dr. Johannes Wislicenus

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The Cover . . .

Johannes Wislicenus (1835-1902), shown when he was Professor of Chemistry and Rektor, U. Würzburg, 1882.
[See article by P. J. Ramberg in this issue.]

FROM THE EDITOR

With this issue of the **Bulletin** we come to a turning point in this publication by the History of Chemistry Division of the American Chemical Society. Dr. William B. Jensen, founder and original editor of the **Bulletin**, has made the decision to step down from this responsibility. It is with a deep sense of humility that someone would assume the editorship of this publication, recognizing the high standard of quality that is to be maintained. Nevertheless, there is a strong conviction that this journal serves historians of chemistry in a vital way, and thus its publication must be continued with as smooth a transition as can be managed.

For those potential authors who await the appearance of your articles or notification of the status of your manuscripts, we offer our assurance that plans are in place to handle these matters promptly. To HIST members and other subscribers, we pledge our goal to produce issues of the **Bulletin** in a timely manner.

All HIST members should have received a complimentary copy of **INDEX TO THE HISTORY OF CHEMISTRY**, prepared by 1995 HIST Chair Martin D. Saltzman, in late 1995. This will serve as a valuable bibliographical resource for chemical historians.

We invite historians of chemistry to submit manuscripts for consideration for future issues of the **Bulletin**. Please consult the "Instructions for Authors" below. All inquires should be addressed to the Editor.

Paul R. Jones

INSTRUCTIONS FOR AUTHORS

Articles of 4–12 pages, typed, double-spaced (excluding references) should be submitted as hard copy (2 copies) and also on diskette, preferably formatted in Word or Wordperfect, to **Editor, Bulletin for the History of Chemistry**, at the University of Michigan. Chemical formulas, to be kept to a minimum, should be computer-generated and printed on separate sheets, with a clear indication of their location in the ms. Authors are encouraged to provide photographs (black and white glossy prints) and drawings (black ink) to enhance the publication. The title of the article should be of reasonable length (up to 15 words); a subtitle may be included if appropriate. Authors should strive to make the title descriptive of the specific contents, for the sake of clarity to the readers.

Format as found in recent issues of the **Bulletin** should serve as a guide. References should conform to the format as illustrated below. Standard **Chem. Abstr.** abbreviations are to be used (see CASSI); title of the article is in quotes; inclusive page numbers are given for an article or partial section of a book.

O. T. Benfey, "Dimensional Analysis of Chemical Laws and Theories," *J. Chem. Educ.*, 1957, 34, 286–288.

G. W. Wheland, *Advanced Organic Chemistry*, Wiley, NY, 1949.

J. R. Partington, *A History of Chemistry*, Macmillan, London, 1972, Vol. 4, 104–105.

L. P. Rowland, Ed., *Merritt's Textbook of Neurology*, 8th ed., Lea and Febiger, Philadelphia, PA, 1989.

Please include a short biographical sketch, to be included at the end of the article.

Readers are encouraged to submit short notes, where appropriate, and letters to the Editor, as well as articles. We would welcome hearing from those who have an interest in refereeing papers and/or preparing book reviews.

APPLICATIONS INVITED

First Glenn E. and Barbara Hodsdon Ullyot Scholarship

The Chemical Heritage Foundation (CHF) is pleased to announce the creation of the Glenn E. and Barbara Hodsdon Ullyot Scholarship Fund. The purpose of the Ullyot Scholarship is to advance public understanding of how important the chemical sciences are to the public welfare. The first Ullyot Scholarship will be awarded for summer 1996; it offers a stipend of \$1,500. The scholarship supports a minimum of four weeks research on the heritage of the chemical sciences utilizing the resources of CHF's Othmer Library of Chemical History in Philadelphia, other area libraries, and associated resources.

The Othmer Library houses primary sources from the sixteenth century through the mid-twentieth century, with emphasis on the last 100 years. The library maintains a wide array of reference books and secondary literature on the history of the chemical sciences and technologies, as well as the personal papers of outstanding chemists and industrialists and the archives of professional organizations. The core of the library—over 40,000 volumes that span the era from the Civil War through World War II—forms an unrivaled resource for the history of American chemical business and technology.

To apply, please send four copies of a curriculum vitae, a one-page description of the proposed research, and the telephone numbers of two referees. The proposal should demonstrate how the Othmer Library's resources are relevant to the applicant's project. Applications must be received by 31 March 1996 and should be sent to Laurel Adelman, Chemical Heritage Foundation, 315 Chestnut Street, Philadelphia, PA 19106. Telephone (215) 925-2222 Fax: (215) 925-1954.

THE 1992 DEXTER ADDRESS

Historic Chemical Instrumentation: From the Cellar Upwards

John T. Stock, University of Connecticut

To begin this address, I need to offer both thanks and an apology. My thanks are to my fellow members of the Division of the History of Chemistry and to the Dexter Corporation, for granting me the 1992 Dexter Award. The apology is simply because I cannot hope to reach the level of erudition of the addresses given by many earlier awardees. My account is merely of my progress towards some understanding of the history of chemistry, especially of its instrumentation.

Becoming a Chemist

When I was about eight years old a neighbor, who was taking his son to the London Science Museum, invited me to join them. We youngsters rushed from exhibit to exhibit, pushing all the buttons that we could find. I had never seen anything like this! At once, I pestered my mother to make many other visits; unaccompanied kids were not exactly welcome in those days. Inevitably, the wardens found her a chair in some quiet corner, while I vanished, to reappear an hour or so later. I got into the Chemistry Gallery, but was not impressed; at that time, there were showcases with lengthy descriptive cards, but no pushbuttons. All of this left me cold; I knew no chemistry. However, a balance with a long cone-like beam caught my attention and I even read the label. After a few more visits, I resolved to become a scientist. How little did I realize the long and tortuous path that lay ahead! Soon after, another neighbor gave me a few monthly-issued parts of a general encyclopedia. As I read my first article on chemistry, I suddenly felt that I had been here before. This sort of feeling has never occurred again.

My 15th birthday passed, so my classmates and I were soon to finish school. We sat for the Schools Certificate examinations, for which the grading scale was "credit" (a very good pass), "pass," and "fail." I got four credits, but two fails. University entrance required five passes, so I was out of the running. This did not seem to matter very much at the time; we were anything but wealthy, so I looked for a job. I could not find any science-related opening, and was finally hired by an accountant partnership. I thought that this was due to my proficiency in arithmetic, but later learned the real reason; I was a teetotaler! The main concern of the business was with licensed premises—pubs, if you like—and I was judged safe to work in the cellars. At least I got to know what goes on behind the bar, as well as underneath it!

After about two years, I took a job in the planning division of a large engineering works. If not exactly scientific, the work certainly involved technology and brought me into close contact with skilled craftsmen. Today, I cannot look at an historic instrument without beginning to visualize how it was made. Before shifting from accounting, I became an evening student at Norwood Technical Institute (now South London College). The fees at institutes like this were very small, sinking to zero if one's attendance had been good. I soon had the run of the laboratories. Although I was awarded both the Ordinary and the Higher National Certificates in Chemistry during the next few years, I still was ineligible to enter a university, even as a part-timer.

Although not very old, the University of London is both large and liberal. Provided that a candidate went through the proper steps and took the examinations, he or she could obtain a degree. Before the War, several

British colleges were unchartered, so their students were examined in London. I believe that Southampton College, now a celebrated university, was one of these. The University of London had realized that some who missed out at school might still make the grade. Thus arose the Special Entrance examinations, open to anyone aged at least 23. I took these examinations as soon as I could and fortunately passed. During my final year at Norwood, I passed the University Intermediate Science examinations and transferred to the Sir John Cass College (now City of London College) which was recognized for degree-level training. Not being able to get time off, I took my annual vacation to coincide with the final examinations, and obtained my bachelor's degree in the summer of 1939. Almost at once, war broke out.

What a change! Anyone professing even a little science was in great demand. I was placed on the National Register and, after many years, my evening studies ended. I was soon on plant control in a wallboarding factory, then moved to a Ministry of Supply establishment in southern England. Initially, we were concerned with possible gas warfare, but later went on to other areas such as smoke screening. With the closing of colleges and the seconding of the faculty, I rubbed elbows with some of the leading scientists of the land. The more fortunate did work that led to post-war publications; with my background, I was assigned to "technical chemistry" and engineer liaison. These were polite terms; for example, I spent a good deal of time hanging on to the turret of a tank while it bumped its way across the countryside, duly emitting its smokescreen. When this was based on the vaporization of oil, I was sometimes involved in spectacular fires! Of course we had laboratory work, usually involving highly unpleasant substances or trying to trace the reasons for the failure of a smokescreen.

I shall never forget the kindness of Professor Neil K. Adam, of Southampton College, some 30 miles south of my location. He gave me the run of the College laboratories on Sundays. The College was some two and one half miles from the railroad station, and the streetcars were not running. Fortunately, I like walking. I wanted to study the polarography of quinoline compounds, but had neither recorder nor pH meter. Nevertheless, by point-by-point plotting, I managed to get the curves at one-half pH intervals over the range 1.5 to 12.0 units. Fortunately, I was well acquainted with the vagaries of the hydrogen pH electrode. After more than a year of Sunday work, the writeup was accepted for publication in the *Journal of the Chemical Society* (1).

Then came another switch, to take over the laboratory of a London food factory. With evenings free, I

used the quinoline work and some other studies to compose a thesis, for which I was granted a London master's degree. I also started teaching in the evenings at, of all places, Norwood Technical Institute. The war was nearing its end and educational establishments were beginning to return to their normal activities. I liked teaching, so became full-time at the Institute in the fall of 1946.

With veterans pouring out of the armed services and numerous groups of students from the soon to be independent African colonies, we were overrun. We taught five and a half days a week, plus two or three evenings. My colleagues and I had little time for research, but we developed a lot of simple apparatus and wrote a couple of texts on small-scale laboratory methods (2, 3). One of these ran through five editions. Because we were short of space, equipment, time, and funds, we used small-scale techniques wherever practical. I also began to study the history of some electrochemical techniques (4, 5).

When things quietened down a bit, I managed to keep Fridays free. So I resumed my electrochemical studies in a corner of the Institute and then wrote a thesis which gained me a London Ph.D. I had become head of department and eventually gained an award for overseas study with Professor I. M. Kolthoff at the University of Minnesota. He fixed me with speaking dates across the country when my wife, small daughter, and I were traveling back home. I was surprised to be offered several jobs. I accepted the offer from the University of Connecticut, arrived there in January, 1956, and have been there ever since.

Chemical Balances

Eventually, I introduced a course on the history of chemistry, but unfortunately this lapsed when I became emeritus. I progressively increased my London contacts, especially with the Science Museum. During my 1965 sabbatical leave, I examined the Museum's fine collection of historic balances. Balances were certainly known to the ancient Egyptians. Quite sensitive small balances, needed for trading in gems, coins, and the like, were in use in the 15th century. The demands of the tax collector may have influenced the design of balances. The British Government needed a means to assess the excise duty on spirituous liquors, and the means chosen required the accurate determination of the specific gravities of standard alcohol-water mixtures. This required a sensitive balance capable of handling a quite heavy load. The famous instrument maker Jesse Ramsden (1735-1800) (Fig. 1) fulfilled this requirement. He was fond

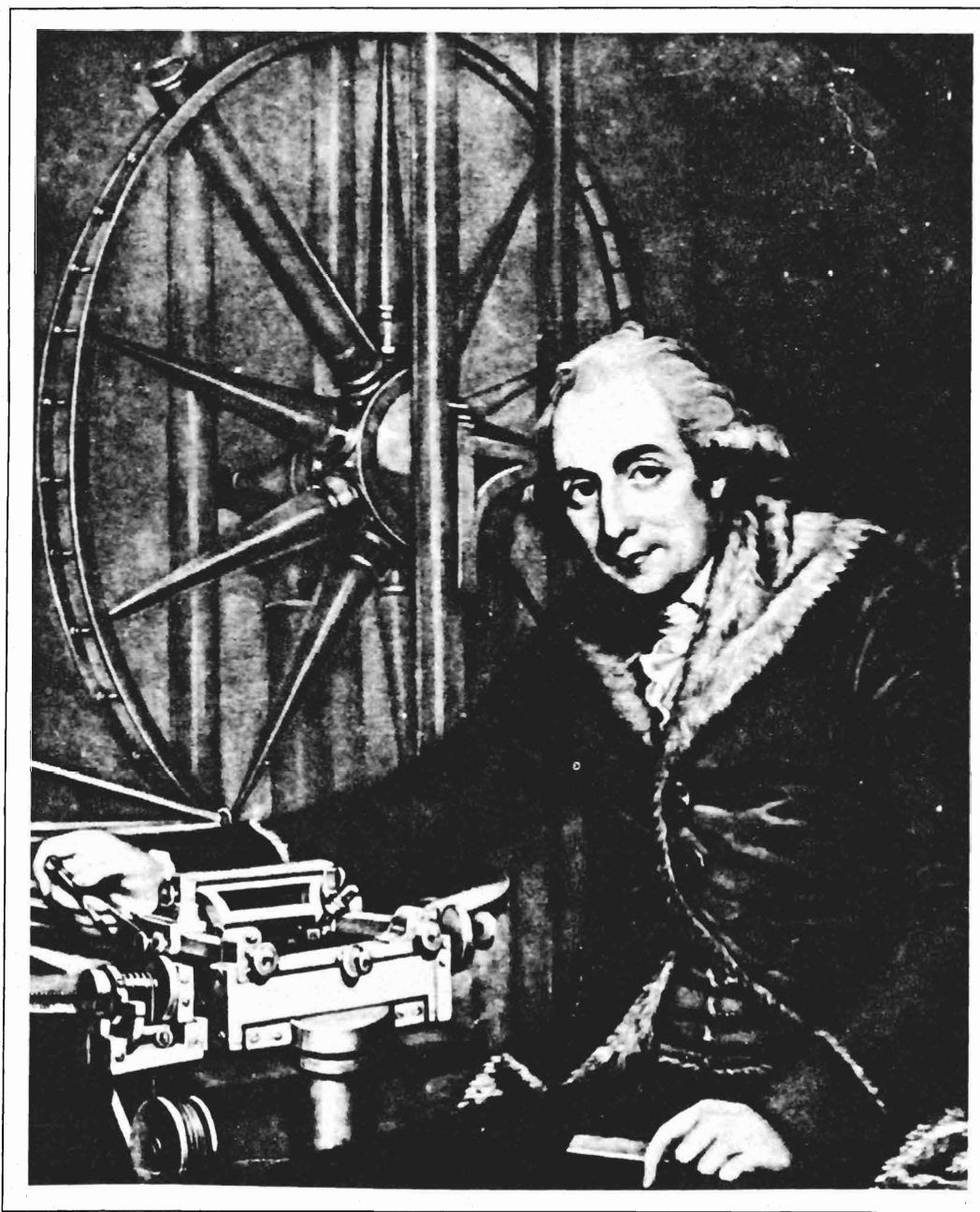


Figure 1 Jesse Ramsden (reproduced by permission of the Trustees of the Science Museum, London)

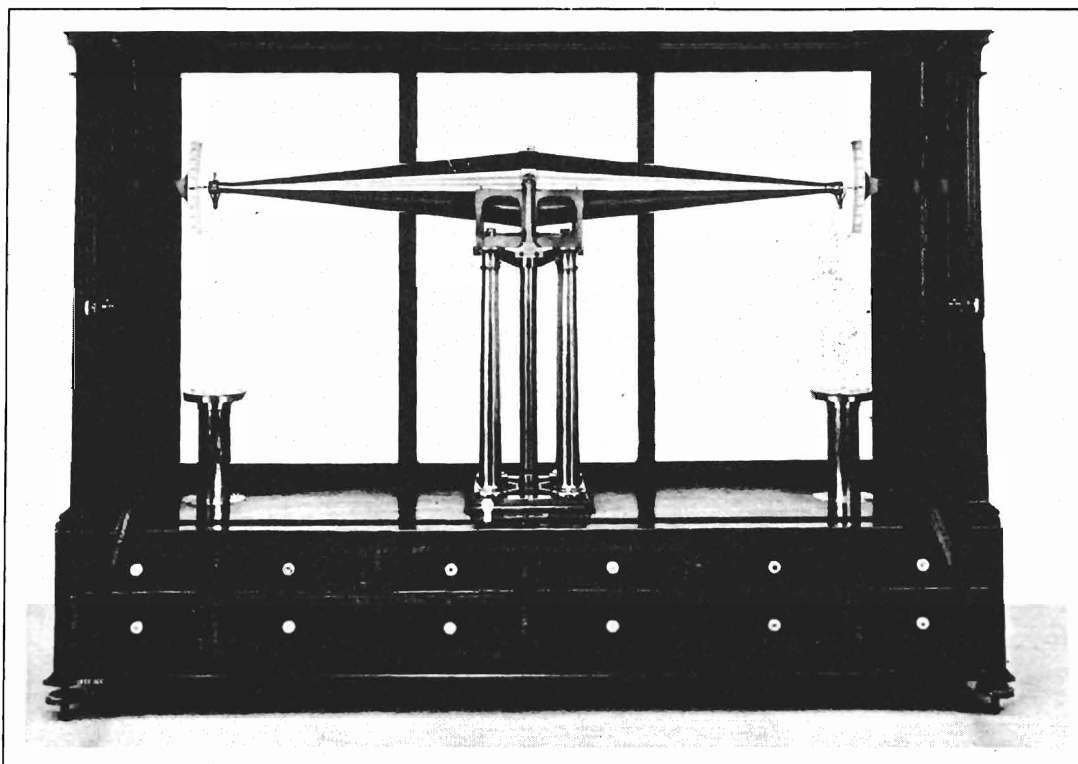


Figure 2 The Ramsden balance (reproduced by permission of the Trustees of the Science Museum, London)

of the rigidity provided by the use of hollow cones; some of these can be seen in the astronomical instrument in the background of his portrait. He made the cone-beam balance shown in Fig. 2 and it was used to make the determinations in 1789. This was the instrument that had caught my eye during my first trip to the Science Museum as a boy. When examined in 1965, the pans were missing, but I reckoned that the sensitivity was better than to one milligram.

Other makers followed Ramsden's design. Actually, the lateral rigidity provided by the cones is quite unnecessary; the beam-bending force is entirely vertical. Hence the triangulated flat beam came into being. A major figure in this development was Thomas Charles Robinson (1792–1841) (6). In 1967, I examined the Robinson balance in the Chemistry Department of the University of Edinburgh. The assumption was that the balance had belonged to Joseph Black (1728–1799). This was, of course, impossible, because the maker was less than ten years old when Black died. A more likely owner was Thomas Charles Hope (1766–1844), Black's successor. This balance, along with a near-copy made by the Scottish firm Adie & Son, is now in the Royal Museum of Scotland.

The intriguing history of the precision balance, described in the Science Museum's account, is too long to go into here (7). I would, however, like to mention a fact and an error. The British standard troy pound was destroyed in a fire of 1834. Three balances, two by Robinson and one by his successor, Henry Barrow (1790–1870), were used in the lengthy work of reestablishment. I know the location of one Robinson balance and the fate of the other. But, after 25 years of searching, I have yet to find the "balance of extreme delicacy, procured from Mr. Barrow" (8). The error concerns the chain balance, in which an adjustable chain eliminates the need for small weights. In company with several others, I had described this type of balance as an American invention of 1916. We now know that the chain principle was introduced in France a quarter of a century earlier (9).

Galvanometers

I had long realized that progress in electrochemistry depended largely on electrical instrumentation. The account by Michael Faraday (1791–1867) of how he made

his own galvanometer intrigued me, so I spent part of my sabbatical leave of 1972 working under Professor Ronald King at the Royal Institution in London. Here Faraday had worked and lived. This was an exciting time, because King was setting up the Faraday Museum in the basement. He suggested that I should write an account of the developments that arose from Faraday's simple instrument.

Around this time, I had been appointed Honorary Research Fellow of the Science Museum and was fully aware of the Museum's outstanding collection of electrical instruments, some on view and some in the Museum stores. Here I must remark that I have seen some interesting instruments in the cellars of various foreign museums. When in Czechoslovakia, I noticed a German copy of an early type of Robinson balance. However, the curator could not tell me how, or when, this had been acquired. In Australia I saw some instruments that had been made locally because of wartime unavailability from overseas. Historic indeed, as examples of instrument-making under stress! However, I must return to the "galvanometer project." After writing a paper or two on limited aspects of current measurement, I joined forces with Denys Vaughan, of the Museum's Department of Physics. It took about ten years of our combined part-time work to get the overall account into print (10).

The siphon recording galvanometer designed by William Thomson (1824–1907), later Lord Kelvin, has always amazed me. It made possible the paper-tape recording of transatlantic telegraph signals. The tiny force available could not possibly drag a pen across paper. Thomson solved the problem by maintaining an imposed potential between the tape and the nearby jet, which moved laterally in response to the incoming signals. Tiny drops of ink were thus projected onto the traveling tape in a frictionless manner. I often wonder if the inventors of the modern ink-jet computer printer were inspired by this device. There is a little electrochemistry associated with the testing of another of Thomson's galvanometers. In 1866, when two cables were working, they were joined at the far end. Thomson transmitted intelligible signals through this total length of 3700 miles, using as a power source a silver thimble containing a little acid and a slip of zinc.

Chemical Automation

Nowadays the automation of laboratory processes is quite common. Attempts to do this are by no means new. I would like to give one example that I noted when

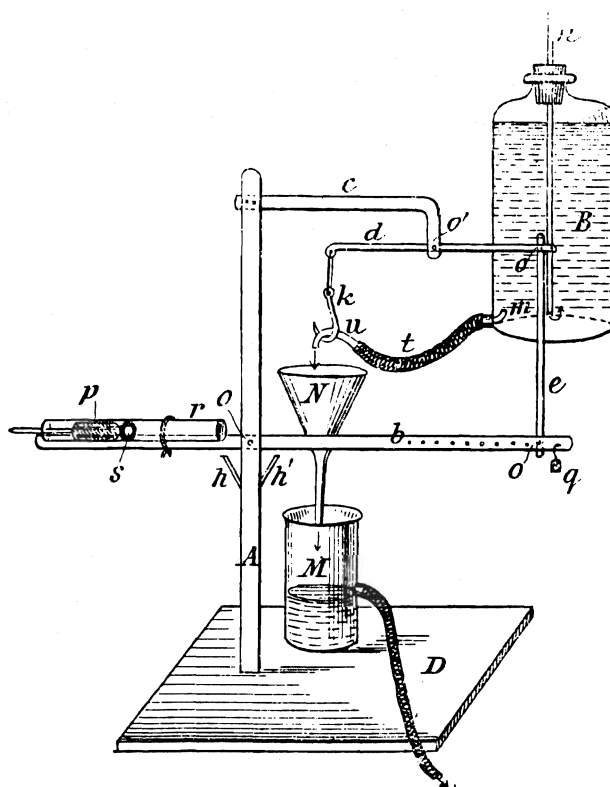


Figure 3 Automatic precipitate washer

surveying this topic some years ago (11). Although not much used today, gravimetric analysis was once a major technique. The washing of a precipitate on a filter paper is a tedious operation; each wash portion should be allowed to drain away before the next portion is added. A method for the automation of this washing, illustrated in Fig. 3, dates from 1893 (12). Suppose that funnel *N*, carrying the precipitate on its filter paper, is essentially dry. Counterpoise tube *P*, closed at the end nearest the upright, carries ball *S* in the position shown. The lever system has depressed the tip of jet *U* below the level of the bottom of control tube in wash liquid reservoir *B*. Liquid runs into the funnel until the increased mass tilts the lever system. This raises the jet and stops the flow. At the same time, the ball rolls right, to the bottom of *P*, thus reducing the counterpoising force. Not until *N* has drained is this reduced force strong enough to reverse the tilt. The flow restarts, the ball rolls back to its original position, and the cycle continues as long as desired.

My varied career has left me with an interest in the history of industrial automation (13). Purely mechanical automation was well known to the ancients, as in the magic opening of temple doors. A somewhat more mod-

ern example is the Falcon loom of 1728, which was controlled by punched cards.

Traditionally, the fuel for steam-raising was coal, which is still in use today. Although the production of carbon dioxide cannot be avoided, there is the obvious need for obtaining good energy efficiency. To achieve complete combustion, somewhat more than the stoichiometric amount of air must be supplied. With too little air, a smoking chimney will soon get the stoker into trouble. To avoid this, he is likely to be over-generous with the air supply. Efficiency is lost in heating the excess air. Efficient operation can be achieved by monitoring at least one component of the flue gases. Some modern devices measure the oxygen content; traditionally, the percentage of carbon dioxide was involved. Gas analyses are possible by the Orsat or similar apparatus. However, boilers run continuously, so any method requiring an operator is virtually impossible. Here we have an excellent case for automation, usually involving flue gases aspirated directly from the chimney (14).

Figure 4 shows the "Oekonometer" of 1893. The density of the gas is continuously indicated by what is

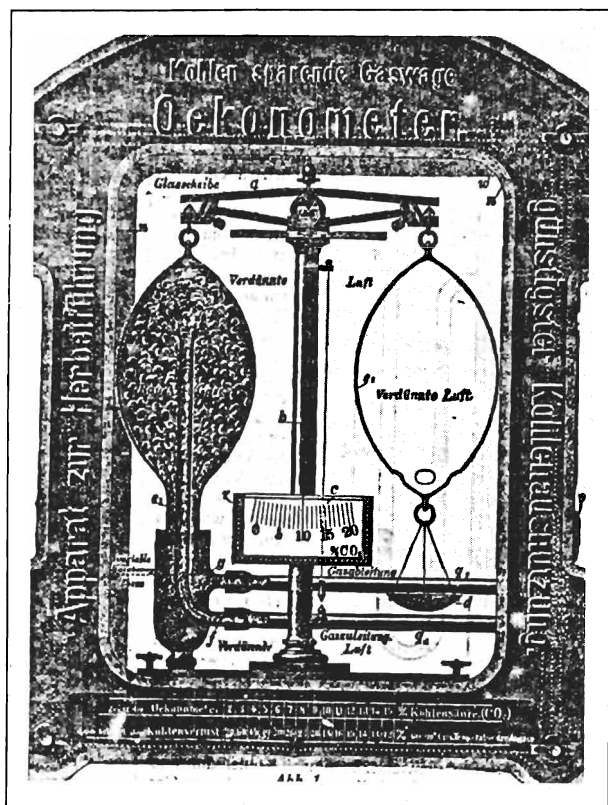


Figure 4 Oekonometer carbon dioxide monitor

essentially a balance in an iron case. The instrument is adjusted so that the pointer scale gives the percentage of carbon dioxide. Another approach is to measure a portion of gas, absorb the carbon dioxide, then measure the residue. A good example of this approach is in the Cambridge Bimeter, introduced in 1910. After passing through a cooler system and a meter, the gas enters an absorption chamber containing slaked lime (calcium hydroxide). With the carbon dioxide now removed, the gas again passes through the cooler to equalize temperatures and then escapes through a second meter. About every two minutes, the differential rates of the meters cause the slowly rotating chart to be marked with a vertical pen stroke of length proportional to the percentage of carbon dioxide.

For use in boilers, the "hardness" of water must be removed. The classical lime-soda treatment requires the titrimetrically controlled additions of calcium hydroxide and of sodium carbonate. The 1906 German patents for the photometric automation of this process were found by sheer luck (15). Looking through early *Chemical Abstracts*, I was puzzled by an entry describing regulated additions "especially to drinking water." In that prefluoridization era, why dose water? The abstractor did not realize that the term "Speisewasser" in the patents, meaning "feed water," is exactly the term used by boilermen. I have never found any reference to the installation of this ingenious but complicated equipment. Only the poorly-responding selenium photocells were then available, and electronics was not yet in sight. The idea was probably before its time.

One Thing Leads to Another

In the study of the history of chemistry an interest in one aspect inevitably leads into another. Perhaps I should give a few examples. I have mentioned the "missing" Barrow balance; I thought that if I found out a little about Barrow himself, this might help in a future search. I was unlucky here; however, I was intrigued to learn that Barrow had been associated with the Great Survey of India. In fact, George Everest (1790-1866) had arranged for Barrow's appointment as survey instrument maker. However, the association eventually broke down, owing, it seems, to the clash of the two strong personalities.

Like most schoolboys, the availability of the celebrated "burner" made me aware that we owed this device to a gentleman named Bunsen. Much later, my interest in electrochemistry turned to the Bunsen cell, another invention by Robert Bunsen (1811-1899). Bat-

teries of these cells were often used by early experimenters; Bunsen himself used them in his experiments on arc-lamp lighting. This got me interested in illumination, both by the gas mantle and by the Edison lamp bulb. A chemist's interest in gas lighting can be readily excused; success was reached through Welsbach's expertise in what we now term lanthanide chemistry (16). But what of electric lighting? Sufficient to say that Edison used electrolytic meters to fix the bills for his customers (17).

In reviewing my long interest in potentiometry, I realized that I knew little about the history of potentiometric titration, except that it had been introduced by Behrend in 1893. On inquiring, I found that Robert Behrend (1856–1926) (Fig. 5) began by studying law, quickly changed to physics, and then decided to become a chemist (18). In 1877 he went to the University of Leipzig, where he was interviewed by the celebrated or-

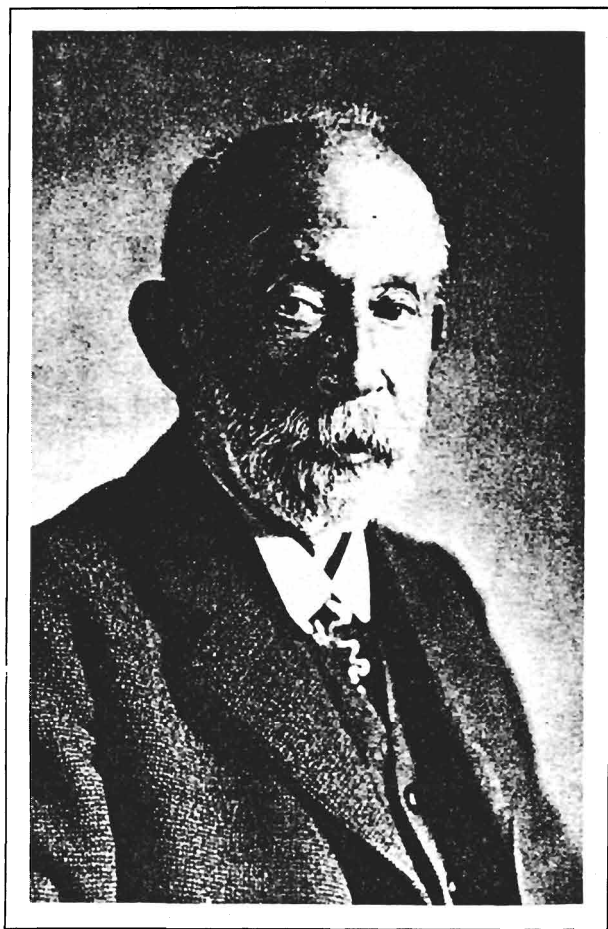


Figure 5 Robert Behrend

ganic chemist, Herman Kolbe (1818–1884), who turned him down. This was because Behrend did not even know the formula of saltpeter! However, he was accepted by a physical chemist and, four years later, obtained his doctorate, *summa cum lauda*. Behrend went on to publish some 100 papers. With one exception, these dealt with various topics in organic chemistry. The exception was his 1893 paper which ended with his description of the first potentiometric titrations. Apparently, Behrend did this work because of apparatus made available to him by his colleague Wilhelm Friedrich Ostwald (1853–1932).

Stock's Law

The conservation of historic instruments is a major concern of mine. I collect nothing; anything offered is steered to a museum, where it will be safe for all time. My experience in searching has led to the conclusion "If an historic item can disappear, it will." The lost Barrow balance that I mentioned has a double importance. First, it must have been a superb instrument. Second, it was the principal balance in the trio used to restore a national standard, thus affecting society in general. Concerning another of the trio, I found the remains of this Robinson instrument, offered restoration at my own expense, but could find no taker for the difficult job.

This leads me to another conclusion, which has almost blossomed into "Stock's Law." This is "A scientist's instruments are his successors' junk." I have just mentioned a sad example of this. For years, I have been urging anyone thinking of scrapping an instrument to check before execution. The item in question may be the last of its kind; if it is a prototype, it is historically unique! A species can be numerous but can still face extinction. Thousands of flue-gas analyzers were, and are, in use. Some years ago, a leading British engineering journal published my request for news of the whereabouts of a pre-1930 analyzer. I still await the first response. I suppose that I should go hunting in boiler houses when I travel around. However, I want to push on with other projects, so I think that I will let this one go. I may yet stumble upon the needful when looking for something else!

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ABOUT THE AUTHOR

John T. Stock, winner of the 1992 Dexter Award in the History of Chemistry, is Professor Emeritus in the Department of Chemistry of the University of Connecticut, Storrs, CT 06269 and is especially interested in the history and preservation of chemical instrumentation.

THE CHEMIST AS CONSULTANT IN GILDED AGE AMERICA

Benjamin Silliman, Jr. and Western Mining

George E. Webb, Tennessee Technological University

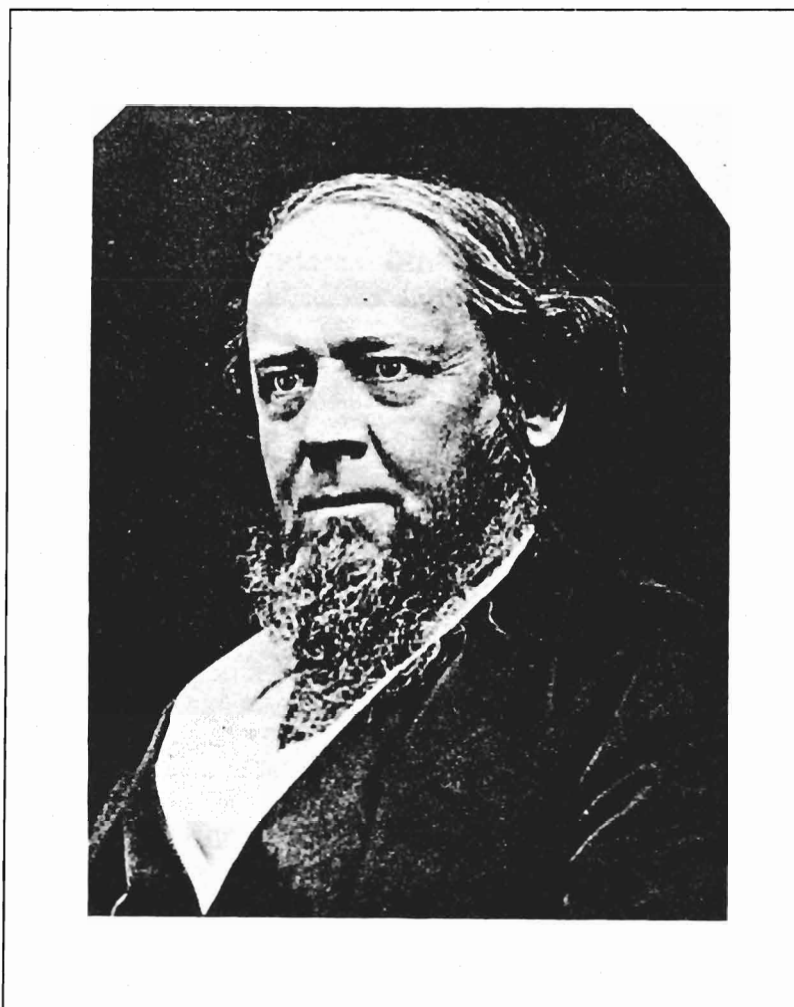
The role of scientists in the growth and development of the American West has only recently emerged as a topic for historical investigation. Although scientists remained an important part of Western exploration, settlement, and economic development throughout the 19th century, historians have generally focused on supposedly more dramatic events surrounding military expeditions, gold rushes, and overland migration. For the historian of chemistry, however, the American West provides many examples of the profession's significance in the development of the region. Among the more important of chemists' activities was their service as consultants to the mining industry which increasingly represented the region's economic base. Mining consultants proved particularly valuable to the industry in two respects. Their scientific knowledge allowed them to suggest more efficient methods to extract and process ores. Equally important, however, favorable reports from consultants would help to attract new investors, who became increasingly important as western mining evolved from placer to hard rock techniques (1). Among the most intriguing of these consultants was the Yale chemist Benjamin Silliman, Jr. (1816-1885).

The younger Silliman descended from a distinguished New England family which included his father, one of the most eminent scientists of the first half of the 19th century. Benjamin, Sr. (1779-1864) served in various faculty positions at Yale and published a standard chemistry text, *Elements of Chemistry*, in 1830 (2). Perhaps his most important contribution to the growth of American science, however, was the establishment of *American Journal of Science and the Arts*, the first issue of

which appeared in 1818. Benjamin, Jr., early expressed interest in scientific matters and, after graduation from Yale in 1837, assisted his father while pursuing graduate studies, receiving the master of arts degree in 1840.

Silliman continued to assist his father for the next half dozen years, after which he gained a faculty appointment as "professor of chemistry and the kindred sciences as applied to the arts." During the next decade, he was primarily concerned with the organization of the Yale (later Sheffield) Scientific School, in which he taught chemistry, mineralogy, and metallurgy. After his father's retirement in 1853, the younger Silliman became professor of general and applied chemistry, as well as giving chemistry lectures in the medical department of Yale College. Silliman was also active in the editorial work of the *American Journal of Science*, serving in various positions from 1838 until his death. In 1847, he published the text, *First Principles of Chemistry*, which appeared in two later editions with a total sales of some 50,000 copies. Silliman wrote another successful text in 1859, *First Principles of Physics, or Natural Philosophy*, revising this volume in a second edition two years later (3).

Because of his interest and expertise in applied science, Silliman frequently served as a consultant to government, business and industry. During the 1840s and 1850s, Silliman travelled throughout the eastern United States, pursuing various mineralogical and chemical investigations. Among the most important of these early activities was his examination of petroleum deposits in Venango County, Pennsylvania, in 1855. Silliman's report on these deposits focused on methods of distillation



Benjamin Silliman, Jr. (1816-1885) (Photo in Polit. Hist.)

and the potential uses of refined petroleum, encouraging the investors who had hired him. Two years after the publication of this report, Edwin Drake initiated the exploitation of the Pennsylvania oil fields by drilling his famous well. Silliman's later consulting activities involved him with diverse clients, including the city of Charlestown, Massachusetts, and a group of mining companies interested in Nova Scotia gold deposits (4). The most dramatic examples of Silliman's consulting activity, however, emerged from the several trips he made to the Far West beginning in the mid-1860s. Focusing on mining and petroleum properties, Silliman became involved in numerous efforts to attract capital to this underdeveloped region, frequently with unanticipated and discouraging results.

Silliman's first western trip began in mid-March 1864 when he sailed from New York with his assistant Frank Semple, a Yale chemistry student. Planning for this trip had begun a few months earlier, after Silliman agreed to examine mining properties for several Philadelphia investors. The major investor in this group was Thomas A. Scott, a vice president of the Pennsylvania Railroad and a well-known promoter of petroleum and mining ventures. Among the properties Silliman was to investigate for Scott were mineral deposits in northwestern Arizona and the New Almaden Quicksilver Mine south of San Jose, California. The Yale professor had also signed a contract with the New York banking firm of Duncan, Sherman & Company, who were primarily concerned with the potential value of gold deposits in

Bodie, Nevada. Small-scale mining activity had been evident in Bodie since 1860, leading the New York bankers to solicit Silliman's opinion concerning these properties. Although hired by two separate concerns, Silliman would be free to arrange other consulting activities once he reached the West Coast.

Arriving in San Francisco on 9 April, Silliman quickly began his western investigations. By the end of the month, he had examined mining properties near Sacramento, visited the mines in Virginia City, Nevada, and travelled to Bodie to gather information for his New York employers. Silliman's report proved extremely enthusiastic, leading to the incorporation of the Empire Gold & Silver Mining Company and his own decision to file a mining claim. Silliman then returned to Virginia City in early May to examine the Potosi Mine. His report encouraged the Potosi owners to continue their mining and milling activities in an effort to tap the rich deposits Silliman assured them were present. The Yale chemist also examined mines in Aurora, Nevada, northwest of Bodie, and revisited Scott's New Almaden Quicksilver Mine before returning to San Francisco's Occidental Hotel on 11 May (5).

Easily securing new clients, Silliman remained in San Francisco only a few days before beginning his second western journey. The last two weeks of May found Silliman at the Mariposa Estate on the Merced River, investigating the gold mines of the Mariposa Mining Company. The directors of this company had paid him \$1500 to visit the mines and prepare a report, which estate superintendent Frederick Law Olmsted found encouraging. During early June, Silliman was back in Virginia City, serving as an expert witness for the famous Gould and Curry Mine in a title suit between his clients and the North Potosi Mine. Silliman's testimony, in which he argued that the Comstock Lode represented one ledge rather than many, convinced the referee to support the Gould and Curry claim. On his way back to San Francisco, Silliman examined mining properties in the Placerville area of California, further establishing himself among mining investors and promoters (6).

Silliman spent the next month examining various properties in California before beginning his next major trip in mid-July. Scott's mining claims in the Fort Mohave region of Arizona had been of intense interest to the Philadelphian since the spring of 1863, when California business associates informed him of promising gold strikes in the area. Quickly organizing mining companies to take advantage of this information, Scott dispatched a preliminary exploring party in December of 1863, shortly before he arranged for Silliman to investigate the mineral deposits more closely. After the

difficult desert journey from Los Angeles to Fort Mohave, Silliman spent ten days investigating the various mining claims along the Colorado River. Although his examination of these claims led to occasional optimistic statements, the gold and silver deposits in northwestern Arizona proved inadequate to justify significant development (7).

After his return from the desert, Silliman continued his consulting activity in California and Nevada. Between mid-September and the end of the year, he examined Nevada's Reese River mining region, approximately 170 miles east of Virginia City, and returned to the latter location to examine further the Comstock Lode. In the employ of a new client, the Empire Mill and Mining Company of Gold Hill, Silliman expressed optimism concerning the long-term prospects of the Comstock Lode, despite its recent decline in production. Silliman spent the next six weeks in California, surveying mines in the Mother Lode region of Sierra and Nevada counties. He was particularly impressed with the gold-bearing quartz veins in the Grass Valley region, becoming part of a syndicate which later purchased the Eureka Mine. Although Silliman intended to return to the East via the Idaho and Colorado mining regions, he cut short his western trip after learning of the death of his father. Quickly completing a few remaining tasks, Silliman left California in early January, arriving home by the end of the month (8).

The last few months of Silliman's western trip, however, involved him in a new venture which would have far-reaching consequences. Upon his return from the Arizona desert, Silliman increasingly focused his efforts on the petroleum deposits of southern California, again at Scott's request. From his initial investigation of Rancho Ojai, seven miles east of Ventura, Silliman emerged as one of the most optimistic observers of the area's oil lands and encouraged Scott and his associates to invest heavily in southern California. Silliman's report on the Ojai property served as the basis for the prospectus of the California Petroleum Company, which Scott capitalized at \$10,000,000. The Yale chemist's positive comments on other oil properties not only convinced Scott to purchase various holdings, but also fueled the speculative orgy which characterized the southern California oil boom of the mid-1860s. Unfortunately for Silliman's reputation, the boom collapsed almost as rapidly as it inflated, leading investors to question Silliman's optimistic reports. Rumors of salted petroleum samples and negative comments concerning Silliman's scientific integrity also surfaced, casting gloom over the Yale professor's trip (9).

Despite the long-term difficulties Silliman would face as a result of his western journey, his trip nonetheless proved profitable. Several articles based on his investigations appeared in the *American Journal of Science*, accompanied by three papers read at meetings of the National Academy of Sciences (10). Equally important, Silliman gained a significant amount of financial security from his initial western trip. His consulting work in the West netted him \$40,000 in gold from more than two dozen clients. When added to fees from his earlier work in Nova Scotia, Silliman's consulting income for 1864 was over \$54,000 as contrasted with his Yale salary of less than \$3000. Later reports and commissions from his western endeavors brought Silliman nearly \$30,000 during 1865 (11). Not surprisingly, his connections with Eastern capital led Silliman to extol the virtues of outside investment in the Far West. In a letter to his wife written a few days before Christmas, 1864, Silliman contrasted the outlook of southern Californians with the dynamic perspective of his clients. Echoing a common sentiment among Eastern observers viewing the Hispanic traditions of California, Silliman referred to "semi barbarous Santa Barbara" and told his wife that he had been indirectly responsible for "doing an incalculable benefit to California" by encouraging people like Scott to invest in the state. Silliman emphasized that outside capital would result in "the opening of a new era of material prosperity" for California, as well as introducing "entirely new and improved social and moral elements into a part of the State hitherto sunk in the deepest Spanish degradation." He expressed similar observations of the importance of capital to California in a letter to the *New York Times* on 17 March 1865. Describing mining activity in California and Nevada, he stressed that "cheap capital is much needed in California," and predicted that the investment of such capital would be "amply rewarded" (12).

Silliman's interest in and devotion to the economic aspects of western mining and petroleum development may well have clouded his professional judgment, as a growing number of critics suggested after his return to New Haven. In fact, Silliman spent most of the rest of his life attempting to regain the scientific credibility which had been damaged by his association with questionable enterprises in the Far West. The southern California oil fiasco was, perhaps, the most dramatic of these unfortunate events, but Silliman's western trip also involved him in similar difficulties with mining ventures. His optimistic report on the Bodie area served as an important part of the 1864 prospectus issued by the Empire Gold & Silver Mining Company to promote the

sale of 10,000 additional shares to gain funds for development. Although this sale brought some \$300,000 into the company's treasury, the sum proved inadequate to make the Bodie mines profitable. By the end of 1865, Bodie was virtually deserted, once again involving Silliman in a seemingly fraudulent venture. Silliman's identification with questionable western enterprises led to a decline in his reputation at Yale as well. Questions concerning his scientific integrity led to a gradual ostracism by many of his colleagues and Silliman's decreasing activity in the affairs of the college. By 1870, he had resigned from both the Sheffield Scientific School faculty and the academic department of Yale College, although he continued to lecture in the medical department until his death (13).

The various challenges to Silliman's credibility and integrity led him to arrange another trip to California in the spring of 1867. Although he described the purpose of the trip as an effort to clarify the salted petroleum sample incident, Silliman provided no new information and became primarily concerned with various mining endeavors in the Mother Lode country. This trip proved much less profitable than his first journey, as potential clients appeared wary of hiring a consultant whose reputation had declined. Silliman investigated various mineral deposits in Calaveras County, joining investors from San Francisco and Grass Valley in the development of gold and silver deposits at Quail Hill. Pledging his own Eureka Mine stock, he lost heavily in the Quail Hill efforts, as did other investors. The Yale chemist's second western trip ended in early January 1868 and proved both economically and professionally disappointing (14).

Silliman's next major western adventure focused on the famous Emma Mine south of Salt Lake City. In October of 1871, he travelled to the Utah mine in the employ of investors who hoped to tap the intense British interest in mining ventures. First located in 1868, the Emma Mine remained largely undeveloped because of the lack of capital, a situation Silliman's employers hoped to rectify through a favorable report on the property. The Yale chemist examined the property, preparing a favorable report and, later, a technical article for the *American Journal of Science*. The London firm coordinating the investment activity in Britain arranged for the telegraphic transmission of Silliman's report from Utah at a cost of \$3000 and published it as part of the prospectus the following month. The prospectus led to heavy investment in the Emma Silver Mining Company, with shares floated in London for more than one million pounds. Such investment success more than justifi-

fied Silliman's fee of \$25,000 for this and a planned second trip to Utah.

The publicity surrounding the Emma Mine encouraged investment in other Utah properties, leading to a minor boom in the region and continuing to attract investors to the Emma Mine. Silliman thus made his second trip to Utah in February of 1872 to examine recent improvements. He reported that the mine was in much better condition than it had been the previous fall, further encouraging investors and indicating that the Utah property had great promise (15). Unfortunately for Silliman, the Emma Mine failed to live up to his optimistic evaluation. As 1872 turned to 1873, the Emma ore body appeared to be playing out, calling Silliman's reports into question. The Utah situation also suggested damaging parallels to Silliman's earlier involvement with the California oil fiasco and the failure of the Bodie mining properties. Silliman's position became even more precarious as 1873 wore on, as the financial panic of that year led to a disappearance of investment capital which crippled the growing Utah mining industry. That year also witnessed the exposure of the Emma Mine promotion as one of the major swindles of the time. The suspension of dividends in the company in late 1872 raised various questions which, over the next year, convinced many observers that the sole purpose of the Emma promoters was to sell stock in the mine at inflated prices. Silliman's favorable reports had supplied them with the scientific gloss of great value in such schemes.

Silliman's role in the Emma Mine scandal seriously damaged what was left of his reputation. Colleagues at Yale continued to see him as an embarrassment to the college, despite his nebulous connection with the academic program. Several fellow members of the National Academy of Sciences (Silliman had been one of the original 50 members of the Academy) were sufficiently angered at Silliman's involvement with various questionable enterprises that they began a campaign in late 1873 to oust him from the organization. Although unsuccessful, the campaign which lasted several months provided clear evidence of Silliman's declining reputation. Press reports of the Emma Mine scandal frequently mentioned Silliman's role, occasionally reminding readers of his earlier difficulties in California and Nevada (16).

By 1876, continued rumors and disclosures of the Emma Mine scandal had led to a Congressional investigation before the House Committee on Foreign Relations. Information reached the committee that Silliman had been paid a large sum of money as a contingency fee after the sale of Emma stock. In letters to and tes-

timony before the committee, Silliman vigorously denied this charge, carefully detailing the \$15,000 fee he had received for his initial visit and emphasizing that his expenses of \$5000 had been paid out of this sum. During his testimony before the committee on 9 March, Silliman also repeated his belief that the Emma Mine was not the worthless property some had charged. The potential of the mine remained significant, he told committee members. According to the *New York Times* reporter covering the hearings, Silliman's testimony was well received by the committee and removed much of the suspicion that he had been an active participant in what the *Times* had earlier called "that very gross swindle" (17).

After the Emma Mine controversy died down, the remaining decade of Silliman's life proved much less contentious. He continued his connection with Yale through his position in the medical department and remained active as a consultant to various private ventures and public agencies. His consulting work led to several more western trips to investigate mineral properties, as well as to various publications and presentations. In November of 1880, for example, Silliman presented two papers at the National Academy of Sciences meeting in New York, one of which provided an intensive examination of the structure of gold-bearing veins. From his own and others' field work, Silliman also published widely on mineralogical topics. His articles on various minerals from Arizona and turquoise from New Mexico both appeared in the 1881 volume of the *American Journal of Science*. Although Silliman began to suffer from heart disease at about this time, he continued to travel extensively as a consultant, making two more trips to New Mexico. Beginning in October of 1884, however, Silliman's condition slowly deteriorated from a combination of heart disease and pneumonia. He died in New Haven on 14 January 1885 (18).

Silliman's career as a scientific consultant provides an intriguing glimpse into the role played by chemists in both the history of the West and the history of America's Gilded Age. Although academic employment remained important to chemists of the period, consulting opportunities were prevalent and profitable. Whether contributing technical expertise to improve production methods or writing favorable reports to encourage investment, consulting chemists were actively involved in the development of the mineral deposits of the Far West. The career of Benjamin Silliman, Jr., which usually focused on the financial aspect of this development, shows the risks as well as the benefits which came from consulting work. His optimistic reports on mining and

petroleum properties led to involvement with questionable investment schemes and seriously damaged his reputation. Heir to one of the great family names in the history of American science, the younger Silliman became better known as an accomplice in the economic excess which characterized the Gilded Age.

ACKNOWLEDGMENT

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A NOTE ON JOSEPH BLACK AND THE SMELL OF "FIXED AIR"

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Every beginning student of chemistry today knows that carbon dioxide (CO_2) is odorless and that the gas is easily generated by adding dilute acid—say, sulphuric or hydrochloric—to some form of calcium carbonate (CaCO_3), such as marble or chalk. I was, therefore, somewhat taken aback when I first read in Thomas Hankins' excellent book on 18th-century science that Joseph Black identified a certain gas, which he designated "fixed air," as having "a characteristic odor (when he produced it by adding acid to chalk)." In support of this assertion Hankins cites "a letter to Cullen written early in 1754" (1). My first thought was that Black's gas must have contained odoriferous impurities. To check this possibility I decided to begin by reviewing the most accessible secondary literature dealing with Black's work on fixed air. Among the writings I looked at were two by Henry Guerlac (2, 3) and one by A. L. Donovan (4). From these writings I learned, among other things, that in the fall of 1752 Joseph Black began performing a series of experiments on two well-known alkalis, lime and magnesia, in the course of which he discovered "carbon dioxide, the first of the atmospheric gases to be identified as a distinct chemical substance" (5). Also, in Guerlac's entry on Black in the *Dictionary of Scientific Biography*, I came across the statement that "the air produced when chalk was treated with acid . . . had a pronounced but not disagreeable odor" (6). Here, then, it seemed, was Hankins' source (and indeed the bibliographic essay at the end of his book mentions the volume of Guerlac's collected writings containing the *Dictionary of Scientific Biography* entry on Black) (7). But now I was faced with a fresh puzzle because any likely contaminant of Black's fixed air, I concluded, would

have had a *disagreeable* odor. Thus, of the small (though steadily growing) number of (permanent) gases that were being produced, identified, and named by 18th-century chemists—the gases we know as oxygen, hydrogen, nitrogen, sulphur dioxide, ammonia, hydrogen sulphide, and various nitrogen oxides—only nitrous oxide (laughing gas) would normally be characterized as having a "not disagreeable odor," and it could scarcely have been produced from chalk and acid (even nitric acid). In fact, the likelihood of *any* contaminants in Black's fixed air is probably low in view of his explicit determination to work only with pure materials in his experiments on fixed air (8).

Reading for myself the text of the letter (dated 3 January 1754, from Black to his teacher William Cullen) on which Guerlac and Hankins were relying for their puzzling attribution of an odor to fixed air, I found Black describing "an air or vapour," produced from chalk and vitriolic (sulphuric) acid, which possessed the property of extinguishing a candle or a piece of burning paper; and, Black adds, "yet the smell of it was not disagreeable" (9). But why did Guerlac paraphrase Black's "not disagreeable" as "pronounced but not disagreeable"? And, indeed, what do Black's and Guerlac's phrases mean? In contemporary standard English usage, "not disagreeable" generally means "agreeable" (and, so far as I can see, this was also true in the 18th century) (10). The fact is, however, that in certain contexts "not disagreeable" does not necessarily mean "agreeable;" and Black's letter provides precisely an instance of such a context. For, consider the strategic placement of the word "yet" in the clause in question: Black apparently expected a gas that extinguished flames to have a dis-

agreeable smell—any such gas, that is, except fixed air (which Black eventually came to identify with the “gas silvestre” of Van Helmont, produced by burning charcoal or by alcoholic fermentation). All this I learned from Guerlac’s essay on Black’s research on fixed air, where Black is quoted as saying (in 1756) that “for some years, I took it for granted that all those vapours which extinguish flame, and are destructive of animal life, without irritating the lungs, or giving warning of their corrosive nature, are the gas silvestre of Van Helmont, or fixed air” (11).

At this point I thought I was done. I had succeeded in correcting a small though not trivial misreading of a remark of Black’s by noticing that his phrase “not disagreeable,” in its context, could—indeed, should—mean “not disagreeable” rather than “agreeable.” And I had succeeded by appealing to the known properties of carbon dioxide gas, in particular, its odorlessness. Nevertheless, I continued to wonder how such a knowledgeable historian of chemistry as Henry Guerlac could have ascribed a “pronounced” odor of any kind to a gas which he had just a few pages before identified as carbon dioxide (12). Was Guerlac leaning over backwards so as not to judge Black’s observations by later, and so irrelevant, criteria? This methodological issue had, indeed, come up earlier in Guerlac’s “Joseph Black and Fixed Air” when he recounted the alleged success of certain of Black’s predecessors—in fact, two of his medical professors at Edinburgh—in treating kidney stones with limewater: though “we believe today that the remedy is worthless . . . the claims made for [it] were based upon apparently convincing laboratory experiments” (13). Guerlac does not exactly give the champions of limewater the benefit of the doubt but neither does he impugn their experimental techniques. Motivated by this same attitude, then, if Black reports fixed air to have an agreeable odor, the historian may well refuse to question this observation.

Reflecting further, I began to wonder if perhaps I might not have succumbed to Whiggish preconceptions in my too confident belief that Black’s fixed air could be unproblematically equated with modern chemistry’s carbon dioxide. Reminding myself of Alain Corbin’s thesis that an olfactory revolution occurred during the 18th century involving a heightened sensitivity to odors, pleasant and unpleasant, I even found myself raising the question of whether Black’s expectations might have influenced his experience in smelling fixed air (14). Expecting any gas which extinguished flames and destroyed life to possess a disagreeable smell, when he found one which didn’t, might not his olfactory expe-

rience, by some odd psychological quirk, have actually seemed agreeable (or, neither agreeable nor disagreeable but still pronounced—a distinct possibility, at least in my own personal phenomenology of odors)? But why talk of quirks? In the phenomenology of perception, to “actually seem” is to “be.” It must be admitted that—at least to my knowledge—no one else in Black’s day claimed to detect anything agreeable (or pronounced) in the odor of fixed air. Still, we are dealing here with a very small group of witnesses, so why shouldn’t the experiences of one of the most careful observers in the group be at least as normative as anyone else’s? The situation might well have been quite different, say, 25 years later, when, as the following captivating and (I suspect) exemplary incident attests, even children were experimenting with fixed air.

In 1779 Josiah Wedgwood hired an assistant of Joseph Priestley’s, John Warltire, to teach his children chemistry. Since at the time Wedgwood was a patron of both Joseph Wright of Derby and George Stubbs, he thought of commissioning (but never did) one of the two painters to depict his children in the act of performing chemical experiments; more specifically, Wedgwood suggested depicting the following (15):

Jack standing at a table making fixable air with the glass apparatus &c.; & his two brothers accompanying him.
Tom jumping up & clapping his hands in joy & surprise at seeing the stream of bubbles rise up just as Jack has put in a little chalk to the acid.

The three brothers would have learned, and confirmed for themselves, that fixed air is odorless; indeed, it seems reasonable to assume that by this time a consensus had been reached on the properties of fixed air (including its odorlessness) within that small European elite familiar with elementary chemistry—a consensus extending to men, women, and children, practising chemists as well as lay scientific cognoscenti. A decade later Lavoisier was to include fixed (or fixable) air—now significantly renamed “carbonic acid”—in his new chemical system (16).

But Black’s “yet” will not go away. In the last analysis, I believe my solution to the problem (or pseudo-problem) of Black’s odoriferous fixed air must be assimilated to my solution of a trivial textual problem generated, once again, by Guerlac’s apparent inattention to a “yet” locution. What I have in mind is that in one of Guerlac’s accounts of Black’s life we learn that Black’s parents had “a numerous issue of eight sons and four daughters *yet alive* in 1761” (17), while in another, later, account Guerlac omits the “yet alive” phrase and refers to Joseph as simply the “fourth of their twelve

children" (18). In fact, Black's parents had 15 children of whom three had died by 1761; Joseph was the fifth son (the fourth to survive infancy) and ninth child (19).

Properties of gases, human genealogies, standard English usage: each is surely a social construction; but, equally, each is surely, in substantial measure, an intransigent and non-arbitrary feature of any coherent world—including, of course, any historical world—we undertake to construct (20).

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7. Reference 3.
8. Reference 2, 437, 446.
9. *Ibid.*, 437. Donovan also quotes this passage, without paraphrase or comment (reference 4, p. 201).
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12. Reference 3, p. 173.
13. Reference 2, 137-8.
14. A. Corbin, *The Foul and the Fragrant: Odor and the French Social Imagination*, (trans. M. L. Kochan), Harvard University Press, Cambridge, Mass., 1986. Corbin, incidentally, cites a treatise of 1778 by Felix Vicq d'Azyr, in which the eminent zoologist maintains that the gas escaping from an opened sepulchre is Black's fixed air. Breathing this gas is responsible for observed cases of suffocation, though "like most of his contemporaries, [Vicq d'Azyr] continued to think that the principal danger lay in a 'stinking vapor'. Whereas gases 'kill immediately, the second acts more slowly on the nervous system, as well as on the fluids of animals, which it manifestly impairs' " (p. 30).
15. Wedgwood to Bentley, 30th May 1779, quoted by Benedict Nicolson, *Joseph Wright of Derby: Painter of Light*, Vol. 1, Pantheon, New York, 1968, p. 144.
16. A.-L. Lavoisier, *Elements of Chemistry*, (trans. R. Kerr), William Creech, Edinburgh, 1790 (reprinted, Dover, New York, 1965), pp. 64, 69. (This is a translation of Antoine-Laurent Lavoisier, *Traité élémentaire de Chimie*, Paris, 1789). Lavoisier characterizes several gases by their "penetrating" odor: "sulphurous acid" (sulphur dioxide), "muriatic acid" (hydrogen chloride), "ammoniac" (ammonia) (pp. 67, 70, 157). On the other hand, Lavoisier never mentions the odor of carbonic acid, which he characterizes as "the acid resulting from this combustion [of charcoal and oxygen, which] does not condense in the common temperature; under the pressure of our atmosphere, it remains in the state of gas, and requires a large proportion of water to combine with or be dissolved in" (p. 63).
17. Reference 2, 129, my emphasis.
18. Reference 3, p. 173.
19. Reference 4, p. 165.
20. Such features I take to be more or less closely related to the "material or phenomenal constraints" of some recent critical responses to the extreme social constructivist account of science; see, e.g., J. Golinski, "The Theory of Practice and the Practice of Theory; Sociological Approaches to the History of Science," *Isis*, 1990, 81, 494, 503.

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**History of Chemistry Lecture Series
Marshall University, Huntington, WV
March 20—April 17, 1996**

All talks, free and open to the general public, will be presented at 7:00-8:00 pm on the Marshall University Campus.

**Wed., March 20 Derek Davenport, Purdue University
Early Vindication of the Rights of Woman Chemists**

**Tues., March 26 Peter Schmidt, University of Florida
Ancient African Iron Smelting**

**Wed., April 3 William Jensen, Univ. of Cincinnati
Two Centuries of Chemistry Sets**

**Wed., April 10 Sr. Mary Virginia Orna, Coll. New Rochelle
Chemistry at the Art/Archeological Interface**

**Wed., April 17 James Marshall, North Texas State University
Alchemy: Middle East, China, and Europe**

PERSPECTIVES LECTURE

Recent Trends in the Historiography of Science

Charles C. Gillispie, Princeton University

The following lecture was given at Princeton University in July of 1992 to the high school chemistry teachers attending the Woodrow Wilson Summer Institute on the History of Chemistry organized by Dr. Derek Davenport of Purdue University.

Current Historiography of Science

The history of science has become a professional discipline only in the professional lifetime of people who are just reaching retirement. It's still a relatively new and exciting field, and welcome aboard. Professor Davenport has been good enough to provide a copy of the program you are following, and I wish I could take your course. I was a student of chemistry once upon a time and have ventured to write a few things concerning its history. It's gone a bit rusty, however; it will be better to leave history of chemistry proper to Professor Davenport and the other members of your faculty, and to say something of the current posture of scholarship in the historiography of science generally and illustrate it with a few examples related to your theme.

This is not something that will come out of the readings in which you are engaged. They are addressed to history of chemistry proper, as they need to be for your purpose, which is to develop historical material to be used in the teaching of science itself. There is not a lot of current writing in the field that would be applicable to that purpose, a most important purpose. In the last several decades, the emphasis has changed. Partington, Ihde, and I, when writing the chapter in *The Edge of Objectivity* you are now reading, were concerned with

development of knowledge of the forces and structure of nature (1). That was the central thrust of the historiography of science down through the 1960s. The concern now is with the relation of science, not to nature, but to the forces and structure of society. This is not merely a question of what used to be meant by social history, that is to say, studies of the place of scientists in society at large together with the sociological characteristics of the scientific community. The term now is "Social Construction of Science." It signifies that, in the view of practitioners of this approach, the content of science is determined, not by technical consideration, not by its success in giving an accurate account of natural phenomena, but by interactions of the scientists who produce it, both among themselves and in the larger society (2).

The question is not whether a finding is right or wrong, nor whether a theory is true or false. In this view that is as meaningless as saying that a work of art or literature, or political theory is right or wrong, true or false. What determines whether a finding prevails is the persuasiveness, the style, the influence, the professional manipulations, the power ultimately of the scientists who developed it. Facts are not found. They do not reside in nature. They are constructed in the laboratory. All facts are, in a word, artifacts. Thus, the reason that the oxygen theory prevailed over the phlogiston theory was not that it yielded a more rational account of the phenomena of combustion. Not at all. The success of oxygen was owing to the authority Lavoisier exercised in the scientific establishment, and beyond that in the French state. He was administrator of the munitions industry. His laboratory was an official installation in the

Arsenal of Paris. His disciples got the best jobs. Around him gathered an entire team—Fourcroy, Guyton de Morveau, Berthollet, and others. They collaborated in extending the defeat of phlogiston into a general reformation of the system of chemical knowledge, creating a new language in which chemical agents were denoted and classified in accordance with their relations in nature. They devised the nomenclature we still use. Against this powerhouse, what chance was there for a forlorn and unorganized set of preachers, pharmacists, and amateurs like Priestley, Kirwan, Baumé, and the diminishing gaggle of phlogistonists? Lavoisier's Achilles heel was not that he overextended oxygen to make it the principle of acidification as well as combustion, though as you know, he did do that. It was that in the French Revolution, he was hopelessly compromised by his identification with the power structure of the old regime, and went to the guillotine. His overbearing, almost mathematical approach thereupon gave way to the more physical chemistry developed by Berthollet, which prospered in keeping with the activist spirit of the revolutionary Republic and the Napoleonic Empire.

It is not, in short, the structure of nature that determines the findings of science. It is just the other way about. The procedures of science are what construct our notion of nature, in whole and in part. Different procedures would produce different notions, and what determines which ones prevail reduces in the last analysis to a question of the power of its proponents and of the interests they serve. Now, I do not wish to leave the impression that all or a majority of historians of science subscribe to this outlook, or even that all those drawn to study the sociological reaches of science take the extreme position I have stated. Still, in any discipline there is usually a certain set of problems or an approach that is at the forefront at any juncture, and there is no doubt that the hot topics in the history of science nowadays are its sociological and cultural dimensions. I might just say a word about the reasons for that. It is the manifestation in our small discipline of the general movement of scholarship in the humanities that goes by the term deconstruction in studies of art and literature. There the point is no longer to develop appreciation of the picture or the text, nor to judge of its merit aesthetically, morally, or otherwise. Instead, the purpose is to exhibit how any expression of a culture, scientific, literary, artistic, whatever, serves the interest of the power groups that define the society. Thus, all study of culture reduces at bottom to a question of politics.

That problems are posed this way derives in large part from the sea-change that came over sensibility a

generation ago, in the so-called cultural revolution of the late 1960s and early 1970s. It took its impetus from the extreme skepticism which then set in among young people generally concerning the rationale of a liberal society and the possibility of objective and disinterested knowledge or actions. The more radical among the coming generation of scholarship found their prophets in the writings of the French philosopher, Michel Foucault, and the literary critic, Jacques Derrida. With respect to science there is the added incentive of showing that its pretensions to abstract truth or validity or objectivity because of its correspondence to natural reality are illusory and that its statements are no less uniquely derivative from socio-political processes than those of economists, novelists, or painters. The message can seem the more plausible in the light of publicity given in recent years to the scandals of science, the Rochester affair, the Gallo investigation, etc.

Whatever one thinks of this program in general, the emphasis on social processes of science has at least one signal merit. It has focussed attention on the actual conduct of experiment. Among the criticisms leveled at the older historiography is a just one, which is that it concerned itself almost entirely with the history of theory—the Copernican theory, the theory of gravity, the oxygen theory, the theory of natural selection, whatever; and theory is at best half the story. In the view of sociological historians, theory is much the less revealing half. Their concern is with the making of science, and they lose interest in it once it's made. Still, the summons to give experiment its due has been stimulating throughout the discipline, and I thought I would give an account of two pieces of work, concerning respectively Boyle and Lavoisier, one by a pair of scholars who represent the social constructionists at their most extreme, the other by an historian of moderate temper, both focusing on the role of experiment in the fabrication of science.

A Social Constructivist Example

The first, I have to say, is the more amusing. *Leviathan and the Air Pump* by Simon Schaffer and Steven Shapin is a very entertaining book, even if I find it a bit exasperating (3). Published in 1985, it has had a great success. The topic is the dispute between, on the one side, Boyle and the circle of experimental philosophers who set the agenda for the Royal Society, and on the other, the philosopher Thomas Hobbes, author of the classic justification of absolutist monarchy, which he entitled

Leviathan, and which comprised a philosophy of materialism.

The centerpiece is Boyle's famous air pump, which initiated the century-long British research program in pneumatic physics and chemistry. He designed it for the purpose of performing experiments in vacuum as a refinement on the cumbersome hemispheres with which Otto von Guericke, Bürgermeister of Magdeburg, had dramatized the reality of air pressure by failing to drag them apart with two teams of horses. This was a mere stunt. The apparatus was good for nothing else. Boyle's machine was a table-top affair. It consisted of two main parts: a receiver from which the air was to be exhausted and a pumping apparatus. The receiver was a glass globe with a capacity of about 30 quarts and an aperture with a tight seal at the top through which experimental objects could be installed. It was connected through a valve at the bottom with the pump, and a brass cylinder about 14 inches high and three inches in diameter fitted with a piston of tanned shoe leather oiled so as to be practically air-tight. It was operated by a rack and pinion device and sucked the air out of the receiver in successive strokes, each requiring greater effort than the last.

Boyle published his first series of trials in 1660, *Experiments Physico-mechanical Touching the Spring of the Air*. We all know the effects he demonstrated: you see a bell rung and hear nothing; a puff of smoke collapses into powder; feathers fall to the bottom like lead weights; the candle gutters out as the air thins; the mouse slowly expires. With each stroke of the piston, the column of mercury descends in a Torricelli barometer until it is almost level with the reservoir in which it stands—but not quite, for the perfect vacuum is unattainable.

Our authors are concerned only incidentally with all this, however, and they take no interest in the corollary enunciation of Boyle's Law (which, to be sure, Boyle demonstrated in compressing a volume of air by increasing the amount of mercury that confined it in a J-tube, and not in the receiver of the air pump). For it is not the use of experimental method in discovery and demonstration of laws of nature that interests them. What interests them about experimentation is the way in which it serves a public relations campaign designed to establish the authority of the new philosophy, which is to say, science.

And it is true that these experiments do not read like an inquiry. Boyle knew ahead of time what the effects would be that he intended to demonstrate. When a trial came out differently, it was because something was

wrong with the experiment. For example, a pair of thin marble squares with polished, lightly oiled surfaces would stick together under atmospheric pressure. When they did not separate in vacuo as they should have, Boyle described the experiment as a failure rather than taking it as reason to investigate phenomena of cohesion. In all this, his purpose was not to settle the dispute which had raged in the previous generation about the possibility of a void in nature. That he regarded as a merely metaphysical question, an empty question, so to say, which could never be settled by observation. He was interested in what could be seen and felt, in the action of the pump itself as well as in what happened in the receiver and in the reaction when the pump was operated, the "spring of the air," which any one feels who pumps up a tire by hand.

It might be, Boyle says, that the spring of the air can be explained by thinking of the air as corpuscular—"conceiving the air near the earth to be such a heap of little bodies, lying one upon the other, as may be resembled to a fleece of wool"—and clearly he did think in terms of atoms. But that goes beyond the evidence:

I shall decline meddling with a subject, which is much more hard to be explicated than necessary to be so by him, whose business in this matter is not to assign the adequate cause of the spring of the air, but only to manifest, that the air hath a spring and to relate some of its effects.

The tactic is the same as Newton's, a little later on. The cause of gravity Newton does not pretend to know. What he demonstrates is the fact of gravity and of its effects. Such, indeed, is the condition that makes the new philosophy, or science, viable: that it have a boundary separating the establishment of physical matter of fact from speculation about causes, and indeed from everything else.

Staking out claims for scientific method, then: this was the real purpose of Boyle's operations with the air pump. Our authors see the campaign as a rhetorical one, transpiring in three stages, or as they say, making use of three technologies: mechanical, literary, and social. The mechanical technology is the air pump itself. Do not imagine experiments performed in the professional privacy of a laboratory. On the contrary, display was central to Boyle's strategy. The air pump was a very expensive instrument. In the eyes of the public, it became the emblem of the mechanical philosophy, the cyclotron of the 17th century. Only a wealthy man could afford one, and only six or seven were ever built. The demonstrations were spectacular. It was exhibited before

Charles II on the occasion of his first visit to the Royal Society. It was regularly trotted out for ceremonies honoring other dignitaries — the Danish ambassador; the Duchess of Newcastle, who was the first woman ever to attend a meeting. Representations of the air pump on title pages and in works of art make it a prime item in the iconography of science.

The motivation is to persuade opinion that experimental philosophy permits seeing, literally “seeing,” into the operations of nature in a depth and detail inaccessible to the unaided senses. The telescope and the microscope merely enhance the senses. The air pump reaches further. It establishes (but does not explain) the fact of what is not immediately observable, the spring of the air, by exhibiting what happens in the absence of air. For opinion to be persuaded, there have to be witnesses. The demonstrations have to be public. It is not a question of convincing scientific colleagues of the cogency of some set of findings or the validity of a hypothesis. The target is public opinion, which is to be persuaded that such direct contact establishes irrefutable knowledge about the world, unadulterated by philosophical error, religious belief, or political influence.

For that purpose the relatively small number of witnesses who attend demonstrations in person would scarcely suffice. Experiments must be published to win their readers’ assent as vicarious witnesses. The experimental style is not at all that of any prior philosophical or literary genre. The Royal Society enjoins a plain, natural way of writing. The writer effaces himself so as not to intrude upon direct contact between the reader and the facts. Boyle spares the reader no detail. No one could doubt that he actually performed, in just the way he said he did, all the hundreds, nay the thousands, of experiments he reports in this and other writings. His reporting is confident, since it is concerned with matters of fact, but unassuming, since the experimenter must keep out of it. When Boyle does go beyond reporting and ventures a possible explanation of the effects, the tone changes from confident to diffident. Such and such may be the cause, but the best that can be hoped for there is probability

Finally, and we come now to the social dimension, the experimental mode of constituting knowledge of facts has to be the affair of a community and not merely of individuals. It is a public matter. Rules are to be observed. A special kind of conduct is incumbent. Critics are to be countered. Recognition is needed from the authorities, that is from government. Recruits have to be attracted. Careers have to be accommodated. A forum has to be created and maintained. All this, of course, is

the reason for founding the Royal Society, where the rules of discourse were explicit. Evidence could be discussed and criticized, but not persons. All discussion of religion, metaphysics, and politics was forbidden. The distresses of the world were not to intrude upon the serenity of science.

Such, in the account of our authors, were the techniques through which Boyle and his contemporaries persuaded themselves that experimental research merely discovered and established matters of fact. In reality, we are told, they were constructing facts artificially, subject to constraints no different from those that bear on writers, theologians, philosophers, or thinkers in any domain. Boyle is thus an early example, and one of the perpetrators, of the illusion that science is a body of knowledge privileged by its correspondence to natural reality and untouched in content, if not in the civic role of its practitioners, by the play of political, economic, and ideological interest that determines other components of culture. Thomas Hobbes, again according to our authors, saw through that illusion at the outset.

Hobbes, in exile throughout the time of Cromwell and the Puritan Commonwealth, was the sharpest critic of the liberal, pluralistic, corrupt regime of the restored monarchy, the chrysalis of just the modern social and political order from which our authors take the scientific enterprise to be derivative. He published *Leviathan* in 1651 amid the disorders of the Civil War. His purpose was to construct a philosophical system that would guarantee civil order. The foundation of knowledge must be notions of cause. Hobbes’s was a materialistic world in which the prime causes were matter and motion. Any philosophy worthy of attention must demonstrate causality on the model of the certain demonstrations of geometry. It must command assent to physical and to civic propositions as surely as does the demonstration of a theorem in Euclid. Assent must be total. It must be enforced. And what do we have in Boyle? An air pump that leaks purporting to establish physical facts. A pretense that a handful of amateurs looking over a physicist’s shoulder are a guarantee of the factuality of what is going on in an inaccessible device. An argument that claims the status of knowledge for artificially produced appearances while segregating supposed facts from the physical causes underlying them and, worse, which withdraws the sanction of philosophy from civil order. For, so say our authors, the problem of generating knowledge is a problem in politics, and conversely the problem of political order always involves solutions to the problem of knowledge. About that, they hold, Hobbes was right—though they do not say what they

think of the authoritarianism on which Hobbes makes order of both sorts depend.

The History of Experiment

Let us turn now to work of another sort, also focussing on the role of the experiment in the production of scientific knowledge, but not serving a sociological or political agenda. Two recent books have won a good deal of attention: Peter Galison's *How Experiments End* and Frederic L. Holmes' *Lavoisier and the Chemistry of Life* (4). Galison is concerned with team research in recent particle physics and with the criteria for deciding that a project is finished. It is an interesting book, but Holmes's seems to me the more successful of the two, and for us it has the further merit of pertinence. Holmes does have a program in his research, but it's not an ideological one. He considers that historians have paid too little attention to what scientists actually do in the laboratory because they have failed to go beyond the published accounts of the finished work. He has completed a series of studies based on the laboratory notebooks of three major figures important to the history of physiology in three centuries: Claude Bernard, Lavoisier, and Hans Krebs.

The book on Lavoisier is the second of this trilogy. Not all scientists have kept records detailed enough to permit reconstituting their experimental practice. Lavoisier did, fortunately. His laboratory registers—or most of them—in 12 great folios are preserved in the archives of the Academy of Science in Paris. Holmes's central interest is Lavoisier's study of respiration, but in the course of recovering that he has gone over the entire record and gives us a portrait which modifies our sense of Lavoisier the man and Lavoisier the scientist in very significant respects.

He is good enough to cite the conjecture in *The Edge of Objectivity* that it might have been in the laboratory that one could penetrate the facade of rationality and method to the human being underneath, and he gives us a far more sympathetic picture of Lavoisier than others do. Lavoisier's thinking is much more tentative than my book made it out to be. The progress from the research program he outlined in 1772 or 1773 to its realization in the *Reflections on Phlogiston* in 1785 is nothing like so preordained. His notes on the many experiments show the difficulty of distinguishing between fixed air, or carbon dioxide, the only gas known at the outset, and pure air, the still unidentified agent of combustion. This difficulty leads him sometimes to confuse oxidation with

reduction. There are backslidings in which he refers to phlogiston, either out of habit, or because it avoided that confusion, all the way down to the memoir on acidification in 1778. His actual measurements are often less precise than the figures he reports in print, which are rounded off and sometimes adjusted a little to compensate for an error he knew he had made in some procedure that he didn't take time to repeat. Experiments he describes as repeated many times sometimes weren't, or at least he didn't record them, which is unlikely. He paid far more attention to the detail of Priestley's work than appears in the formal acknowledgments.

What is, perhaps, most interesting, his ideas did not become clear simply in the course of analyzing and recombining mercuric oxide, nitric acid, sulfuric acid, metallic carbonates, and all the rest of it. At times he got so interested in the methods he was using that he lost sight of the problem he was investigating and seems to be concentrating on the means instead of on the ends, sometimes interchanging them. In the laboratory he showed a spontaneity that is carefully repressed in his publications. Also, it was in the actual writing of his memoirs, and not in the manipulation of retorts, distilling columns, and scales that he did some of his best thinking, seeing explanations that went beyond the data in the notebooks and adjusting his published account so as to support his conclusions. He was more apt to doctor the order than the results of his investigation. Clearly, then, he cleaned up his act in the printed memoirs. Now, all scholars and scientists do that to some extent, of course, but Lavoisier led the way toward modern practices in that respect too. He cared more for appearances than was characteristic of his time, perhaps because of his admiration for mathematical science, or perhaps that was the effect of his temperament, or both. At all events, the reality was a lot less programmed, a lot less logical than the appearance.

What do we learn about Lavoisier the scientist? The most important thing is that Holmes modifies the sense of the configuration of his career that has been widely accepted, and that appears in my chapter. According to that picture, Lavoisier gets straight the role of oxygen as the combining agent responsible for combustion, for calcination, and—over-reaching himself—for acidification. He thereupon generalizes the methods he has employed so as to work a reformation in the entire science, and the result is modern chemistry. It is the culmination of his career, completed to all intents and purposes in the framing of chemical nomenclature and in publication of the *Traité élémentaire de chimie* in 1789. True, along the way he occasionally mentioned the probability that

oxygen is also the active agent in the respiration of animals, but the subsequent research on respiration, and on organic compounds and reactions, has been seen as an appendix, if not an afterthought, a next stage amputated by the guillotine before it could amount to much.

Not at all, we learn. Holmes's own primary interest is in history of physiology rather than chemistry, but his reconstitution of Lavoisier's physiological research puts the whole career in a new and broader perspective. Lavoisier made tests with animals very early on. In his first experiments on mercuric oxide, for example, he tried to differentiate between the air he got by reducing it with charcoal and the air he got by reducing it without charcoal, that is by heating it. The first test he made was on animals: a bird expired at once in fixed air. Another spent half a minute in the other air and flew away chirping happily when the jar was removed. From then on, he calls it sometimes pure air, sometimes eminently respirable air, sometimes vital air, and this before Priestley taught him that it was a distinctive gas. The eventual shift in terminology to oxygen conceals what is clear from the use of the older term in the notebooks. In fact, its role in sustaining life was always one of the defining properties. For a time, he thought that respiration was a process that separated the vital portion of the atmosphere from air in general. The trouble with that was, of course, that the product of respiration had exactly the wrong properties. Only gradually did he come to appreciate that breathing vitiates air in just the way a candle does. In 1775 he was enormously impressed by Priestley's experiments showing that coagulated sheep's blood changes from dark to bright red and back when transferred between jars of phlogisticated and dephlogisticated air. Where does the change occur in the body? At the surface of the lungs? In the bloodstream? Beyond that Lavoisier finds that there is a difference between the air produced by respiration and that remaining after calcination, but he's not yet clear about the difference between fixed air—carbon dioxide—and mephitic air—atmospheric nitrogen. The same amount of vital air yields a larger volume of the one than the other; the one precipitated limewater; the other did not.

Gradually, then, Lavoisier developed a theory of respiration concurrently with the development of his understanding of calcination and combustion, and his misunderstanding of acidification. He moved towards his completed oxygen theory along all four lines, and not just the three lines of inorganic chemistry. But none of the respiration experiments fitted into finished pieces of research. The main thing he published on respiration—

apart from passing allusions—were the experiments he did with Laplace in the ice calorimeter. The subject appeared to be the heat generated by the breathing of the guinea pig in that icy jar rather than the creature's physiology, but in fact it is clear in the notebooks that Lavoisier was thinking very much about the process of respiration and that he had considerable experience in animal physiology. His comprehensive memoir on respiration was the first major work he published after *Reflections on Phlogiston* later in the same year, 1785.

Meanwhile, the notebooks show, he had tried experiments on combustion of plant materials, on the organic acids, especially acetic in connection with acidification, on alcohol and its relation to sugar and water; and on what he saw as processes of nature, especially fermentation and putrefaction. Gradually, he arrived at a definition of plant substances as containing carbon, hydrogen, and oxygen in three-way combinations, and a definition of animal substances as containing in addition azote or nitrogen, and in some cases sulfur and phosphorus. With the oxygen theory completed with respect to inorganic chemistry by 1785, he turned attention mainly to what we would call organic chemistry.

It's not a new departure, however, but rather an extension of his reformation of chemistry to problems of life. Five chapters are devoted to them in the *Traité élémentaire*. He fits them into the same scheme of classification that he employed for organic compounds. Plant substances are acids or oxides of double and triple bases composed of varying proportions of carbon and hydrogen. Vegetable acids contain additional proportions of oxygen. The bases of animal substances are triple and quadruple composites, etc. It's true that the tone of these chapters is different. They read like provisional stages in a research program rather than like the finished system of science in the body of the treatise. Lavoisier uses the same balance sheet method of equating input of the substance undergoing analysis, whether by fermentation or combustion, with the yield in gases, liquid, and solid matter. The classifications don't really work. Still, he arrives at very nearly the modern values for the proportions of carbon, hydrogen, oxygen, and nitrogen in many instances. The techniques may properly be considered the point of departure of organic chemistry. The famous final memoirs of the 1790s, in collaboration with a new assistant, Armand Séguin, are addressed to the animal economy. The purpose is to extend the analysis from respiration to all physiological processes, digestion, excretion, transpiration, that maintain the steady state of matter and heat in the animal body. That work

was never finished. What the notebooks show, however, is that it was continuous with the whole course of Lavoisier's reformation of chemistry and also of agriculture, and not a new departure once the chemical revolution was finished.

Critical Conclusion

In conclusion, and for whatever my opinion may be worth, it is obvious that I have a great deal of sympathy for Holmes's treatment of Lavoisier in particular, and more generally for the current historical emphasis on recovering the detail of experimental practice. At the same time, I do have fundamental reservations about the more extreme approach of the social constructionists, the "strong program," as they call it. For one thing, it seems to me hoist by its own petard. If the findings of scientists are thought to be determined, not by the structure of nature but by the sociology of the investigators, is it not equally or still more probable that the same is true of statements by sociologists concerning the structure of science?

That is merely a debating point, however. More substantively, it seems to me that the micro-sociology of research projects can be very illuminating when it is a question of the making of science. But the sociology of research fails when it becomes a question of explaining the success of the outcomes that prevail. Technical considerations and the fit with nature are therein paramount. Though undoubtedly framed by individual persons and groups of persons in a social environment, science has the capacity to transcend the personalities and circumstances of those who produce it. The relation of the finished piece of work to its creator is not the same in science as it is in art or literature. It is obvious that Hamlet and the Mass in B-Minor would not exist if Shakespeare and Bach had never lived. It is otherwise in science. The planets would still move subject to the inverse square law of gravity if Newton had died in infancy or (as he threatened) suppressed the *Principia*. No one else would have composed it, but it is clear that everything in it that really mattered to classical physics would soon have been written down by others in some way. Much the same is true of all, or nearly all, the significant contributions to modern science. The well-known phenomenon of simultaneous and usually independent discovery is all the evidence needed.

Moreover, although the introduction of a piece of science will bear the mark of its creator and of the circumstances in which he worked—of Lavoisier's clarity of

mind, in the case of the oxygen theory, and of his interactions with the people around him—still, the personal and social elements that went into the original formulations make no difference to the practice of workaday science once a contribution has left the hand of its creator, and that happens immediately. No one has to retrace the road he took to discovery. Instead, the discovery must be verifiable and workable by any qualified scientist if it is to be science at all. So it is with the cultural context. Until very recently, science was uniquely a product of western civilization. Nowadays, however, the Japanese and Indians, among others, work it in the same way as Europeans and Americans do, and in some instances more effectively. The same cannot be said of the legacy of art, poetry, religion, or political theory originating in the West.

In my view, not perhaps a very fashionable one at the moment, that is because science, though produced in society, is about nature.

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A LETTER FROM FRANKLIN BACHE TO ROBERT HARE

William D. Williams, Harding University

It is always intriguing to relate a historical artifact to the people and events of its original use. The following letter from the author's collection has prompted some interesting investigation into the collaboration of two prominent early Philadelphia chemistry teachers (1):

Dear Doctor: Philada. Jan. 8. 1835

Allow me to thank you for the check you were good enough to send me this morning for one hundred & twenty-seven Dollars; 27 Dlls for medical services and 100 Dollars for my services in relation to the new Ed. of your compendium.

Very respectfully & truly yours:

Franklin Bache
To Dr. Hare

Robert Hare's *Compendium of the Course of Chemical Instruction* . . . was the most original American chemistry text published during the first half of the 19th century. Hare (1781-1858) taught chemistry at the University of Pennsylvania Medical School from 1818 to 1847 and spent much of that career developing his textbook. It was not designed for general use, but rather as a transcript of his own unique lectures and ingenious experiments. It was preceded by three shorter precursor works: *Minutes of the Course of Chemical Instruction* . . . (1822-25), *Supplement to Minutes* . . . (1824), and *Engravings and Descriptions* . . . (1826). These were combined and enlarged into his *Compendium*, which went through four successively larger editions from 1827 to 1843 (2).

Franklin Bache (1792-1864), great-grandson of Benjamin Franklin, also had a distinguished career. A physician in his early years, he gradually turned to chem-

istry as his main interest. He taught chemistry at the Franklin Institute (1826-32), the Philadelphia College of Pharmacy (1831-41), and Jefferson Medical College (1841-64). He wrote *A System of Chemistry* (1819), edited the *Supplement to Henry's Elements* (1823), edited four American editions of Edward Turner's *Elements of Chemistry* (1828-41), and coauthored, with George B. Wood, the *Dispensatory of the United States* (1833), a pharmaceutical reference that has gone through revisions up to the present (3).

There is evidence that Hare was continually rushed with his textbooks. They were often published in parts as the school term progressed and frequently contained apologies for certain parts not being ready. More than once, he called upon Bache for assistance when he did not have time to finish assignments. As early as 1821, when Hare was editing an American edition of Andrew Ure's *Dictionary of Chemistry*, Bache was called to finish the publication. The preface explained that Hare was pressed for time and "pursuant to my advice, the publisher engaged Dr. Franklin Bache to revise the work and read the proofs" (4).

In 1822, Bache edited, "with the approbation of Dr. Hare", a new American edition of William Henry's *Elements of Experimental Chemistry*, which Hare had edited in the previous edition (5). Apparently Hare was too busy with his own *Minutes* and experimentation with his new "Galvanic Deflagrator" to undertake another edition.

Bache served as a reader for the first edition of Hare's *Compendium* in 1827 (6) and was editor of the 1836, third edition "in the absence of the author." Hare explained in the preface that "The health of a portion of my family having rendered it expedient for me to sail



Robert Hare

to Europe, I was under the necessity of engaging my friend Dr. Bache to superintend the printing of this edition" (7).

The exact dates of Hare's trip or which member of his family was ill is not known. His presence in England in August 1836 is mentioned in one of his published letters.(8)

Internal evidence in the 1836 *Compendium* suggests that Hare made the revisions before he left. Additions by Bache were enclosed in brackets and occurred in only eight places, totaling about three pages (9). Apparently Bache's main job was overseeing the printer.

The date on Bache's above letter, however, presents a puzzle; January 1835 appears too early for payment for editing the 1836 edition. Perhaps Hare prepaid Bache for work yet to be performed. Perhaps Bache, as we all have done, automatically put the previous year (1835) on his letter written early in the new year (1836). Or, perhaps work on the 1836 edition was already well under way prior to January 1835.

What payment would be reasonable for Bache's editing work? Typical printings of the period were one-thousand copies. Hare's classes were 300 to 400 stu-



Franklin Bache

dents per year (10). Even though leather bound, such a book would have sold at that time for less than five dollars. If Hare's royalty were 50 cents per copy, he would have collected \$500 on the edition; \$100 might have been a plausible payment to Bache.

Although Bache's letter leaves us with unanswered questions, it is fascinating to know a little more of the human side of these chemists of yesteryear.

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CHARLOTTE ROBERTS AND HER TEXTBOOK ON STEREOCHEMISTRY

Mary R. S. Creese and Thomas M. Creese, University of Kansas

In 1892 Charlotte Fitch Roberts, a young woman of 33 and an associate professor of chemistry at Wellesley College, was given leave from her teaching duties for graduate work at Yale University. She received her Ph.D. in 1894—the first in chemistry given to a woman by Yale. Her dissertation was a notable analytical and expository work in which she surveyed the relatively new field of “Chemistry in Space” or “Stereochemistry.” Published in 1896 as a 189-page monograph, *The Development and Present Aspects of Stereochemistry*, it formed a substantial addition to the English language literature on a subject where most of the primary publications were in German or French, and it served as an advanced textbook for a number of years (1). However, within little more than two decades the field caught up with it and, indeed, passed it by. The development by G. N. Lewis, Irving Langmuir, J. J. Thomson, and others of the electronic theory of chemical bonding, and its rapid acceptance among chemists, made the theoretical speculations Roberts’s book presented of little more than historical interest (2). As with other replaced theories, the practicing chemist saw little reason to pay them any attention. However, as a concise record of ideas current 100 years ago about the three-dimensional structure of organic compounds, and apparently the only such record written by an American chemist to that time, the book is still of historical interest (20).

Roberts’s studies in stereochemistry probably began about nine years before she went to Yale. In 1885–86 she had spent a year at Cambridge University where she attended lectures by the Scottish chemist, Sir James Dewar. Though perhaps now remembered more for his later work on the liquefaction of gases, Dewar also carried out a considerable amount of research in organic

chemistry and contributed his share to the development of ideas of molecular structure (3). For Roberts, although she made no original contributions to the area, stereochemistry was to remain a major interest throughout her life. During the 1890s, at the time she was writing her monograph, experimental observations were being turned out by European chemists at an ever-increasing rate, but after the grand generalizations of van’t Hoff and Le Bel in the 1870s, theory had failed to keep pace; the field was without any coherence or unity. Despite the confusion, however, Roberts’s last chapter, with its summary of current ideas, demonstrates that some of the working hypotheses then being put forward have interesting correspondences with more modern concepts.

Being a textbook in chemistry, the work makes rather dry reading for the non-chemist historian concerned with women’s contributions to science. An introductory chapter summarizes the background and the state of the field by the mid-1890s. Topics discussed include the discovery of isomerism, starting with Pasteur’s work on optical isomerism in the tartaric acids in the 1860s and that of Wislicenus on the lactic acids in the 1870s. Roberts relates how this led directly to ideas of different arrangements of atoms in space and to the concept of geometrical form in molecules. The story continues through the critical work of Le Bel and van’t Hoff and the introduction of the idea of the tetrahedral distribution of the valencies of the carbon atom, with the representation of linked carbon atoms as tetrahedrons having the carbons at the centers and one solid angle in common (4). Van’t Hoff’s hypothesis of free rotation about single carbon-carbon bonds is covered, Victor Meyer’s suggestion of limited rotation in certain special cases (such as the di-



Charlotte Fitch Roberts, 1890. Photo by Partridge
(Courtesy of Wellesley College Archive)

carboxylic acids) is discussed, and the troublesome problem of multiple carbon-carbon bonds gone into at some length (5). From this follows a stereochemical explanation for the isomerism observed in compounds such as maleic and fumaric acids.

Chapter 2 amplifies these topics, presenting further illustrations and applications. Chapter 3 deals with the structure of aromatic compounds, detailing the arguments and conflicting evidence brought forward *pro* and *con* in support of the various representations of benzene, including those suggested by Kekulé, Claus, Dewar and Armstrong (7). Claus's diagonal formula had the advantage over Kekulé's of limiting the number of possible disubstitution products to three. On the other hand, it also predicted that the formation of addition products would require the breaking of single bonds. As to Dewar's suggestion, Roberts commented that it seemed to have no advantage over Kekulé's and had the disadvantage of containing two different kinds of carbon atom, which should give rise to two mono-substitution products; further, the formation of a hexa-addition product required the breaking of a single bond. Armstrong's "centric" formula was an attempt to explain "the unwillingness of benzene to form addition compounds," the "energy" being "directed toward the center of the molecule instead of holding together any two particular atoms" (8). To a modern chemist, it appears to be a groping towards an explanation for the properties which would later be seen as associated with the stable π -cloud of benzene. The stereochemical problems presented by



Charlotte Fitch Roberts c 1900(?) (Courtesy of Wellesley College Archive)

THE
DEVELOPMENT
AND
PRESENT ASPECTS
OF
STEREO-CHEMISTRY.

BY

CHARLOTTE F. ROBERTS, PH.D.

BOSTON, U.S.A.

D. C. HEATH & CO., PUBLISHERS.

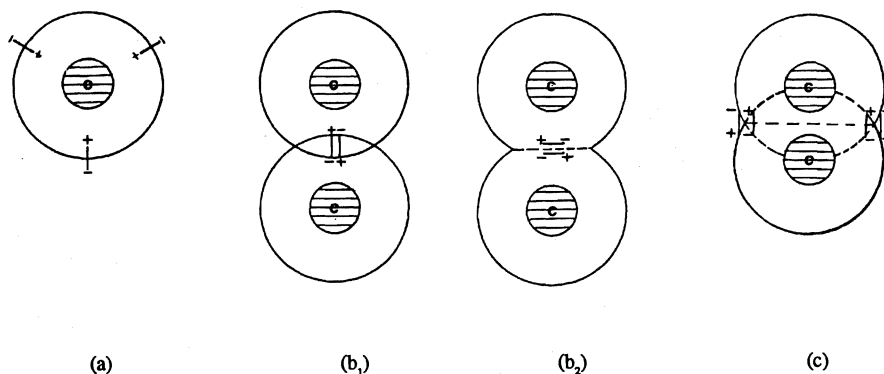
1896.

organic compounds containing nitrogen merited a chapter to themselves, the varying valence of nitrogen being one unresolved difficulty and isomerism in compounds containing a carbon-nitrogen double bond, especially the oximes, another.

A short chapter on the relation of stereochemistry to optical activity and to crystallography completed the literature survey, and led to Roberts's final and perhaps most interesting chapter, summarizing speculations about fundamental questions concerning atomic structure and the nature of valence. The major outstanding questions she posed as follows (9):

Is [valence] an inherent property of the atom, or is it first called into existence by the approach of other at-

oms? Has it definite location in the atom, is it exerted in certain definite directions, is it to be considered as originally to be divided into parts in the atoms; or is it more of the nature of other attractive forces, an undivided whole, until the near approach of other atoms causes it to be divided among them? In what does the difference of valence in different elements consist? Does it correspond to the difference in different magnets, a difference in the amount of attractive force; or to a difference in the motions of the atoms, perhaps a different number of vibrations in a unit of time; or to a difference in the number of certain particular parts of the atom which we may call valence places? What do we mean by double and triple linking between two carbon atoms, and what conceptions of valence can explain the fact that doubly linked carbon atoms are not held to-



Meyer and Riecke's representation of the carbon atom with surrounding ether envelope in the surface of which are embedded electrical dipoles: (a) isolated carbon atom (the fourth dipole is hidden behind the central carbon); (b₁) and (b₂) carbon atoms joined by a single bond; (c) carbon atoms joined by a double bond (14).

gether with twice the strength of two singly linked atoms, and triply linked with three times that strength?

Stereochemistry had raised these questions but had failed to provide many answers. There seemed, however, to be little doubt that valence had direction, which further implied, given a geometric form for an atom, that there must be definite "valence places" on the atom. Hence valence and atomic form or shape would seem to be linked. Van't Hoff's conception of the carbon atom as the center of a tetrahedron with attractive forces concentrated in the four solid angles explained many situations, but ran into difficulties when doubly or triply linked carbon atoms had to be accommodated. Lossen, Wislicenus, von Baeyer and others all contributed their ideas to the problem of multiple linkage, but difficulties remained (10).

In 1888 Victor Meyer and Eduard Riecke had published an electrical explanation of valence, taking an approach which organic chemists had tended to avoid (11), although the idea that there was a close and definite relationship between atoms and electric charge went back to the electrochemical research of Michael Faraday in the 1830s and even earlier (12). Meyer and Riecke pictured the carbon atom as surrounded by a spherical "ether envelope," of diameter several times larger than the atom, the surface of the envelope being the "seat of valence," and each of the four valences being an electrical dipole freely rotatable in the ether envelope (13). Thus, in the figure, single bonds are represented in (b₁) and (b₂), and double bonds in (c), the electric dipoles lined up as in (b₁) representing the situation where there was free rotation about the carbon-carbon axis, while (b₂) depicted restricted rotation—as, for instance, in the

dioxime of benzil. In (c) rotation about the carbon-carbon axis was forbidden. This picture of overlapping "envelopes" is remarkably suggestive of the later concept of orbital overlap.

Roberts ended on a cautious note (15):

Granting, then, the existence of inherent valence-places, there is still diversity of opinion as to whether these are caused by a qualitative difference of matter at these points, or whether they are the results of a polar condition either in the atom itself or its ether envelope; and in regard to this point stereochemistry has nothing to say. Having thrown down the postulate of the existence of valence-places, stereo-chemistry withdraws, having apparently no facts to offer in explanation of the cause and nature of such places. These subjects seem at present to be left largely to the domain of pure speculation, though there is an undoubted and proved connection between electricity and valence which cannot be overlooked in any explanation of the latter.

It is plain, then, that stereochemistry offers no distinct and definite representation of an atom. It only emphasizes certain attributes of the atom, and has already been very fruitful in stimulating speculations concerning atomic structure and valence. Whether any one of the theories now before the public, or one yet to be evolved, will ever receive experimental verification enough to be yielded universal acceptance, and thus give a definite conception of the atom or not, time alone can tell. . . .

Roberts had as a model for her work van't Hoff's *Stéréochimie*, the revised and expanded, but still remarkably concise, third edition of *La Chimie dans l'Espace*. Published in Paris in 1892, it presented in a style that was clear and lively a review of experimen-

tal data and current theories. To some extent she followed van't Hoff's general organizational scheme, while giving considerably more space to work carried out by other authors. An English translation of van't Hoff's monograph appeared in 1898, two years after Roberts's book, and was most favorably reviewed in the *Journal of the American Chemical Society* (16). Indeed, it was seen as becoming a standard textbook in stereochemistry. Strangely enough Roberts's book, which covered much the same ground, was not mentioned in the review. Another important work in the same area, the *Handbuch der Stereochemie*, edited by C. A. Bischoff, came out in two volumes in 1894 and 1895, the second volume—from Roberts's point of view the more important—appearing too late to be consulted by her before her monograph went to press. Being nothing short of an encyclopedic reference work of research relating to practically all aspects of stereochemistry, it hardly took the place of a textbook. However, it and the translation of van't Hoff's book may to some extent have overshadowed Robert's contribution. Both the European works had the advantage of being written by acknowledged experts in the field.

Charlotte Roberts taught at Wellesley College from 1880 until her death in 1917, progressing from an assistantship to full professor and head of the chemistry department by 1896, when she was still in her 30s. Beyond five papers on analytical methods written while a graduate student of Frank Gooch at Yale (1892–94), she published little experimental research, and the monograph is clearly her most significant contribution to the chemical literature (17, 18). She had three study leaves in Europe over the course of her career and spent some time in van't Hoff's laboratory in Berlin in 1899–1900, but would appear to have been concerned mainly with keeping abreast of current developments in chemistry rather than attempting any research of her own.

Indeed, with poor facilities and equipment in their laboratories and heavy teaching loads, few of the turn-of-the-century women chemists at small women's colleges like Wellesley carried out experimental work after completing their graduate degrees, even when granted study leaves. Roberts, perhaps as a result of the handicaps she faced, clearly turned her attention to studies of the development of ideas in chemistry rather than attempting laboratory work. By about 1905 she had become interested in the very beginnings of modern chemistry and its evolution from alchemy. She joined the English Alchemical Society, and during her last two study leaves (1905–06 and 1912–13) spent some of the time she had in Europe investigating the life and work of the

later alchemists, particularly Paracelsus, the 16th century Swiss alchemist and physician sometimes called the father of experimental chemistry. This historical research was still in progress at the time of her death and unfortunately none of it appears to have been published.

Roberts grew up in Greenfield, Massachusetts, and first entered Wellesley as an undergraduate in 1876, the year the college opened. After receiving her B.A. in 1880 she stayed on as an assistant in the chemistry department and became instructor two years later. Following her year in England, she was promoted to associate professor and taught for six years before going to Yale to study for her Ph.D. In 1917, at the age of 58, she died suddenly at her home in Wellesley of a cerebral hemorrhage. Popular with her students and well-liked by her colleagues, she was remembered especially for her lively and fun-loving personality; among her special pleasures were her activities in the college theater group, in capacities ranging from author to manager and actor. Wellesley was her home for most of her adult life, and her career there almost coincided with the first 40 years of the college's existence. The Charlotte Fitch Roberts endowed professorship in chemistry commemorates her name (19).

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FROM SMALL MISUNDERSTANDINGS MIGHTY DISPUTES GROW

E.D. Hughes' American Paper

Martin D. Saltzman, Providence College

In the well over 200 papers that Edward David Hughes (1906–1963) published there is a single short paper that appeared in the *Journal of the American Chemical Society* in 1935 (1). Why did Hughes choose to publish this paper entitled "Hydrolysis of Secondary and Tertiary Halides" in an American journal when all the rest of his publications appeared in British journals?

An attempt will be made in this paper to produce a scenario that led to the publication of this 1935 paper in an American journal. In doing this some of the problems American chemists had with the assimilation of the principles developed by the "English school" will be illustrated.



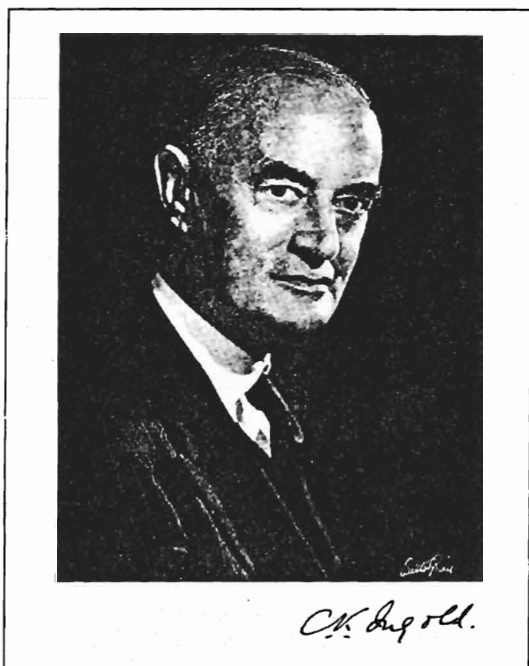
There are several reasons that can be advanced for the difficulty American organic chemists had with applying electronic theory to organic reaction mechanisms. Though Gilbert Newton Lewis (1875–1946) and Irving Langmuir (1881–1957) had, between 1916 and 1920, produced a comprehensive theory of bonding involving the electron pair and the octet theory, they unfortunately produced few if any examples relating to organic compounds. Neither Lewis nor Langmuir was particularly interested in organic chemistry so there was little momentum generated to apply their ideas to organic reaction mechanisms. Applications by American chemists in the 1920's were few and far between. Among those who attempted to use Lewis-Langmuir theory were James Bryant Conant (1893–1978) of Harvard University in his 1921 study of addition to carbonyl compounds and Howard J. Lucas (1885–1963) of Cal. Tech., who published a series of papers on electron displacements in organic compounds from 1924 to 1926 (2,3). Morris Kharasch (1895–1957) of the University of Chicago published two papers in the *Journal of Chemical Education* in 1928 and 1931 on the electron in organic chemistry. Except for these scattered examples there was unfortunately not a single example of a research program dedicated to the application of Lewis-Langmuir theory to the process of organic reaction mechanism by any American chemist until the late 1930's. By way of contrast in Britain, both Robert Robinson (1886–1973) and Christopher K. Ingold (1893–1970) had adopted Lewis-Langmuir theory in the 1920's. They had produced an extensive set of papers dealing with applications to a group of very diverse types of organic reactions.

American chemists had also been traumatized to some extent about the use of electronic theory as applied

to organic reactions by the overly enthusiastic application of the ideas of John Joseph (J.J.) Thomson (1856–1940) by a group of American chemists in the period between 1904–1920. In 1904 Thomson had presented a model of bonding which in essence was a modern revival of the dualistic ideas of Berzelius. This led to the presumption of an ionic type of bonding in organic molecules which of course led to problems. Practioners of this electropolar conception principally were Harry Shipley Fry (1879–1949) of the University of Cincinnati, George Falk (1886–1953) and Charles Nelson (1876–1965) of Columbia University, Julius Steiglitz (1867–1937) of the University of Chicago, and William Albert Noyes (1857–1941) of the University of Illinois. Their theories were quickly shown to be unworkable and this may have caused organic chemists who followed the controversy to be put off by electron theory.

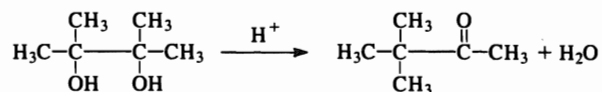
C.K. Ingold has written of the scientific work of Hughes the following (5):

It can certainly be said that this work has changed the aspect of organic chemistry, by progressively replacing empiricism by rationality and understanding. . . . This revolution of approach has been completed . . . essentially because his particular combination of scientific and human insight enabled him . . . not only to provide the required scientific concepts, but also to achieve their general acceptance, even though this task in communications involved a campaign to break through a sustained opposition.

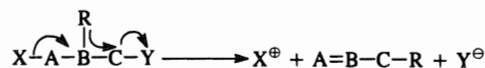


I hope to show that it was just this sort of opposition and misunderstanding in the United States that led to the publication of Hughes' 1935 paper in an American journal. The chief protagonists in this drama on the American side were Frank C. Whitmore (1887–1947) and Everett S. Wallis (1899–1965) and on the British side Hughes and Ingold.

The series of events began in 1928 when C.K. Ingold, acting as one of the reporters for the *Annual Reports on the Progress of Chemistry*, made the following comments in reviewing studies related to molecular rearrangements (6)

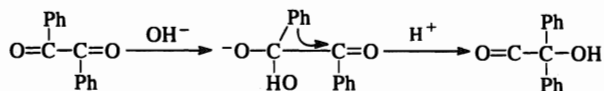


A general expression, involving what is called the "pinacolic electron displacement," and embracing the pinacol-pinacolin, Wagner-Meerwein and related transformations, has been given in the following form:



in which the tendency of X to part from, and of Y to retain, electrons during ionization or combination with a reagent supplies the driving force of the mechanism.

In the changes mentioned, X is usually an ionizable hydrogen atom and Y a potential anion such as hydroxy or halogen, but in certain cases a preliminary reaction is necessary to provide the complete system; for instance, in the benzil-benzilic acid change the effect of X is provided by a negative pole formed by the preliminary addition of hydroxide.



In 1932 there appeared one of the landmark papers in the history of American physical organic chemistry "The Common Basis of Intramolecular Rearrangements" (7) by Frank C. Whitmore. In this paper Whitmore presents a rationale for the benzil-benzilic acid rearrangement as follows (7):

Although rearrangement of compounds containing carbonyl groups and a group corresponding to the X in the systems discussed so far might be expected to follow a very different course, such may not be the case. The only difference is that an atom with an open sextet may be formed by the addition of a positive ion instead of the removal of a negative ion. Thus the first step in the benzilic acid rearrangement becomes:

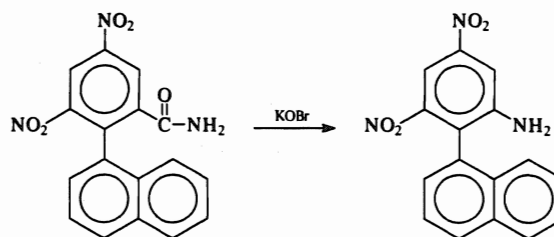
Whitmore in his paper on the Hofmann rearrangement stated that by means of a private communication from E.S. Wallis they both had agreed upon the negative nature of the migrating group. Thus E.S. Wallis became a participant in the unfolding controversy with Hughes and Ingold.

The next stage occurred when George A. R. Kon (1892–1951), as the reporter for the homocyclic division of the 1933 *Annual Reports*, commented upon the work of Whitmore and Wallis concerning molecular rearrangements which had appeared in 1932 (13). Kon was a close associate of C.K. Ingold as both had been at Imperial College during the period that Ingold had been a student and later a junior member of the staff (1913–1924). In his report Kon first summarized the crux of Whitmore's hypothesis concerning the common basis for intramolecular rearrangements. He paid particular attention to points in the original paper and subsequent papers of Whitmore's which presented ambiguities. In particular, Kon pointed to the paper on the Hofmann rearrangement where the neopentyl group was said to be negative yet in the formation of halide from neopentyl alcohol it was viewed as positive because re-

arrangement occurred. In addition, Kon pointed out the problem in the Whitmore interpretation of the benzil-benzilic acid rearrangement previously cited. In a footnote concerning this rearrangement Kon stated "The reporter wishes to thank Prof. C.K. Ingold for drawing his attention to this point." It appears obvious that Ingold was very familiar with Whitmore's work, and the mechanism that Whitmore had proposed was the just the inverse of that described by Ingold in 1928. The following statement by Kon most likely triggered the events which followed (13):

There appears to be some danger that hypotheses of this kind, helpful though they are in interpreting the course of numerous reactions, may be too widely generalised and it is well to recognize their limitations. For instance, there are changes which cannot be satisfactorily reconciled with an ionic mechanism, and of these the Hofmann rearrangement of the optically active amide to an active amine constitutes an important example.

Kon then went on to criticize the interpretation that Wallis had given to the retention of optical activity in the rearrangement of 3,5-dinitro-2- α -naphthylbenzamide to the corresponding amine:



The activity of the original compound is due to the restricted rotation, owing to the steric effect of the carbamyl and the nitro-group in the *o*-positions: the blocking effect never ceases, as would doubtless be the case if the migrating group were to leave the system as an ion prior to its transfer to a nitrogen atom.

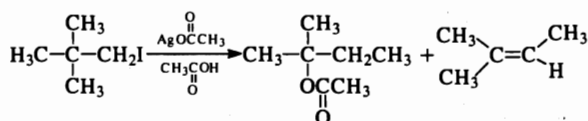
In essence Kon attributed an ionic mechanism to the Hofmann rearrangement even though Wallis very firmly stated in his summary to the paper where this reaction was reported, "These results preclude the possibility of migration of the optically active group in any free form, either positive, negative or neutral free radical." (12) Either Kon had not understood what Wallis had written or was wedded to the idea of intramolecular rearrangements being ionic in nature. He went on in his report to present other evidence in papers that had appeared in 1933 that could lead to the interpretation of the Lossen, Beckmann, and benzidine rearrangement in terms of an ionic mechanism.



E.S. Wallis

We cannot with any certainty know how much of what Kon wrote was the result of the input of C.K. Ingold, but certainly he must have seen the manuscript in advance and would certainly have called Kon's attention to any gross errors in his report. One can only surmise this from Kon's acknowledgment of Ingold's contribution concerning the benzilic acid rearrangement.

Whitmore and Wallis reacted to the comments of Kon in the *Annual Reports* very quickly because there followed in 1934 two short papers, the first from Whitmore and Flemming in the *Journal of the Chemical Society* entitled "Electronic versus Ionic Mechanisms for Intramolecular Rearrangement" (15), and the second from Whitmore and Wallis in the *Journal of the American Chemical Society* entitled "The Electronic Mechanism of Intramolecular Rearrangement" (16). In essence both of these short papers claimed that the "British school of organic chemists," as Whitmore referred to them, had completely misinterpreted the points that he and Wallis had made regarding the nature of intramolecular rearrangements. These processes do not occur by ionic mechanisms at all, but by transfer of the migrating group with its electrons. The migrating group never leaves the molecule and hence these mechanisms cannot be ionic. In the *Journal of the Chemical Society* paper the authors describe the steps involved in the reaction of neopentyl iodide with silver acetate in glacial acetic acid at 60°C which produced tert-amyl acetate and trimethylethylene:

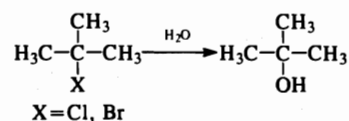


In the *Journal of the American Chemical Society* paper Whitmore and Wallis argued that the work of either of them offered evidence for the correctness of each other's interpretation (16):

We do not agree with this implication; in fact, careful reflection will show that the reaction of Wallis and Moyer, in which an optically active amide of a sterically hindered diphenyl derivative gives an optically active amine, is the strongest existing evidence for the correctness of this modern electronic viewpoint as contrasted with the older ionic mechanisms. A concise electronic explanation of the steps involved in the Hofmann reaction from an electronic standpoint was given to show that the reaction is truly intramolecular and not ionic. In all of this Whitmore never directly addressed the problem of the benzilic acid rearrangement or his use of positive and negative radicals in his paper on the Hofmann rearrangement. He did say that chemists may

not have really understood the implications of his work. They assumed that he was presenting an ionic hypothesis such as ones already available in the literature to explain rearrangement in compounds that can undergo ionization to some extent. He pointed to the work of Meerwein appearing in *Annalen* in 1927 (17).

Whitmore and Wallis submitted their short notes concerning what they perceived as the misinterpretation of their views in April and May of 1934. No doubt when these appeared in print they must have caused great consternation in the Ingold group. At this time there existed a good deal of trans-Atlantic enmity between many of the American chemists of Whitmore's generation and the Ingold school (18). Much of this was probably due to the lack of understanding of the revolutionary insights that Ingold and his collaborators had brought to the understanding of organic reaction mechanism. I believe the Hughes paper was an attempt to show the ignorance of Whitmore with respect to the power of the ideas advanced by Ingold *et al.* The impetus for this paper was the appearance of the first paper in a series on the hydrolysis of tertiary halides by Whitmore in the June, 1934 issue of *Journal of the American Chemical Society* (19). In this paper Whitmore presented a series of observations concerning the hydrolysis of tertiary butyl and amyl halides to the corresponding alcohols.



Whitmore found that tertiary halides were far more resistant to hydrolysis than he had expected. In either cold water or cold aqueous sodium hydroxide the reaction produced some alcohol but mostly alkene, whereas in hot water only alkene was formed. In the same issue as Whitmore's paper there was a publication from A.E. French, W.H. McShan, and W.W. Jöhler of the University of Missouri on the "Action of Inorganic Bases on Secondary and Tertiary Butyl Bromides." (20) In this study the ratio of alkene to alcohol formation was determined by varying the type and concentration of metallic hydroxides. Their results indicated that secondary butyl bromide gave increasing amounts of alkene as the base concentration increased. In the case of tertiary bromides the maximum formation of alkene was only 2%, the rest being the alcohol.

Hughes' paper on secondary and tertiary halides was received on November 30, 1934 and published in April, 1935. In this paper Hughes gave a mechanistic expla-

nation of the results of Whitmore and French *et al.* It should be mentioned that at this time Hughes was a junior member of Ingold's department at University College, London, and was most likely acting as a surrogate for Ingold. Hughes had come to University College in 1930 to do post-doctoral work with Ingold, who himself had just arrived from a previous post at Leeds University. Hughes had just recently received the Ph.D. degree at the University of Wales under the tutelage of Herbert B. Watson (1894–1975). From Watson, Hughes mastered techniques of kinetic analysis which Ingold was to use to such great advantage in the 1930's. Watson himself had been a student of Kennedy J.P. Orton (1872–1930), one of the undisputed masters of kinetic analysis in Britain and head of the department at University College, Bangor (Wales) where Hughes studied. Hughes' life and career were completely dominated by Ingold, and it would seem quite strange why he would have submitted this paper in question to the *Journal of the American Chemical Society* unless asked to do so. Hughes began his paper as follows:

Comment has been recently passed on the relative proportions in which alcohol and olefins are formed by the hydrolysis of secondary and tertiary alkyl halides. We wish to direct attention to some considerations relating to the same. (1)

There followed a discussion of the mechanisms of substitution and elimination using the S_N1 , S_N2 , $E1$, $E2$ notation developed by Ingold. Hughes specifically indicated that the intent of his paper was to report that he had found the changeover point from S_N2 to S_N1 in dilute aqueous alcoholic solution as being between the ethyl and isopropyl group. The work of French *et al.* on secondary halides, Hughes pointed out, is consistent with the operation of a combination of S_N1 and $E2$ mechanism. Tertiary halides reacted much more rapidly than the secondary halides and produced little olefin because this is consistent with an S_N1 mechanism which predominates over the $E2$ mechanism. With respect to the work of Whitmore, it was pointed out that in *t*-amyl chloride, $E1$ now becomes a significant pathway as the halide becomes more highly substituted. Whether dilute aqueous acid, base, or neutral medium is used, it plays no role in the process as it is purely unimolecular. The pathway of this reaction is consistent with S_N1 and $E1$ mechanisms and experimental evidence for this was offered by Hughes. One wonders how many American chemists reading this paper in 1935 had any idea of what Hughes was writing about!

There is no recorded reply to this paper by Hughes, and curiously this series on tertiary halide hydrolysis

began and ended with paper I. Perhaps Whitmore knew if he published any thing further it would be a subject for further papers pointing to his lack of an understanding of the mechanism of the processes he was studying. Certainly Ingold through Hughes had achieved his purpose!

It should be mentioned that a very short note appeared in the August, 1938 *Journal of the American Chemical Society*, "The Common Basis of Intramolecular Rearrangements. IV A Correction: The Benzilic Acid Rearrangement." (21) Whitmore stated in a face-saving way that "no facts have been found contrary to the assumption of the basis of molecular rearrangements as due to a carbon with an open sextet. However, the extreme extension of the hypothesis to the benzilic acid rearrangement, involving the addition of a proton to benzil to form a positive ion, cannot be supported." (21) Whitmore had no alternative but to publish this retraction a decade later, not because of what Ingold had published in 1928 nor the criticism leveled at this mechanism by Kon in 1934, but because of the work of several American chemists.

Frank Westheimer (22) had shown in 1936 that the benzilic acid rearrangement was second-order and a function of hydroxide concentration. Irving Roberts and Harold Urey (23) in 1938, performing oxygen exchange experiments in alkaline media, showed that there was rapid and reversible addition of hydroxide to form a negative ion intermediate, which was then followed by rearrangement. Roberts and Urey concluded their paper with the following remark. "This mechanism is entirely consistent with the organic evidence and with the theory of reactivity of organic compounds as a function of electron displacements as developed by English workers". (23) Reluctantly, Whitmore admitted his error and that his mechanism was indefensible, in the face of the accumulated evidence.

It is hoped that this curious episode has shown that the radical revolution created by Ingold and other members of the so-called English School in the understanding of organic reaction mechanism was one that proceeded with some difficulty in the United States. Even among chemists such as Whitmore who was interested in applying electronic concepts to reaction mechanisms the transition was difficult. It would remain for the new generation of chemists who were free of many of the restrictions of the past, such as Saul Winstein (1912–1969), Paul Bartlett (1908–), Herbert C. Brown (1912–) and Frank Westheimer (1912–) among others, to facilitate the transition. Through their efforts and those of others, American chemists would become the

leaders in the field of physical organic chemistry in the post-war era.

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COMMENTARY

Johannes Wislicenus, Atomism, and the Philosophy of Chemistry

Peter J. Ramberg, North Dakota State University

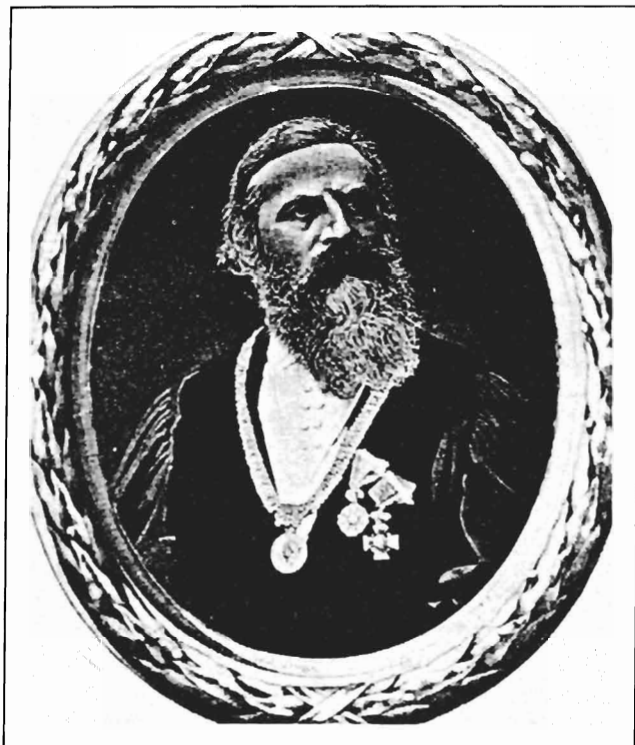
Johannes Wislicenus (1835–1902) is known as the chemist whose work on the structure of lactic acid inspired van't Hoff's theory of the asymmetric carbon atom, and who then sponsored the translation into German of van't Hoff's *La chimie dans l'espace* (1875). He was subsequently forced to suffer the scorn of Hermann Kolbe, who in his attack on stereochemistry declared Wislicenus to have left the arena of the exact sciences. Naturally, Wislicenus thought otherwise, but his side of the story, surprisingly, has never been told (1). As the earliest and strongest supporter of van't Hoff's theory of the tetrahedral carbon atom, Wislicenus clearly recognized the implications that the study of "chemistry in space" entailed for both chemical theory and practice, and he was willing to endure the criticisms brought about by his scientific commitments. The ability to study the arrangement of atoms in space, declared Wislicenus, was a definite sign of progress for the science of chemistry.

In 1888 Wislicenus published a clear and succinct defense of the then young science of stereochemistry, as a reply to a request from Wilhelm Lossen (1838–1906), professor of chemistry at the University of Königsberg (2). Despite its brevity, it reveals several aspects of Wislicenus' theoretical and methodological commitments, and therefore occupies a central position for understanding his science. I present here some introductory comments on the historical context of the paper, followed by a translation of the complete text.

Wislicenus had long been sympathetic to the idea that knowledge of spatial relationships of atoms was necessary for the success of chemical theory. He himself never found success, however, in producing a satisfactory way of investigating these relationships. During his

decade-long research on the constitution of the lactic acids, he struggled to interpret the differences he found (primarily the appearance of optical rotation) between the four known acids, and invented the term "geometrical isomerism" to indicate that these differences could be traced back to some sort of difference in the three-dimensional arrangements of the constituent atoms (3). He was unable to produce anything more concrete than this vague insight. It was not until the fall of 1875, when he became acquainted with van't Hoff's theory of the asymmetric carbon atom, that he realized what kind of three-dimensional arrangement would be useful for chemical theory.

In 1873, Wislicenus had reached a theoretical dead-end and had abandoned the further study of lactic acid, in part because of experimental difficulties in preparing pure samples of lactic acids. More importantly, however, another source of his frustration can be found in the traditional theoretical interpretation of the term "structure" that confined Wislicenus to a particular interpretation of chemical notation. According to its original meaning, as envisaged by August Kekulé and later clarified by Aleksandr Butlerov, a chemical structure represented the chemical arrangements of atoms in a molecule, and represented those atoms as "chemically" indivisible units, and not as discrete parts of matter in space (4). The phrase "chemical structure" therefore meant something unique—a picture or summary of the chemical behavior of a substance towards other substances; it did not mean a picture of the actual physical form of the molecule (what it "actually" would look like, if we could see it). Before he read *La chimie dans l'espace* in the fall of 1875, Wislicenus always regarded chemical structures according to this accepted interpretation.



Johannes Wislicenus (1835–1902)

The solution to Wislicenus' dilemma lay, of course, precisely in the theory of the tetrahedral carbon atom that van't Hoff laid out in his short book. The founders of stereochemical theory, van't Hoff and Le Bel, interpreted "structural formula" in a way different from its original meaning and assumed that atoms shown to be located near another atom in the molecule's chemical structure were also located near that atom in the molecule's physical form. The original aim of both theories was an explanation of optical activity, but the beauty of van't Hoff's thesis in particular lay in the recognition that all chemical drawings could contain more information than their original purpose had implied (5). According to van't Hoff, structures did not simply

represent the sequence of chemical connections in a molecule, i.e., which atom was connected with which, but could also imply the spatial relationships between them. These spatial relationships were obtained by the assumption of an equivalence, or at least a correspondence, between the chemical structure of a molecule and its physical form. One could obtain a model of the physical form of a molecule by assuming each carbon atom in its chemical structure to have the physical form of a tetrahedron.

Van't Hoff offered a method for modelling the physical form for all organic molecules, in the process proposing a means of representing the connections between carbon atoms. He modelled single, double, and triple bonds by joining, respectively, two corners, edges, or faces, as depicted in Fig. 1. The model in Fig. 1 was incapable of rotation about the line containing the carbon atoms, and thus predicted the existence of two different spatial isomers (i.e. *cis* and *trans* isomers) when

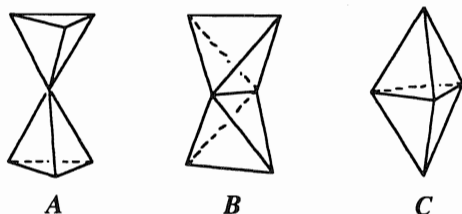
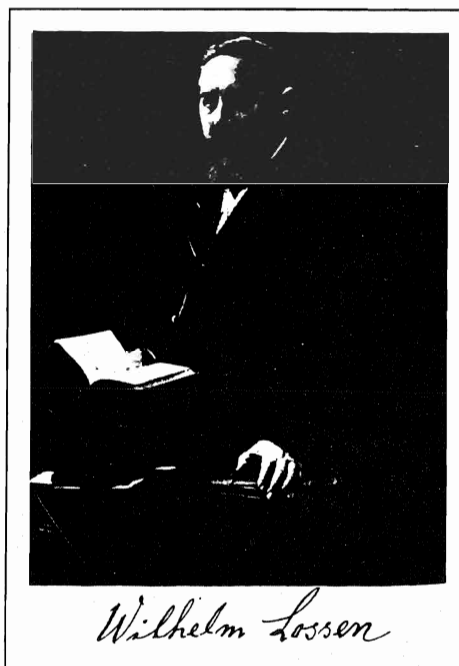


Figure 1 The van't Hoff-Wislicenus models for (A) single; (B) double; and (C) triple carbon-carbon bonds (after Wislicenus)

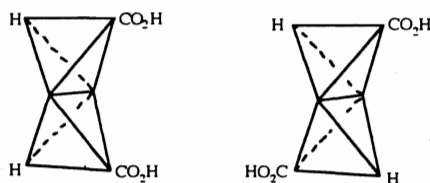


Figure 2 cis and trans isomers (after van't Hoff and Wislicenus)

each carbon atom contained two different radicals. This prediction accounted exactly for the existence of several known pairs of acids, such as maleic and fumaric acids (Fig. 2) that could not be differentiated theoretically by appealing to different chemical structures (that is, by connecting the atoms in a different way). Although van't Hoff's explanation of optical activity by means of the asymmetric carbon atom was generally adopted, this theory of geometrical isomerism in the unsaturated acids was ignored until 1885, when Wislicenus began his major work on the confirmation and expansion of van't Hoff's theory of unsaturation.

In the spring of 1887, Wislicenus published the results of these investigations in a major work entitled "On the Spatial Arrangement of Atoms in Organic Molecules and its Determination in Geometrically Isomeric Unsaturated Compounds" (6). Wislicenus adopted the models in Fig. 1 and provided a means of assigning *cis* and *trans* configurations (in Wislicenus' terms, "planesymmetric" and "axialsymmetric") to the unsaturated acids. In the 1877 edition of *Die Lagerung der Atome im Raume*, van't Hoff had already indicated a means of making such an assignment and had also given preliminary arguments for making such claims, but Wislicenus took these suggestions and elaborated upon them to reproduce a detailed version of van't Hoff's arguments, and applied the same reasoning to other pairs of acids. In the history of chemistry, Wislicenus' work occupies a unique position because of his explicit and comprehensive adoption of mechanical methods to solve chemical problems and its thoroughly mechanical attempt to explain chemical transformations. It is not necessary here to go into the intricacies of Wislicenus' mechanical arguments. They were complex and involved the consideration of intramolecular motions and chemical attractions, as well as the genetic chemical relationships of these acids to their derivatives.

Wilhelm Lossen responded to Wislicenus' paper in late December of 1887, directing his criticism to the van't Hoff theory and its assumptions about molecular

form in general, and not to Wislicenus' modifications (7). The argument was essentially a summary of his two earlier articles published in 1880 and 1881 on the nature of valence, which he defined simply as the number of atoms that were located in the "binding zone" of another atom (8). To Lossen, valence was a simple number indicated by the chemical structure and he made no commitment to a single valence number for any given atom (for example, carbon had a valence of either two, three or four). He found the concept of a multiple bond an absurd idea, since he interpreted this to mean that an atom could find itself in the "binding zone" of another atom twice; an atom was either there and bound or it was not. Presumptions of multiple bonds were an effort, in Lossen's view, to save the theory of constant valence, and rested furthermore on the assumption that atoms were divisible, since two different parts of an atom must attract two different corresponding parts on another atom. To be able to divide atoms in such a way, however, one must know what the atoms themselves were like, and at the current state of science, this was not accessible to observation.

Therefore, Lossen conceived of atoms as simple points, and gave the following simple analysis of the consequences of van't Hoff's theory. The theory of saturated compounds, that is, the model for optical activity and the model for single bonds, he found (9):

... compatible with the assumption that atoms are material points. The given figures become perhaps somewhat less clear, but not essentially changed, if all of the edgelines are removed. The endpoints of the remaining lines—dotted in the figures—then indicate the position of atoms in space, and their lines of bonding indicate the direction in which the force that unites the atoms with one another acts; this direction is exclusively dependent on the position of the atoms [Fig. 3].

He subjected van't Hoff's model for double bonds to the same analysis and found that it (10):

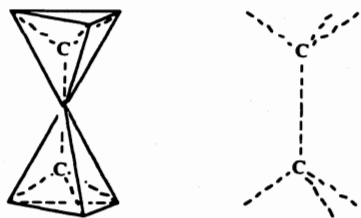


Figure 3 (after Lossen)

... can no longer be reconciled with the assumption that atoms are material points. It is not apparent therefore why in this case a rotation of the two triangles in opposite directions should not be possible [rotation about the C-C axis in Fig. 4]. Van't Hoff does not stop at [specifying] the position of atoms in space, but goes further, and also presents an arrangement of the affinity units in space, independent of the positions of the atoms ... In fact, the direction of lines CA and CB in Fig. 4 no longer indicates the position of atoms, since at A and B there are no atoms. In other words, in Fig 4 the affinity units possess an independent position in space.

The presumed restriction of rotation about the carbon-carbon bond, so crucial to van't Hoff's explanation of the isomerism between the unsaturated acids, was actually not possible if one followed Lossen in considering the position of point-mass atoms in space. Nor did the model for the double bond make physical sense to Lossen, since the lines of bonding did not lie along a straight line between the carbon atoms. The van't Hoff model had assumed that the atom had a shape and therefore had parts (11):

In my opinion [van't Hoff's] conception leads necessarily to the assumption that multivalent atoms cannot be considered as material points at all, that rather there are

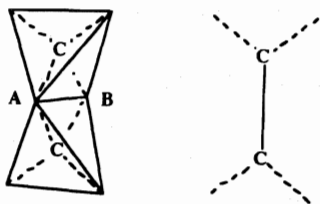


Figure 4 (after Lossen)

parts of them to distinguish, from which emanates their influence on other atoms.

Lossen then inquired how van't Hoff and Wislicenus could know anything of these parts.

It was unacceptable, according to Lossen, simply to speculate regarding the form of the carbon atom and its parts, and then construct the spatial properties of molecules. Although Lossen did not argue that the spatial distribution of atoms was unknowable, he did object to van't Hoff's claim to a knowledge of the spatial distribution of affinity units on the atom, that is, the shape of the atom itself. Lossen was quite specific about the sequence of events chemists should follow to gain knowledge of a molecule's spatial properties. One could only consider the position of atoms in space after the determination of the specific atomic form, and after the location of the seats of chemical affinity were located (12).

Lossen's critique was therefore methodological as well as theoretical. Van't Hoff and Wislicenus had addressed the problem exactly the other way around. They had first assumed an atomic form and a spatial distribution of affinities, bypassing completely even a preliminary definition of "affinity unit" (valence bond), and then constructed the form of molecules that led to certain observable predictions, namely the appearance of different configurational isomers. Lossen emphasized this "deficiency" in logic, and asked Wislicenus and van't Hoff to explain further what they actually meant in their models by affinity units.

This methodological criticism, that essentially advocated an inductivist over a hypothetico-deductive approach, provoked Wislicenus' response, which appeared in the *Berichte der deutschen chemischen Gesellschaft* in February of 1888. Wislicenus simultaneously defended the principles of stereochemistry against Lossen's theoretical argument, and the use of hypothesis in chemical theory against Lossen's methodological criticism. Wislicenus had remarkable linguistic skills, and in a forceful and articulate manner in a scant four pages of the *Berichte*, he made many interesting and insightful observations about the nature of chemical theory (13).

Two aspects of Wislicenus' scientific thought dominate this paper. First, and most obvious, is his explicit commitment to a physical atomism that would benefit chemical theory. Early in his career he followed the traditional interpretation of structural formulas, and separated the belief in indivisible physical atoms from his interpretation of chemical formulas. In his 1859 *Doktorarbeit* and *Habilitationsschrift*, "The Theory of

Mixed Types," he ascribed no physical reality to chemical formulas whatsoever, and considered them only as reaction formulas. Until his major 1887 work on stereochemistry, he made no public statements on the use of a physical atomism for chemical theory (14).

During his extended study of the lactic acids during the 1860s and 1870s, he attempted to reach definite conclusions about the physical arrangements of atoms to explain the differences between them, but it was not until the fall of 1875, when he became acquainted with van't Hoff's theory, that he saw a way that a physical atomism could be applied to chemical theory. By 1885 or 1886, when he began his study of the unsaturated acids, and probably much earlier, he had completely accepted van't Hoff's premise of the correspondence between the chemical structure and physical form of molecules. And in 1888 he felt confident enough to present publicly his conception of those physical atoms.

What then, did Wislicenus mean by atoms? His 1888 paper was the most explicit public statement of his beliefs—he said that the carbon atoms were tetrahedrally-shaped carriers of chemical energy. But this statement must be considered carefully. It is clear elsewhere in his response to Lossen that Wislicenus did not regard the *Berichte* as the place for such lofty speculations, and he made them only out of courtesy to Lossen; he did not regard this belief by any means as scientifically justified. At the most, it was perhaps a hunch or a feeling, based on his work so far. He was, on the other hand, absolutely committed to a broad conception of a tetrahedral carbon atom, since he was convinced that the experimental evidence confirmed this basic assumption. Presumably, he did not want to be "tied down" to a specific interpretation of the nature of the tetrahedron, i.e. the ultimate stuff that composed it, the actual cause of chemical affinity, or to the precise nature of the affinity unit, as Lossen had requested. These reservations no doubt also were related to his methodological commitments.

Perhaps the most interesting aspect of Wislicenus' atomism was his conviction that spatial arrangements of atoms were "accessible to experimental test," and that the proof of these configurations led precisely to a deeper understanding of atoms and furthermore, to a knowledge of subatomic structure. The "Uratoms," as components of the recognized elementary atoms, were the carriers of chemical affinity. This was the closest he ever came to defining an affinity unit, but he fell short of actually producing a concrete definition, and he remained content merely to make an analogy between the Uratoms and atoms of compound radicals at a higher

level. The idea that the known elements were possibly divisible was not a new or unique idea with Wislicenus, as he himself was quick to point out. It can be found in the speculations of Adolphe Wurtz, August Kekulé, and Crum Brown in the development of structure theory, and permeates much of chemical thought in the 19th century (15). Particularly innovative here, however, was Wislicenus' conviction of the relationship he offered between the confirmation of stereochemical theories and a knowledge of subatomic structure (16).

After 1888, Wislicenus was never again as explicit about the nature of these Uratoms. In a lecture given in 1892, in honor of the 25th anniversary of the Deutsche Chemische Gesellschaft and the observance of the death of A.W. Hofmann, and in 1893, in a tantalizing lecture given as the Rector of the University of Leipzig, "Chemistry and the Problem of Matter," he discussed similar ideas as in 1888, without going into as much detail about the actual nature of these Uratoms (17).

Wislicenus' response to Lossen also offers clues about his methodological and epistemological commitments. It is only through the manipulation of molecules, said Wislicenus, that chemists have gained knowledge about the nature of the constituent atoms, and the same process will elucidate the nature of the parts of those atoms. This, Wislicenus claimed, put him squarely in the middle of traditional research in organic chemistry. He considered research on geometrical isomerism to be a natural outgrowth of that empirical, inductive tradition.

Wislicenus declared at the same time, however, that the study of geometrical isomerism departed from this tradition, because it emphasized a deductive methodology. The theory of the tetrahedral carbon atom was not a cautious hypothesis, built from the slow accumulation of facts and observations. On the contrary, it was a set of bold assertions about the physical nature and actual appearance of carbon atoms and of organic molecules, and could not be confirmed by direct experience. It was precisely this speculative aspect of the theory that had provoked Lossen's criticism.

Speculation, Wislicenus admitted, was less certain than the cautious method of induction, but it nonetheless provided a quicker path to successful theories, provided such speculations could be supported by empirical investigation. They certainly may be wrong, but that should not prevent us from making them and testing them. Wislicenus made similar comments about the usefulness of hypotheses in a long letter to Hermann Kolbe defending van't Hoff's theory. Since new hypotheses generate new facts, even if these hypotheses be wrong, the facts they generate could be reinterpreted by later

generations of chemists to create a better theory. The future, and not the present, Wislicenus declared, was the best judge of scientific work (18).

Among organic chemists of his generation, he was perhaps the most explicit about the usefulness of hypotheses in chemistry. He advocated vigorously the advantages of hypotheses and the imagination not only in 1888 but also in his 1892 and 1893 lectures, and recognized in fact a methodological change from a predominantly inductive chemistry earlier in the century to a predominantly deductive chemistry that depended on the imagination. Like the incorporation of physical atomism into chemical theory, Wislicenus' scientific life was also coincident with a conversion of chemistry from an inductive, natural-history oriented science, to a theory-driven science that depended on the empirical confirmation of predictions (19).

With his commitment to a physical atomism and to a deductive chemistry, Wislicenus perceived clearly the existence of new trends in the theory and methodology of chemistry, and promoted these trends vigorously. He was prepared to endure the complaints and criticisms of Lossen and others who thought he took stereochemical principles too far, and who thought he had not remained tied to the facts. In part these criticisms were justified; he was almost too eager to see his principles work, and thought spatial properties would solve all difficult cases of isomerism. As Arthur Michael would show in the 1890s, some of Wislicenus' conclusions rested on empirically shaky ground (20). But Wislicenus' occasional overenthusiasm does not detract from his reasoned and articulate defense of stereochemistry. He clearly and gratefully acknowledged the debt he owed to past theoretical accomplishments in chemistry and to its inductive methodology, and indeed placed himself within these traditions, but would never agree with his opponents that chemists should be permanently fastened to them.

The following translation is an attempt, if it is possible, to be both literal and free, and I have also attempted to recreate Wislicenus' style as much as possible. Wislicenus held strong opinions, in religion and politics as well as chemistry, and was able to express them articulately and forcefully, both in print and in speech. It is, I believe, one of the factors that contributed to his influence in stereochemistry. Several German words that are difficult to translate have been included in the text, and all emphases are Wislicenus'. W. V. Farrar translated small portions of the text in 1968, and I have diverged considerably from his version. The most significant departure is explained in the notes.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. To date, the best and most sympathetic account of Wislicenus' life is by his assistant, colleague and friend at Leipzig, Ernst Beckmann, "Johannes Wislicenus," *Ber.*, **1904**, *37*, 4861-4946. I am currently evaluating Wislicenus' contribution to stereochemical theory.
2. J. Wislicenus, "Ueber die Lage der Atome im Raum. Antwort auf Lossen's Frage," *Ber.*, **1888**, *21*, 581-585.
3. N. Fisher, "Wislicenus and Lactic Acid: The Chemical Background to van't Hoff's Hypothesis," in O.B. Ramsey, ed., *Van't Hoff-Le Bel Centennial*, American Chemical Society, Washington, DC, 1974, pp. 33-54.
4. A. J. Rocke, "Kekulé, Butlerov, and the Historiography of the Theory of Chemical Structure," *Brit. J. Hist. Sci.*, **1981**, *14*, 27-57, and *idem*, *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*, Ohio State University Press, Columbus, 1984.
5. Le Bel made no such commitment, and considered each class of organic compounds separately. He agreed with van't Hoff only in his explanation of optical activity.
6. J. Wislicenus, "Ueber die räumliche Anordnung der Atome in organischen Molekülen und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindungen," *Abhandlungen der mathematisch-physischen Classe der königlichen sächsischen Gesellschaft der Wissenschaften*, **1887**, *14*, 1-77; the article was translated early in this century: "The Space Arrangement of the Atoms in Organic Molecules and the Resulting Geometrical Isomerism in Unsaturated Compounds," pp. 61-132, in G. M. Richardson, Ed., *The Foundations of Stereochemistry: Memoirs by van't Hoff, Le Bel and Wislicenus*, American Book, New York, 1901. I have retranslated the title.
7. W. Lossen, "Ueber die Lage der Atome im Raum," *Ber.*, **1887**, *20*, 3306-3310. Arthur Michael (1853-1942) began the other, ultimately more devastating criticism in 1888; see "Zur Kritik der Abhandlung von J. Wislicenus. 'Ueber die räumliche Anordnung der Atome in Molekülen,'" *J. Prak. Chem.* **1888**, *36*, 6-39.
8. W. Lossen, "Ueber die Vertheilung der Atome in der Molekel," *Ann.*, **1880**, *204*, 265-364 and "Ueber die

- sogenannte Verschiedenheit der Valenze eines mehrwertigen Atoms," *Ber.*, 1881, 14, 760-765.
9. "Die vorstehenden Ausführungen, deren Einzelheiten besonders in der ersten Auflage von van't Hoff's Broschüre entwickelt sind, sind vereinbar mit der Annahme, dass die Atome materielle Punkte seien. Die gegebenden Figuren werden vielleicht etwas weniger deutlich, der Sache nach aber nicht geändert, wenn man alle in denselben gezeichneten Kanten weglässt. Die Endpunkte der bleibenden (-in den Figuren punktiren-) Linien bezeichnen dann die Lage der Atome im Raum, die Verbindungslinien derselben die Richtung, in welcher die Kraft, welche die Atome mit einander vereinigt, wirkt; diese Richtung ist ausschliesslich abhängig von der Lage der Atome," Lossen, reference 7, p. 3307.
 10. "Diese letzere Auffassung lässt sich nicht mehr vereinigen mit der Annahme, dass die Atome materielle Punkte seien . . . Sodann ist nicht einzusehen, weshalb in diesem Fall eine Drehung der beiden Dreiecke im entgegengesetzte Sinn um die Linie CC nicht möglich sein soll . . . bleibt er [van't Hoff] nicht stehen bei der Lage der Atome im Raum, er geht darüber hinaus und stellt auch noch eine von der Lage der Atome unabhängige Lage der Affinitätseinheiten im Raum dar . . . In Fig. 4 dagegen ist die Richtung der Linien CA und CB nicht mehr gegeben durch die Lage der Atome, denn in A und B befinden sich keine Atome. Mit anderen Worten, in Fig. 4 besitzen die Affinitätseinheiten eine selbstständige Lage im Raum," *ibid.*, p. 3309.
 11. "Diese Auffassung führt nach meiner Meinung notwendig zu der Annahme, dass das mehrwertige Atom sich überhaupt nicht als materieller Punkt betrachten lässt, dass vielmehr Theile desselben zu unterscheiden sind, von welchen die Wirkung auf anderen Atome ausgeht," *ibid.*
 12. Lossen, reference 7, p. 3309.
 13. His linguistic abilities were apparently not limited to German. His English students also indicated an excellent proficiency with English, although he never published in it. This likely was primarily due to his three-year residence in America, although it seems likely he learned English in Germany before then.
 14. J. Wislicenus, "Theorie der Gemischten Typen," *Zeit. Gesamm. Naturwissen.*, 1859, 14, 96-175. According to Nicholas Fisher, Wislicenus was already thinking in three dimensions as early as 1863. At that time, however, Wislicenus did not have any concrete ideas about the nature of the physical form of molecules. This is supported by two observations. First, in 1863 Wislicenus continued to use the old type theory notation, which did not lend itself easily to three dimensional thought. Second, in 1863, when Wislicenus elaborated on the meaning behind chemical notation, he spoke primarily of different pictures of molecules with regard to their chemical behavior, and not to their physical form. See Fisher, reference 3, p. 43.
 15. See A. J. Rocke, "Subatomic Speculations and the Origin of Structure Theory," *Ambix*, 1983, 30, 1-18, and W. V. Farrar, "Nineteenth Century Speculations on the Composition of the Elements," *Brit. J. Hist. Sci.*, 1965, 2, 297-323.
 16. Wislicenus' belief in simpler atoms was also noted by W. V. Farrar, "'Chemistry in Space' and the Complex Atom," *Brit. J. Hist. Sci.*, 1968, 4, 65-67.
 17. J. Wislicenus, "Die wichtigsten Errungenschaften der Chemie im letzten Vierteljahrhundert," *Ber.*, 1892, 25, 3398-3410 and *Die Chemie und das Problem von der Materie*, Edemann, Leipzig, 1893.
 18. Wislicenus to Hermann Kolbe, 24 November 1877. Standnummer 3550, Archives, Library of the Deutsches Museum, Munich.
 19. Alan J. Rocke has pointed out this trend which occurred in the mid-19th century, and has assigned it as a possible cause for the pathological nature of Hermann Kolbe's attacks on structural chemistry as well as against Wislicenus and van't Hoff. See A. J. Rocke, "Kolbe vs. the 'Transcendental Chemists': The Emergence of Classical Organic Chemistry," *Ambix*, 1987, 34, 156; for a more general exploration of this trend earlier in the century, see also A. J. Rocke, "Methodology and Its Rhetoric in Nineteenth-Century Chemistry: Induction versus Hypothesis," in E. Garber, Ed., *Beyond History of Science: Essays in Honor of Robert E. Schofield*, Lehigh University Press, Bethlehem, 1990, pp. 137-155.
 20. Michael, reference 7, and "Untersuchungen über Alloisomerie. II." *J. Prakt. Chem* 1892, 46, 209-305; 381-427, "Untersuchungen über Alloisomerie. III." *J. Prakt. Chem* 1895, 52, 289-372.
 21. The figure of Wislicenus is taken from *Alma Julia. Illustrierte Chronik ihrer dritte. Seularfeier*, Thein, Wurzburg, 1882, p. 107.

ABOUT THE AUTHOR

Peter J. Ramberg was in residence at the Library of the Deutsches Museum in Munich in 1991-1992 as a Fulbright pre-doctoral fellow and completed his Ph.D. dissertation on the early history of stereochemistry at Indiana University the following year. He currently teaches general and organic chemistry in the Department of Chemistry, North Dakota State University, Fargo, ND 58105-5596.

PRIMARY DOCUMENTS

Johannes Wislicenus, "Concerning the Position of Atoms in Space: An Answer to W. Lossen's Question"

*Translated from Berichte, 1888, 21, 581-585
by Peter J. Ramberg*

In the final issue of last year's *Berichte*, W. Lossen publicly challenged van't Hoff and me to reveal our views concerning the nature of affinity units on the basis of our geometrical ideas, by asserting that the question of the position of affinity units in space must be considered *before*, and not *after*, addressing the question of the position of atoms in space and, above all, a definition of affinity unit must be given" (1).

I agree completely with Lossen that our considerations about the configuration of molecules exclude the assumption that atoms may be "material points." One cannot avoid imagining them as spatial objects, thereby transferring the location of the units of chemical effect [Wirkungseinheiten] on multi-valent elementary atoms into different regions of these spatial objects. In principle, this idea is in no way hindered by difficulties, provided we conceive the so-called elementary atoms not as atoms in a strict sense, but as composed of groups of still more fundamental atoms [Urelementaratom] of a simpler sort—similar to the more compound radicals at more complex levels.

This notion is, however, neither peculiar nor new. The majority of chemists interested in this question might well share it today. Considering the proof of periodicity in the relationship between the properties and weights of the elementary atoms, in which they resemble by decisive analogy both the compound radicals of organic compounds, and, in their periods, to the homologous and heterogeneous series of the latter, the complexity of elementary atoms is certainly more probable than their simplicity. This view is also supported by physics, especially by the most recent research in spectroscopy.

While recognizing that Lossen's request is justified in general, I must, on the other hand, decisively reject the point raised by the above statement. Exactly the opposite: only *after* the spatial arrangement of elementary atoms in molecules is determined, and not *before*, is it possible to consider Lossen's question seriously. As I have shown in my paper "On the Spatial Arrangement of Atoms in Organic Molecules" (2) and will shortly show in detail on the basis of experimental research, the question concerning the spatial arrangement of atoms is

accessible to experimental test. On the basis of recently concluded investigations, I have convinced myself and am thoroughly satisfied that it also passes these tests. As a result, the initially purely hypothetical assumption is reinforced, that the independent rotation between two mutually monovalently bound carbon atom systems is prevented whenever they enter into a divalent linkage [zweiwertige Verkuppelung] (3). These facts now give quite important evidence for the existence of a double bond between neighboring carbon atoms and also for their corporeality.

For the moment, however, investigations on the configuration of molecules offer the only way to reach conclusions about the form of elementary atoms and the spatial distribution of their spheres of influence [Wirkungssphären], designated as affinity units. Or does Lossen know another way? The things that we chemists manipulate are chemical molecules—only from *their* properties, through *inductive* inferences, have we acquired our knowledge about the properties of the elementary atoms. As long as we had only extremely limited knowledge about the properties of molecules, each inductive conclusion remained uncertain, and the speculations based on them, the *deductive* conclusions, remained deficient, even sometimes positively wrong.

The empirical study of the quantitative compositional relationships of chemical compounds led initially to the law of multiple proportions and then towards a new scientific atomism. The efforts made towards determination of the atomic weights, however, remained for a long time very unsatisfactory and controversial—at least as far as their true values were concerned—until—and this is predominantly the accomplishment of organic chemistry—truly comparable molecular weights could be ascertained for a large number of chemical compounds. Only from these molecular magnitudes were actually comparable atomic weights derived. Furthermore, after establishment of the atomic weights, the study of molecular composition resulted in the concept of valence, out of which, again only from the study of compound molecules [Verbindungsmoleküle], emerged the law of atomic linkage, and so forth. The empirical elucidation of the way in which atoms are spatially distributed in molecules will follow an entirely similar course, and this distribution will in turn yield clues about the geometric properties of the atoms of our elements. These properties will become all the more certain as our empirically gained knowledge about the geometric properties of molecules becomes more certain.

Today these conceptions about atomic form and the positions of their areas of chemical effect [Wirkungs-

zonen] can only remain very uncertain. We certainly have the need, of course, to form such conceptions, but must always bear in mind that all theories derived by way of speculation are still very unreliable. Of course, that should not prevent us from forming deductive conclusions. We must certainly be aware, however, that the value of these conclusions, in combination with inductively derived knowledge, lies in the fact that they direct the imagination along the new avenues of empirical research which it seeks. Sometimes, indeed, the imagination is led along false paths, but between these paths lie the routes leading to the goal.

In view of today's situation of compelling facts that are urgent to such studies, exact scientists certainly have the right to occupy themselves with the further empirical pursuit of inevitable (4) hypotheses concerning the spatial distribution of atoms within the molecule, without immediately discussing the deeper lying reasons for each relationship before the general public. On the other hand, he who desires more speculation certainly has the right to make the attempt, and to provide the paths of *his* thoughts to his contemporaries; he is not, however, entitled to demand the same from others.

So I could, of course, simply reject Lossen's statement of "before" and "after" and his request, by challenging him with full conviction that a speculative discussion of the relationships in question could bring more clarity than the certain, admittedly long, path of empirical research. Nevertheless, once challenged, I want to grant the wish of my honored colleague at least as far as I can with good conscience.

Thus, I believe it more probable that atoms are spatial objects composed of atoms of simpler elements [Urelementen], than of point-like carriers of energy. Therefore, it appears more probable to me than any other assumption, that the atoms may be compared to compound radicals, and that like them, their affinity units are located in certain parts of those atoms from which they act.

I believe it possible that with time we shall not only obtain certain ideas about the form of elementary atoms, but also about the position of the relative locations of their spheres of influence [Wirkungssphären], and also that we will ultimately elucidate the actual essence of the specific chemical form of potential energy.

I do not consider it impossible that a carbon atom may be an object whose form more or less [perhaps quite closely] resembles a regular tetrahedron; further, it is not impossible that the causes of every effect that actually manifests itself in the affinity unit concentrate

themselves in the corners of this tetrahedral object, and for analogous reasons, would possibly be similar to the electrical effect of an electrically charged metal tetrahedron (5). The actual carrier of this energy would ultimately be the primitive atoms [Uratome], just like the chemical energy of compound radicals undoubtedly is a product of the inherent energy of the elementary atoms within them.

These are, more or less, the ideas that I myself have already had for some time about the very question imposed on me by Lossen. By no means do I attach to them the value of scientific conviction and I prefer not to be "nailed down" to them. Nor do I wish to get involved in a purely speculative discussion, since I voice these thoughts here not only in free personal discourse—how could it be otherwise—but from a position which above all is dedicated to the results of exact science. Such discussions are actually valuable only for their critical aspects if they are not conducted quite strictly on the basis of sufficient facts: they can contribute towards clarification in a negative sense, by detecting the untenability of expressed theories or theoretical opinions, but they are able to bring us no further in a positive direction. At the most they succeed now and then in bringing a precise expression to factually derived knowledge. From this standpoint I also judged, for example, Lossen's earlier longer paper "On the Distribution of Atoms in the Molecule" (6), without, however, agreeing with all the points contained in his critique.

This has turned out longer than I originally intended. It may remain unabbreviated as a critique of Lossen's viewpoint in relation to "before" and "after." Lossen's claim is the proof that even we chemists do good from time to time by making completely clear to us the path that we have to follow for the development of concepts. We must take actual obtained knowledge, and not a justifiable desire, as the starting point for our advancement into the unknown.

In conclusion, with full conviction of its greater justification, I oppose Lossen's thesis once again with the antithetical statement: not *before*, but only *after* establishment of the spatial position of elementary atoms in a compound's molecules can we address the question concerning the position of affinity units in the spatial objects of elementary atoms with the prospect of success. Ultimately these considerations can likely also lead to a satisfactory definition of affinity units.

Leipzig, Early February 1888
(Received on February 16)

REFERENCES AND NOTES

1. W. Lossen, "Ueber die Lage der Atome im Raum," *Ber.*, **1887**, *20*, 3306-3310 on p. 3309, second paragraph.
2. J. Wislicenus, "Über die räumliche Anordnung der Atome in organischen Molekulan und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindungen," *Abhandlungen der mathematisch-physischen Classe der königlichen sächsischen Gesellschaft der Wissenschaften*, **1887**, *14*, 1-77.
3. Wislicenus is referring here to the transformation from Fig. 1(A) to Fig. 1(B) in the preceding commentary, that is, to an elimination reaction. The rotation about the carbon-carbon bond is removed in these transformations. The idea of free rotation was originally van't Hoff's, but Wislicenus developed the idea to a much greater extent in his 1887 essay.
4. The German word here is "unabweisbare," which usually translates as "irrefutable." The sentence, however, is not entirely clear with "irrefutable." The reviewer of the first draft of this translation suggested that "unabweisbare" was a misprint or misreading of Wislicenus' manuscript for "unbeweisbare," which would translate literally as "unprovable" or perhaps "indemonstrable." Neither of these alternatives seems better than "irrefutable," however. "Inevitable" seems to fit better with the content of the paper and of the sentence itself.
5. A fragment of this sentence in German reads as follows: ". . . nicht für unmöglich ferner, daß die Ursachen jener Wirkungen, welche in den 'Affinitätseinheiten' zur tatsächlichen Erscheinung kommen, sich in den Ecken dieses tetraëdrischen Gebildes concentrieren . . ." Farrar translates this fragment as follows: ". . . that the causes of the effects which enter our actual experience as affinity units might be concentrated in the angles of the tetrahedron . . ." This, I believe, is a mistranslation, since there is no reference to "our" experience in Wislicenus' sentence. Farrar's subsequent footnote is therefore also inaccurate. Wislicenus was not a positivist, but he made no claims of actually seeing an affinity unit. See W. V. Farrar, "'Chemistry in Space' and the Complex Atom," *Brit. J. Hist. Sci.*, **1968**, *4*, 65-67, p. 66.
6. W. Lossen, "Ueber die Vertheilung der Atome in der Molekel," *Ann.*, **1880**, *204*, 265-364.

OLD CHEMISTRIES

Steele's "Fourteen Weeks in Chemistry"

William D. Williams, Harding University

Fourteen Weeks in Chemistry, by Joel Dorman Steele, was America's most widely used high school chemistry text from 1868 to 1900 and is one of the most frequent "old chemistries" found in today's rare book market. It was the first of a series of science texts by Steele with the similar titles: *Fourteen Weeks in Chemistry* (1867); *Fourteen Weeks in Natural Philosophy* (1869); *Fourteen Weeks in Astronomy* (1869); *Fourteen Weeks in Geology* (1870); *Fourteen Weeks in Physiology* (1872); *Fourteen Weeks in Zoology* (1872); and *Fourteen Weeks in Botany* (1879). His *Key to Practical Questions in Steele's Sciences* (1871) contained answers to questions in the first four books. These works, along with a series of history texts which were coauthored with his wife, sold over one million copies. Several were published in Japanese, his *Astronomy* in Arabic, and his *Chemistry* in a Braille edition. In 1879, his *Chemistry* was used in 60 out of 122 public high schools in larger cities (1). Seven of his texts were still in print in 1928, 42 years after his death. His books made a significant contribution to the popularization of science in America.

Steele made countless addresses to educational, civic, and church meetings. One of particular interest to chemical historians has been preserved. In July 1884, at the Centennial Anniversary of the University of the State of New York, Steele delivered his last public address, "The History of Science Teaching in the Academies of this State." He recalled the early texts of Marcet, Comstock, Phelps, Cleveland, Eaton, etc. He surveyed the apparatus available at various schools and dates, and presented tables of science enrollments from 1800 to 1884. He observed changes in education and technology over the years and closed with his own philosophy of science teaching (2).

A

FOURTEEN WEEKS

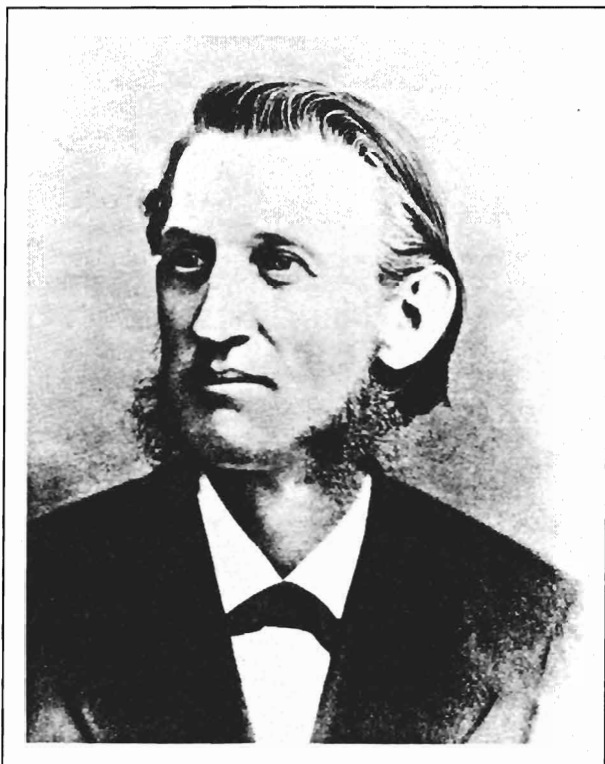
COURSE IN CHEMISTRY.

BY

J. DORMAN STEELE, A. M.,
PRINCIPAL OF ELMIRA FREE ACADEMY.

"Bright and glorious is that revelation
Written all over this great world of ours."
LONGFELLOW.

NEW YORK:
A. S. BARNES & Co., 111 & 113 WILLIAM STREET.
BOSTON:
WOOLWORTH, AINSWORTH & Co.
1869.



Joel Dorman Steele

Steele was born on 14 May 1836 in Lima, NY, the son of an itinerant Methodist minister. Graduating in 1858 from Genesee Wesleyan College (later part of Syracuse University), he enthusiastically chose teaching as a career. He was teacher and principal at Mexico, NY (1858-62), Newark, NY (1862-66) and Elmira, NY (1866-72). Recognized as a gifted teacher, he was exceptional in motivating students (3).

While in college Steele had emphasized Latin, literature, and debating. Apparently his science was self taught as he prepared for his own teaching. Although his first book (1867) listed him with an "A.M." degree, there is no evidence that he ever took any graduate work. The degree may have resulted from his four years at Genesee or it may have been honorary. In 1879, he was awarded an honorary Ph.D. for excellence in teaching by the University of the State of New York.

At the outbreak of the Civil War, Steele served as Captain of Company of the 81st New York Volunteers. He was severely wounded early in the fighting at the battle of Seven Pines, VA. After lying near death for some time, he was discharged and returned to his teaching.

Although he taught many subjects, science was Steele's favorite. Finding the available texts too cumbersome and unappealing, he developed his own set of chemistry notes and methods of presentation. He emphasized exploration, imagination, and critical thinking rather than rote memorization of recitation questions, as earlier texts had done. In 1866 he made plans to have his chemistry notes published by a local press. Publisher A. S. Barnes learned of his project and encouraged him to write a simpler chemistry text intended only for high schools. Steele described his feelings upon its publication (4):

What a Lilliput it seemed—only two hundred and twenty-five 14mo pages of coarse, well leaded type—and what a contrast to the standard Brobdingnags of the day! But it sold! I could scarcely believe the news that came. I had never dared hope that anybody outside the circle of my personal friends would care to buy my book. Yet so it was. An edition of two thousand copies had gone at once and a second edition was to be printed immediately.

The most distinctive features of *Steele's Chemistry* were the brevity and the abundance of every-day applications. Claiming no originality, he stated that his contribution was "simple, interesting language." Large type, familiar applications, short, declarative sentences, and the absence of abstract theory made the book more inviting to typical students. Its wide success was testimony to Steele's desire for "a pleasant study which the pupil can master in a single [14 week] term" (5).

The book was divided into four sections: (I) A brief Introduction; (II) Inorganic Chemistry, covering the more common non-metals and metals; (III) Organic Chemistry; (IV) An Appendix with experiments, review questions, and a qualitative analysis scheme. The "Inorganic Chemistry" section, covering over half the pages, was a descriptive treatment of each successive element following the common outline: sources; preparation; properties; uses; compounds.

Steele's emphasis on applying chemistry to every-day life may be seen in special paragraphs on photography, matches, glass, ceramics, mirrors, etc. Some of his historical anecdotes are still a delight to read: the term "carat" was derived from a dried bean used for weighing by diamond merchants in India; "crucibles" were so named from the sign of the cross placed on them by the alchemists as a prayer for a safe, non-explosive experiment; "antimony" came from "anti-monk," which 15th-century monk, Basil Valentine, called his newly discovered metal. To test its properties, he fed it to the monastery pigs and found that they thrived upon it. A

similar experiment on his fellow monks caused some to die—hence “anti-monk”; “cobalt” was named by miners for Kobolt, the evil spirit of the mines, because the promising ore crumbled to ashes upon roasting (6). A devout Methodist, Steele also inserted frequent references to a benevolent Creator providing chemicals that man would be able to use.

The appendix on “Directions for Experiments” gave detailed instructions for performing experiments described in the text. In the back of all editions, the publisher advertised sets of chemicals and apparatus. A basic set cost \$15.00 and an enlarged set \$30.00. Prior to 1873 the sets cost \$20.00 and \$40.00, but, in addition, special apparatus was offered for making oxygen (\$22.50), nitrous oxide (\$22.50) and an oxygen-hydrogen blowpipe (\$40.00).

The first edition of Steele’s chemistry, published in 1867, was titled *A Fourteen Weeks Course in Chemistry* (261 pp, 25 figures). A reprint in 1871 shortened the title to *Fourteen Weeks in Chemistry*. A revised edition in 1873 (312 pp, 78 figures, \$1.50) adopted the new nomenclature that was appearing in all texts of the period, though the older version, “with the Old Nomenclature,” continued to be reprinted and was advertised as available as late as 1880. The 1873 edition also added a section to the appendix, “Qualitative Analysis for Beginners” by Edward J. Hallock (1846-1884), of Columbia College. In his autobiography, Steele explained that specialists in the various subjects had assisted him in his writings (7):

In getting up these various books we spared neither labor or expense . . . I associated with myself also the best help I could find . . . In chemistry I was aided greatly by Edward J. Hallock of Columbia College, whose lengthy studies in German laboratories had furnished him with a fund of experience.

It is unclear what contributions Hallock made in addition to his appendix on qualitative analysis. The “New Nomenclature” edition, with an 1873 copyright date, went through many printings with no date on the title page and continued to be used even after a third edition appeared in 1887 (8).

The third edition, copyrighted in 1887, changed the title to *A Popular Chemistry* (327 pp, 81 figures). It was printed in larger type and the introduction and chapters on organic chemistry were rewritten. Steele had died in 1886 and his eyesight had been failing for several previous years. In 1885 he wrote of trying to “get my Chemistry and Physics revised before they [eyes] fail entirely” (9). Apparently he was unsuccessful, since the

preface of *A Popular Chemistry* was titled “Publishers Preface” and lacked the “author” comments of previous editions. A contemporary review observed that “the revision has been done by competent hands,” but whose hands remains a mystery (10). Hallock’s appendix on qualitative analysis was still present, this time with “Ph.D.” after his name, but since Hallock had died in 1884, he could not have made the revisions. Another possibility is Mrs. Steele, who was said to have revised some of the books.

A Popular Chemistry was reprinted for many years with no date on the title page and the same 1887 copyright date. About 1890, the American Book Company was formed from A. S. Barnes and several other publishing houses. American Book Company continued to publish *A Popular Chemistry* with the same plates that Barnes had used. In 1895, Steele’s wife re-copyrighted his 1873 second edition of *Fourteen Weeks in Chemistry* and put it on the market. Perhaps she was no longer receiving royalties from *Popular Chemistry*.

Steele’s other texts were equally successful. Immediately after his first chemistry in 1867, A. S. Barnes proposed additional works in science. The *Fourteen Weeks* series was widely used. Steele continued both to teach and write until 1872, when he reluctantly left the classroom to devote his time exclusively to the preparation of textbooks. In collaboration with his wife, Steele also wrote a series of history texts. To avoid any criticism of his reputation in science, he refused to let his name appear on the history works. Later it was inserted on the title page after they were selling in extremely large figures.

First Edition—*A Fourteen Weeks Course in Chemistry*
1867 A. S. Barnes; 261 p.; c1867.

1868-71 A. S. Barnes; 288p.; appendices added to previous; c1867.

First Edition—*Fourteen Weeks in Chemistry*

1871-79 A. S. Barnes; same contents as previous; 288 p.; c1868; ads for this edition continued in 1873-1879 editions below.

Second Edition—*Fourteen Weeks in Chemistry*—(all c1873)—about 25% rewritten.

1873-76 A. S. Barnes; 312 p.; dates on title page.

< 1879 A. S. Barnes; 312 p.; no date on title page; Steele’s *Botany* (1879) not in ad.

> 1879 A. S. Barnes; 312 p.; no date on title page; Steele’s *Botany* (1879) is in ad.

> 1887 A. S. Barnes; 310 p.; no date on title page; Steele’s *Popular Chem.* (1887) is in ad.

~ 1890 Same as previous except American Book Co.

> 1895 Same as previous except c1895 by Mrs. Steele.

Third Edition—A Popular Chemistry—(all c1887)—no dates on title pages. (About 50% rewritten).

1887-90 A. S. Barnes; 329 p.

~1890 American Book Co. from press of A. S. Barnes; 329 p.

1890-97+ American Book Co.; 329 p.

Although his books were quite simple, Steele struggled with their production. He read every available work on each subject and agonized over the best way to condense the material. He remarked about one of his history books that he had "spent six months in sandpapering the manuscript" (11), and regarding his 1873 chemistry revision, he wrote (12):

My brain turns out its best product one when driven at high pressure, day after day. If I take things easy my sentences are dull, heavy and cumbersome. Only when my whole nervous system is on fire do my sentences sparkle and my style become lively and entertaining. Every paragraph, therefore, worth keeping or that at all satisfies me, takes just so much of my life force, and exhausts me to that extent. A good sentence consumes something which meat and drink do not promptly supply . . . Then there is a vast amount of study in connection with my book work. Perfection comes from labor, and I expend much of it on my books. But I never grudge any pains or time given to revising, polishing, or verifying. It may sometimes seem of little account, yet it goes to make up the value of my books.

An honorary Ph.D. was conferred upon Steele in 1870 by the University of the State of New York. While none of his biographies mention another degree, his earlier books list "A.M." after his name. He was elected a Fellow of the Geological Society of London and a trustee of Syracuse University.

Steele was in frail health in his later years. He died on 25 May 1886 at Elmira, NY at the age of 50. A deeply religious man, he frequently referred to Divine creation in his science books and endowed a chair of "Theistic Science" at Syracuse University. His beloved wife, Esther Baker Steele, directed that his gravestone read: His true monument stands in the hearts of thousands of American youth, led by him to "look through Nature up to Nature's God." Mrs. Steele also contributed to the "Steele Memorial Library" in Elmira and the "Esther Baker Steele Hall of Physics" at Syracuse University.

REFERENCES AND NOTES

1. F. W. Clarke, *A Report on the Teaching of Chemistry and Physics in the United States*, Circulars of the Bureau of Education, No. 6, 1880, Washington, DC, 1881, pp. 170-175.
2. Mrs. George Archibald (pseudonym of Anna C. Palmer), *Joel Dorman Steele. Teacher and Author*, Barnes, New York, NY, 1900, pp. 190-215.
3. Reference 2 is the best biography of Steele. It not only contains a short autobiography by Steele himself, but reprints some of his addresses and correspondence. Other biographies are found in W. Miles, *American Chemists and Chemical Engineers*, American Chemical Society, Washington, DC, 1976, p. 454; D. Malone, Ed., *Dictionary of American Biography*, Scribner's, New York, NY, 1935-6, Vol. IX, Part 1, p. 556; *The National Encyclopedia of American Biography*, White, New York, NY, 1893, Vol. III, p. 265; J. Wilson, Ed., *Appleton's Encyclopedia of American Biography*, Appleton, New York, NY, 1888, Vol. V, p. 660.
4. Reference 2, p. xxxi.
5. J. D. Steele, *Fourteen Weeks in Chemistry*, Barnes, New York, NY, 1876, pp. vii and viii.
6. Reference 5, pp. 65, 77, 173, and 123.
7. Reference 2, p. xxxii. Little-known chemist Edward John Hallock was born in Peekskill, N Y in 1846. He received an A.B. degree in 1869 and an A.M. in 1872 from Columbia College School of Mines. He worked at the same school from 1871 to 1877 as Assistant in General Chemistry under Charles F. Chandler. He was among those attending the Joseph Priestley Centennial at Northumberland, PA in 1874. From 1872 to 1884, he wrote extensively in the *Boston Journal of Chemistry*. Hallock's "Qualitative Analysis for Beginners," which Steele appended to his text in 1873, was also serialized in the *Boston Journal of Chemistry* (Volumes 7 & 8, 1872-73). While studying in Europe in 1877-79, he sent frequent letters to this journal. He was awarded the Ph.D. at Heidelberg in 1878. He was Professor of Chemistry at Southern Medical College, Atlanta, GA in 1880-81 and was appointed Director of the Analytical Laboratory of the *Boston Journal of Chemistry* in 1881. He also contributed articles to *Popular Science Monthly* and other periodicals. He died 22 March 1884. (Biographical information from *Boston J. Chem.*, 1877, 12, 68-69, 172, 208-209; 1879, 13, 28, 40-41; 1880, 14, 28-29; 1881, 15, 7; 1884, 18, 71).
8. Around 1880 the appendix of the 1873 copyrighted, "New Nomenclature" edition was revised. Although the total number of pages remained unchanged, the "Qualitative Analysis" section was shortened and the "Directions for Experiments" section was enlarged and reset in smaller type.
9. Reference 2, p. 161.
10. "Book Reviews," *Science*, 1888, 12, 107.
11. Reference 2, p. 160.
12. Reference 2, p. 155-156.
13. This portrait of Steele was used as a frontispiece in all printings of his *A Popular Chemistry*.

GEORGES DARZENS (1867–1954): INVENTOR and ICONOCLAST

Pierre Laszlo, *École polytechnique*

Georges Darzen's name is absent from the *Dictionary of Scientific Biography*. This is a regrettable omission, on three grounds. He was a creative organic chemist, to whom we owe both the thionyl chloride conversion of alcohols into chlorides and the "Darzens reaction"—an addition-fragmentation which can be seen as the forerunner to the Wittig reaction. He was a perceptive observer of the scientific scene, keen on informing his students of the latest scientific developments during the first quarter of this century regarding the structure of the atom and the quantum theory of spectra. And this genuine Renaissance man, by his multi-faceted talents, by the diverse degrees he took, by his prolific academic and industrial activities, was also endowed with a remarkable independence of spirit. Thus, we offer here a summary of his life and work.

Early Years

Georges Auguste Darzens was born on 12 July 1867 in Moscow. His family came from the Aude region in Southern France. His father, Amable Rodolphe Darzens (1823–1886), settled in Moscow, following there cousins who probably came from France when Napoleon invaded Russia. The father was engaged in trade between the two countries.

Sent to Paris for his education at the age of 13, Georges Darzens became a boarder at Collège Sainte-Barbe. He prepared there for the competitive examination to the École polytechnique, where he studied (class of 1886) before becoming a professor (1913–1937). During his studies at the École, he was attracted to astronomy. However, this budding vocation was quashed when the medical staff diagnosed eyesight problems and gave Darzens glasses to correct them. At that time, un-

less a student completed the École polytechnique curriculum with a very high ranking (the first 15 or 20 would enter government service as high-level technical councilors), he would be inducted into the French Army. Most Polytechniciens became Army captains and served out life-long careers within the military. Not so with Darzens—even though his final rank was 39th out of a class of 226, his poor eyesight spared him from an Army commission.

Turned away from astronomy, Darzens embraced chemistry. His mentor at the École polytechnique, Édouard Grimaux (1835–1900), was at the time of Darzens's studies (1886–1888) one of the few French organic chemists to disobey the decree of Marcelin Berthelot against teaching atomic theory. As Darzens would later write, "These atomistic theories, renovated by [Adolphe] Wurtz and his school, were responsible for my entering organic chemistry" (1). During the period 1888–1897, Darzens served as an assistant to Grimaux in his laboratory at École polytechnique.

At that time, another former Polytechnicien became world-famous. Captain Alfred Dreyfus had been convicted of treason to his country and had been sentenced to Devil's Island in French Guyana. Grimaux and Darzens were both convinced of Dreyfus's innocence and they vigorously supported his cause. This took considerable courage in the military milieu at École—they were voices crying in the wilderness—and they suffered for their stand. Grimaux was even summarily dismissed from his chair.

The Renaissance Man

Conventional wisdom sees old age as a slow-motion disaster. Young adulthood, however, is seldom a success



Georges Darzens, in the uniform of a student at École polytechnique, in 1887

story. The person has yet to firmly grab a career; and elders offer resistance. The Darzens biography magnifies the former stereotype. This young man was splendidly unfocused. His unbridled energy was daunting. He was helping Grimaux as an assistant and he later became *répétiteur* at the École. During the last decade of the 19th century, Darzens continued to explore various careers. Already in possession of a B.S. degree in mathematics, and of another in physics, he studied for, and in 1895 also passed, the *agrégation* in physics. This certification exam would have allowed him, had he so chosen, to teach in secondary schools. As if he were not busy enough studying chemistry, mathematics, and physics, all at an advanced level, in 1890 Darzens also enrolled in medical school, receiving his M.D. in 1899. He doubled up, in much more than a consulting position, from 1897 on, as director of the research laboratory of the L. T. Piver perfumery company—a position that he held until 1920. Yet another avocation of

Darzens was physiological optics. As he later wrote (in the third person), “at the onset of his career, at a time when he was still undirected, he published (in 1895) a physical theory of the perception of colors by the eye” (2).

The Inventor

This was also the time of the birth of the automobile and Darzens launched himself into the new era with characteristic passion. While his brother, Rodolphe, was organizing the first car races (in which he also drove), Georges conceived, designed, and built three or four automobile prototypes in the period 1890–1910 (3). If Darzens was an inventor in his spare time, his inventiveness also marked him as a scientist. Following Vlado Prelog, one can classify scientists into four sub-groups: improvers of the state of knowledge; providers of general explanations for sets of facts; authors of discoveries; and inventors. Darzens clearly belongs with the last.

His chemical inventions include a general method for $-OH$ to $-Cl$ substitution, which Darzens himself described thus (2):

... in order to prepare the α -chloropropionic ester, he has devised a novel procedure for substituting chlorine for the hydroxy group in a molecule. This procedure uses the action of thionyl chloride [$SOCl_2$] in the presence of a tertiary (amine) base. It has been put to universal use for performing such a substitution in fragile molecules such as terpene alcohols and sterols.

His inventive talent is also obvious from his contributions to the composition of perfumes and from his involvement in the development of explosives during the First World War (4). Appointed to Service des Poudres on 31 October 1914, Darzens immediately improvised a makeshift manufacturing process for making picric acid from aniline. This production was started at the end of 1914. By the time of the Battle of the Marne, he was submitting numerous classified reports to the scientific commission for powders and explosives.

Darzens's main contribution to chemistry is the reaction that bears his name. It puts him in the first rank of French organic chemists during the first half of our century, along with such names as Victor Grignard (5). I can do no better than to let Darzens himself (without undue modesty) summarize his contribution (6):

As early as 1904, he set up the handsome method of glycidic synthesis of these two important classes of compounds, aldehydes and ketones. This method has become a classic and is in universal use. It bears his name.

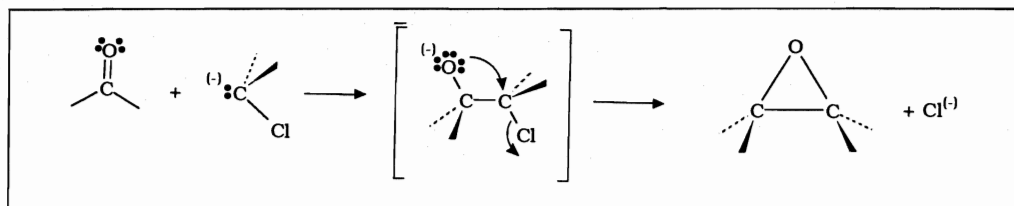


Figure 1 The Darzens reaction

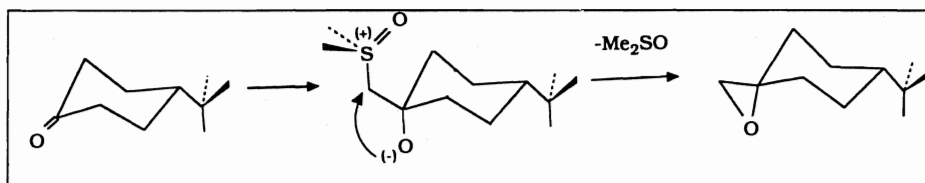


Figure 2 The Corey-Chakovsky reaction

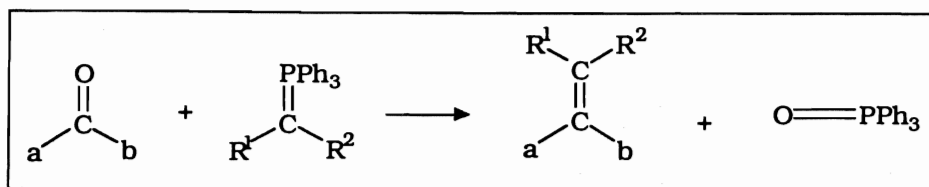


Figure 3 The Wittig reaction

This method consists in the condensation of α -chloro esters with ketones or with aldehydes under the action of sodium ethoxide or of sodium amide. In this manner one obtains glycidic esters that can be saponified easily into the corresponding acids. These are decomposed by a simple distillation into, depending upon the case, new homologous aldehydes or ketones. . . This glycidic method of synthesis, besides its exceptional generality, has led to preparation of the most diverse aldehydes and ketones in all fields of organic chemistry.

A continuous thread connects this reaction with other, more recent, name reactions. The Darzens reaction is an addition-fragmentation (Fig. 1). Among its other merits, it gives ready access to those activated and extremely useful intermediates—the epoxides. The first step is addition to a carbonyl of a chlorine-bearing carbanion. The second step is internal displacement of chloride ion by the back-side attack of the charged oxygen nucleophile produced in the first step. An epoxide results. The Corey-Chaykovsky modification (Fig. 2) uses a carbanion $(^-)CR_1R_2X$ in which the X leaving group is a stable, neutral entity—either dimethyl sulfide or dimethyl sulfoxide. Epoxides are also produced, and in a highly stereoselective manner. The Wittig reaction (Fig. 3) adds a phosphorus ylid to a carbonyl. While it

resembles in mechanism the Corey-Chaykovsky procedure, the Wittig reaction differs from it, because of both kinetic and thermodynamic factors, in producing an olefin (together with a phosphine oxide as the side-product).

The Educator

Darzens was a keen follower of new developments, not only in chemistry but in science in general. To give an outstanding example of his percipience, while the Millikan determination of electronic charge was performed during the period 1909–1913, Darzens included it in his very first lectures at École polytechnique in 1913–1914. Likewise, in the 1930s, his course in general chemistry juxtaposed the Mendeleev periodic classification and the shell model of the atom borrowed from J. J. Thomson and N. Bohr.

This taste of Darzens for the new and daring in science was very helpful to his institution. Quantum mechanics entered the École very late, with the appointment of Louis Leprince-Ringuet to a chair in physics in 1936. Fortunately, during the whole period between the two World Wars, when the physics professor, Lafay,

was deaf to new ideas and silent on relativity and quantum theories, Darzens's general chemistry teaching went some way toward filling the void. He made his students aware of the new discoveries in atomic physics. From the very first pages of his lecture notes, the reader learned about electrons, X-rays, and Rutherford's nuclear model of the atom.

Was the organic chemistry course also ahead of its time? If framed in the classic mode, it does not compare badly with that given by J. B. Conant at Harvard. Darzens brings in not only natural products with pharmacological activity and applications to industrial chemistry, but also cites compounds of potential military use. One of his comments reads: "very toxic and easily flammable, some spontaneously—phosphines might find use as aggressive compounds in warfare."

Another merit of his lectures is their historical dimension. Thus Darzens pays homage—and this was rare at the time—to the pioneering work of the Russian genius Mikhail Vasilievich Lomonosov (7):

Systematic observation of the numerical relationships between the various chemical phenomena seems to have had as its precursor the Russian chemist and writer Michael Lomonosov (1711–1765). Not only does this scholar introduce the concepts of relationships, but also those of volumes, of pressures, and of temperatures. He applied mathematical methods to the study of chemistry. He even developed, using the example of nitre, a theory of crystal structure that makes him the first crystallographer.

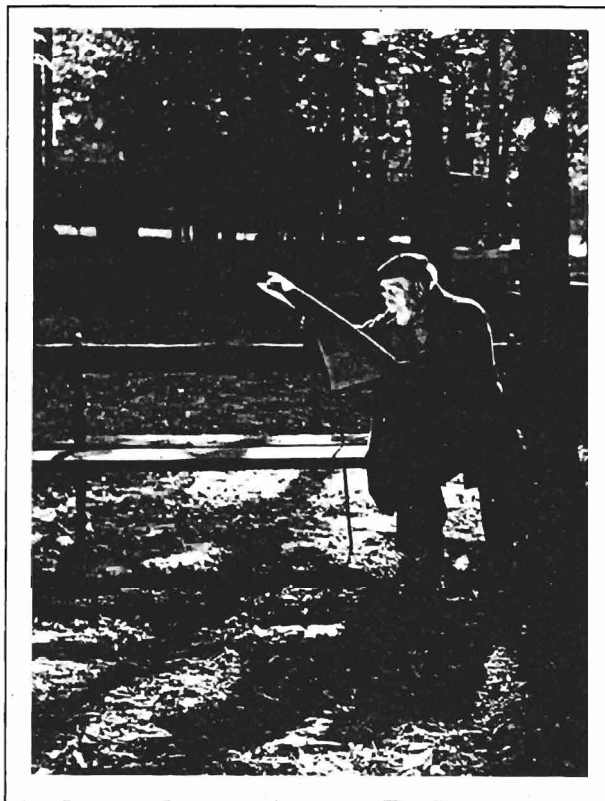
Darzens provided his students with a very modern presentation, not only relative to their outdated physics course, but also in an absolute sense. He was, for instance, very much interested in what we call "reaction mechanisms"—which he termed the "theory of a reaction."

The Nonconformist

Darzens had considerable self-assurance. While still a *répétiteur* at École polytechnique, he published a booklet on chemistry for the layman (8). The subtitle, "A Textbook Estranged from Any Program," was characteristic of him. As we already noted from his behavior during the Dreyfus affair, Darzens was brave and did not hesitate to take other unpopular and lonely stands. At a time when France was bent on revenge on Germany for its rout during the Franco-Prussian War of 1870, and at a time when it was deemed antipatriotic, if not treasonous, to praise anything German, Darzens expressed his admiration for German chemistry. With Cassandra-like

lucidity, he was preoccupied by the economic and scientific advances of Germany as compared to those of France. He saw clearly that the vigorous health of the German chemical industry was rooted in a firm experimental basis (the laboratory training introduced by Liebig), in patent regulations that allowed protection of a new process (and not just the discovery of a new molecule, as in France), and in its methodical organization. There was at least one clash between the administration of the École and Darzens's publicly-expressed admiration for German chemistry during his first year of teaching; and the *directeur des études* had to tell him to be more circumspect (9). Apparently his unorthodox personal life and his militant Free-Masonry (he became a dignitary in one of the French branches), together with his other traits of independence, ensured that he was never elected to the French Academy of Sciences, to which he so obviously should have belonged.

Darzens retired from École polytechnique in 1939. In 1945, while he was attending a conference in Italy, his laboratory was taken away from him. His protest letter to the German general then heading the École is a valu-



Georges Darzens, after his retirement, in the Luxembourg Gardens, in Paris ca. 1940 (picture by Brassai)

able document for the historian, as Darzens uses it to summarize the highlights of his teaching career at the École. Despite this loss, he continued to address himself to chemical problems, publishing communications in *Comptes rendus de l'academie des sciences* until the early 1950s. During his last years, he continued to enjoy Parisian life, going to the Opéra and Opéra Comique, continuing to work on some of his pet projects outside chemistry (major scientific problems, such as the expansion of the Universe, a theory for lepra, and one for cancer), having a very active social life (he loved the company of people and especially that of women), and running a complex personal life. He died on 10 September 1954.

His Vision of Chemistry

Early in his career, Darzens—who wrote a handsome prose—proposed this metaphor (8):

The chemist appears to me in the guise of a traveller climbing on an endless mountain. Clouds mask the perspective. Glimpsed from afar, those trees, he fancies, are his goal; and those grandiose landscapes beyond which nothing is apparent. However, as soon as he gets there, as soon as he has traversed the fog, other horizons spring up beyond this first horizon. They are wrapped also in the same deceiving haze. And our chemist is infected with the crazy desire to progress yet further. He covets getting to a point where he alone will be left to admire the splendors now left behind him. Indeed his temerarious and haughty climb gives him so many wonders to look at that they enthrall him. He catches himself fantasizing about what may lie beyond and his intuition does not betray him.

This accurate report of the joy of discovery from an extremely creative scientist is worthy of the attention of psychologists.

Darzens made other extremely interesting statements about chemistry. He saw it as a science lying somewhere between the empirical and the mathematical (10):

Convinced that chemistry had much to gain from acquiring general methods to solve its numerous problems, that differ much more by their appearance than in their intimate nature, I developed the desire to devote myself to such a study. The reader will find out that most of my work aimed at establishing such general methods. *They are to chemists the equivalent of equations to mathematicians.* I have met with a degree of success.

This reflected his deep ambivalence towards organic chemistry. Sometimes he compared it to mathematics for its inner logic and for lending itself to formalization,

whereas, at other times, he put the accent on the unavoidable empiricism (11):

Its domain remains much more that of intuition than of rigorous deduction. Its practitioners need to become steeped in a peculiar form of knowledge. It is more akin to a "wisdom" than to a "science"; and it is acquired only through lengthy and almost physical intimacy with chemical substances. **HERE ONE THINKS WITH ONE'S HANDS** ought to be engraved on the entrance to all our laboratories.

Besides such insights into the nature of organic chemistry, Darzens had other incisive remarks, as when he noted that (10):

The greatest advances have occurred whenever a new inorganic reagent has been introduced in organic chemistry.

ACKNOWLEDGMENTS

This article has much benefited from a biographical essay written by Mr. Georges Darzens, Jr. (1900–1978), as well as from a letter of Mr. Claude Darzens to the author, 24 November 1987. I have also been able to take advantage of papers and mimeographed lecture notes in the archives of École polytechnique, for whose consultation I am indebted to Mrs. Francine Masson, chief librarian, and to her staff.

NOTES AND REFERENCES

1. G. Darzens, *Recherches et travaux scientifiques de M. Georges Darzens*, J. Dumoulin, Paris, 1912, (printed résumé presented by Darzens as a candidate to a chair in chemistry at École polytechnique).
2. "Note sur les travaux scientifiques de M. G. Darzens, "undated manuscript, c 1949, possibly prepared in support of yet another, aborted candidacy to the French Academy of Sciences, to which Darzens was never elected; kindly communicated to the author by Dr. Jean Jacques.
3. One of these designs led to a small series of six to ten vehicles. The innovations Darzens introduced were the lengthening of the ride of the pistons with respect to the "square" arrangement that had been the norm till then; the introduction of ball bearings in the hub of the wheel, that met with his friend Louis Renault's utter skepticism: "You are making a mistake! Roller bearings are no good, nothing beats a smooth hub;" and the equality of the sizes of the front and rear wheels.
4. While at Piver, he designed such classic perfumes as "Floramyne" and "Tréfle Incarnat." Later on, having moved to other companies, he continued formulating

successful perfumes at Grenoville (1921–1924) and at Dior (1926–1931). During the latter period, he started the manufacture of various synthetic nitro musks.

5. P. Laszlo, "Un grand Polytechnicien, Darzens (1867–1954)", *La Jaune et la Rouge*, 1988, 18–20.
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7. G. Darzens, *Cours de chimie générale*, École polytechnique, Paris, 1913–1914, p. 3.
8. G. Darzens, *Initiation chimique*, Hachette, Paris, 1912.
9. P. Laszlo, "Le Chatelier, Public Prosecutor of Darzens," *Ambix*, in press.
10. G. Darzens, *Cours de chimie générale*, École polytechnique, Paris, 1919–1920 (emphasis added).
11. G. Darzens, *Cours de chimie organique*, École polytechnique, Paris, 1937–1938, p. 11.

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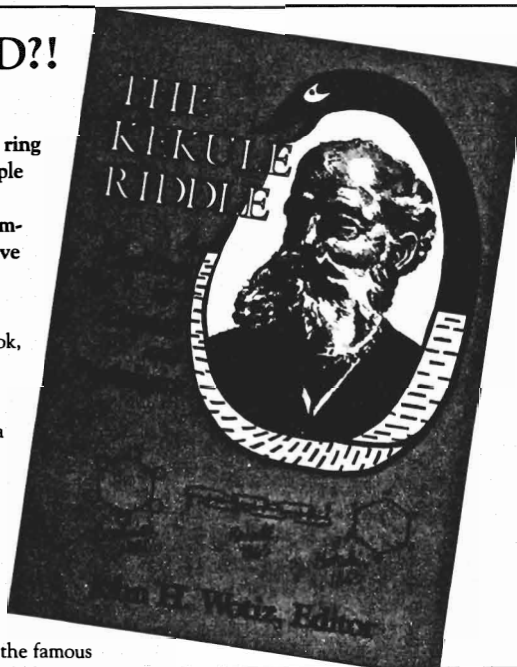
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