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NEW EDITOR FOR THE *BULLETIN*

Effective January 1, 2011, **Carmen J. Giunta** will assume the position of editor of the *Bulletin for the History of Chemistry*.

Paul R. Jones is the second editor who has served since 1995.

The founding editor, Dr. William B. Jensen, initiated the journal—only one of two English-language periodicals dedicated exclusively to the history of chemistry—in 1988, with the publication of issue "Number 1."

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HISTORY OF HIST. II. ON PROBATION (1, 2)

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Introduction

One of the more important results of the reorganization of the American Chemical Society (ACS) in 1890 was the advent of the national meeting, in which the society broke from its cocoon in New York City and spread its wings to envelop chemists throughout the country as active participants (3). Registration statistics for the last decade of the nineteenth century are meager, but it appears that no more than a few hundred people attended this usually biannual affair.

The growth of chemical activity in both academe and industry during that time led inevitably to specialization as chemists in general and the society in particular attempted to cope with a flood of new information. The first time papers at a national meeting were segregated by subject occurred at the World's Congress of Chemists in Chicago in 1893, when 76 presentations were arranged in nine different categories (4). Nevertheless, for the next ten years national meetings of the ACS consisted of single sessions, often with long general interest papers and what seems to be considerable emphasis on social events.

In 1903 the ACS Council appointed a committee to study the feasibility of forming divisions organized along technical lines. At its next meeting the Council rejected the committee's recommendations that five groups be formed (5). Yet at the next national meeting in Philadelphia in December, 1904, the large number of papers submitted required a new mechanism to fit them into the four-day period. For the first time the initial general session was followed by simultaneous sessions for papers in five specialties—physical, organic, inorganic, and industrial chemistry, plus a larger group that included agricultural, sanitary, and physiological chemistry (6).

Pressure was building on the society from another direction as well, however. A number of new organizations were being formed that focused on a specific area of chemistry, and many ACS members were joining these new societies (Fig. 1). In January, 1908, the ACS Council formed the ACS Division of Industrial Chemists and Chemical Engineers. By the end of that year there were four more divisions: agricultural and food chemistry, fertilizer chemistry, organic chemistry, and physical and inorganic chemistry. All of these groups had been loosely organized into what were called sections since the Philadelphia meeting and now were given a formal status (7). According to ACS Secretary Charles L. Parsons, "Each division has every advantage which can come to an entirely separate organization and enjoys likewise the great additional advantage which comes with union and strength in numbers, functioning independently and conducting their specialized affairs and programs with almost complete autonomy (8)." In fact, each division had "the right to elect their own officers, to draw up their own by-laws subject to approval of the Council. . .and to collect, control, and manage funds to be expended for their own purposes (8)." It was an obvious attempt at

Year	Society	Percent Charter Members also ACS
1902	[American] Electrochemical Society	29% (of 350)
1906	New York Section, Society of Chemical Industry	25% (of 3079)
1906	American Society of Biological Chemists	50%
1908	American Institute of Chemical Engineers ("many," including all officers)	

***Figure 1**. New Organizations Formed out of the ACS 1902–1908 (10)*

preventing more ACS members from bolting from the society and forming new specialty organizations.

By the time Edgar Fahs Smith and Charles A, Browne held the first HIST meeting under a shade tree on the campus of Northwestern University in August, 1921 (2), five more divisions had been added; and five more were in the required "probationary" period. Called "sections" rather than "divisions," these probationary groups had to hold "a sufficient number of successful meetings to prove the need for them" and thus be approved by the ACS Council (8). At the end of the second informal HIST meeting held in Rochester, NY in April, 1921, Smith rejected a suggestion to form a "Section of Historical Chemistry," preferring to "let things develop freely and spontaneously." Smith was convinced that there would be more interest developed in this manner rather than a formal schedule of papers as a section or division might arrange (2).

Preparing for the New York Meeting (Fall 1921)

That situation was soon to change. During the summer of 1921 Smith and Browne continued to correspond, exchanging photographs, books, autographs, and information about recent additions to their respective collections (9). In addition, they discussed the forthcoming ACS meeting in New York, at which a portrait of Priestley, copied from the original by Stuart, would be presented and subsequently be given to the National Museum in Washington. They were also concerned about the fate of the Priestley house in Northumberland, and Smith expressed the feeling that "I can't get it out of my head that the house ought to become the property of the American Chemical Society (10)." In late May Smith told Browne, "We must try hard to have a meeting of those interested in the history of science at the next general meeting of the Society in September. I fancy there will be a great many more attend than came the last time (11)."

Two months later Browne told Smith that his "announcement about our **historical section** has set me to thinking and last night I went over my papers to see what I could find of interest (12)." In view of the expected visitors from England, Browne solicited Smith's opinion about his discussing "the relations between Old England and New England in alchemy and chemistry," including the relations of Robert Boyle and others with George Starkey, John Winthrop, Robert Child, and Jonathan Brewster (12, 13).

Just a month before the New York meeting Smith told Browne that he "had a letter from Professor [Lyman C.] Newell of Boston, who tells me that he is coming to New York and hopes our little history section will meet, as he has some portraits and letters he would like to show (14)." Browne responded three days later, indicating that he would have a "twenty-minute paper subtitled 'A Sketch of Alchemy in Seventeenth- century New England' for the historical section, **if we meet**, and some photographs of old letters (15)." Smith responded somewhat petulantly, "Of course the History Group will meet. [Frank B.] Dains will be there. Newell is coming with letters and books, and [Wilder D.] Bancroft desires three minutes for the presentation of some ancient point. Adolph, a professor from China, is prepared to give us some points in early chemistry in that land (16)."

Evidently prompted by Browne's preparation of a paper, Smith sent Browne a short manuscript that he thought he would read "before our Section on the History of Chemistry." Titled "The First History of Chemistry in the English Language," it discussed the "Introductory Lecture" written by Thomas Cooper and published in Carlisle, PA in 1812. Smith claimed it was the "first history of science in our tongue, and written here in America." He asked Browne, "Do you think it will do (17)?" Browne assured him that "your contribution will, I am certain, interest everyone in our history section." He then indicated that he was bringing to New York photostatic copies of the early alchemy letters written in New England between 1630 and 1660, a copy of the earliest bill (1632) for chemicals and apparatus shipped to America, a copy of George Starkey's letter—the first chemical letter written by the graduate of an American college in 1646, a copy of one of Jonathan Brewster's manuscripts upon alchemy written in 1653, and copies of letters written by Sir Robert Boyle, Robert Child, and others (18).

In that same letter Browne committed a potentially egregious error by adding after his comment on Cooper's history, "There was a *Sketch of the Revolutions in Chemistry* published by T. P. Smith in Philadelphia in 1798. Have you ever seen this and does it deal at all with the history of chemistry?" Smith wrote back the very next day, although he kindly slipped his response to Browne's question between two other topics (19). "I have a copy of the *Revolutions in Chemistry* by Thomas P. Smith, and I had it reprinted in my book entitled *Chemistry in America* published by Appleton's in 1914 (20). I may bring the copy over." Somewhat sheepishly Browne confessed that "it is strange that I should have forgotten the account of Thomas P. Smith in your *Chemistry in America*, which has been constantly within arm's reach of my desk ever since it appeared in 1914. I immediately re-read your account of him; his oration on the *Revolutions in Chemistry* impressed me as a remarkable effort for a young man of 21 (21)."

Smith did compliment Browne, however, pointing out that "those are perfect treasures which you are going to show us in regard to the alchemists, and in my Address to the Society I am going to mention them as having been brought to light by you (22)." Smith then continued, "Shall we try to give our Section on the History of Chemistry more prominence? Do you think we could prevail upon Dr. [Charles] Herty to give us a page of his *Journal* in which to place such things as may interest American chemists in the history of Science? (18, 23)" Thus it is clear that in spite of Smith's remarks about not wanting a Section at the Rochester meeting, his exchanges with Browne during the summer of 1921 show that by the time of the New York meeting in September he had all but abandoned that feeling and was already talking about the group as a Section of the History of Chemistry (even though it did not formally exist), encouraging others to participate, and even thinking about getting items published in the Society's literature.

The New York Meeting (Spring 1921)

The 62nd national ACS meeting in New York was an elaborate affair that attracted 1557 registrants, the third largest in the Society's history to that date. It was billed as "Chemistry's Greatest Rally" because it was sandwiched in between two other important events. The British Society of Chemical Industry was meeting at McGill University in Montreal from August 29–31, after which the overseas delegation and many Canadian members visited Canadian chemical industry sites in Toronto and Ottawa before crossing the border to meet in joint session with the ACS on September 5–11. A special train carrying the foreign guests was met at the border by a delegation headed by the governor of New York and including Smith (as ACS president), Charles Chandler, Ira Remsen, Marston T, Bogert, and William H. Nichols. After tours of American chemical industry sites in Niagara Falls, the group traveled to Syracuse, where they were given a tour of the Solvay plant. From there they proceeded to Albany, and took a night boat down the Hudson to New York. After the ACS meeting closed on September 11, the Seventh National Chemical Exposition opened the next day at the East Coast Armory, thus providing a complete package of chemical activities (24).

The history of chemistry group is not mentioned in any of the advanced notices for the meeting's sessions, but registrants received a small 4 x 8.75 inch program that fit easily into a coat pocket. On page 2 there were several announcements, including one which said (25):

> History of Chemistry—President Edgar Fahs Smith and kindred spirits will meet Friday afternoon, September 9, in Room 301, Mines, to discuss their hobbies.

Friday was the last day of the official meeting, with Saturday scheduled for "golf and tea" and Sunday a "boat trip and tea." As at Rochester (2), Smith tacked this session on to the end of the meeting and in fact did not specify a time. But it was shrewdly scheduled to follow the inaugural meeting of the Section of Chemical Education (CHED), which Smith had organized (26). Since Smith chaired the CHED session, it must have been easy for him to segue into the history session. More than 100 people, swelled by CHED attendees, assembled into the little crowded room at Columbia to hear Smith and others "discuss their hobbies," undoubtedly surprising but pleasing Smith and Browne.

There is no indication that Smith read his paper on Thomas Cooper, but he did start the program by talking about his favorite subject, Joseph Priestley, and "the benefits derived from a study of the history of … American chemists (27)." Lyman Newell explained methods for preserving letters and documents, and how the collecting of old portraits and books could be used in the teaching of the history of chemistry. Charles Browne did describe the history of alchemy in New England. In addition to these three who would become HIST stalwarts, other speakers included a Dr. Goldsmith, H. G. Byers of Cooper Union, Charles A. Doremus, a Dr. Adolph of Shanttung, Christian College, K. C. Pandya from India, and Ernest Cohen of the University of Utrecht (27).

At the conclusion of the session, which included an impressive display of old books, letters, autographs, and portraits, "several men spoke enthusiastically of the proposed plan of having regular meetings devoted to the history of chemistry. This meeting was an inspiration to those who were familiar with the history of chemistry and a revelation to many whose interest in this field was sincere but dormant." As a result of the large turnout and supportive response, steps were taken in New York officially to form a Section of the History of Chemistry (28). It seems to have been a lively session that must have ended late. For Smith it was a tiring day. Not only had he chaired two sessions that afternoon of the two groups he was instrumental in organizing, but he was scheduled to deliver his presidential and public address that evening at 8 P.M. (22).

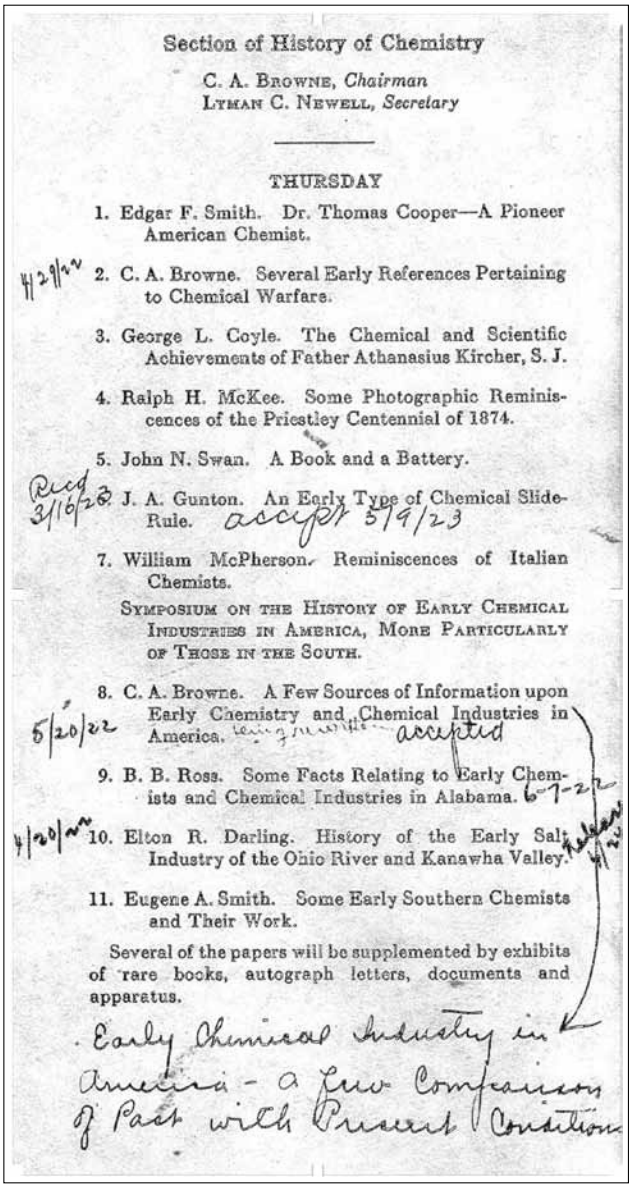
On to Birmingham

Five days after this meeting, Smith wrote Browne thanking him for what he "did for the group on the History of Chemistry (29)." Wondering if "we are not going to get a pretty big Section on the History of Chemistry," Smith noted that he had "just written Dr. Parsons that we wanted to have a definite period set aside for us at Birmingham and at Pittsburgh next Spring and Fall. Some of us will be there and we want to continue these conferences (29)."

The correspondence between Smith and Browne during the interval between the New York and Birmingham meetings continued at a steady pace. Smith promised Browne that he would "do everything to advance the meetings of the Section on the History of Chemistry" and encouraged Browne to "take up the very earliest chemistry of this country and develop it. Let it be your field (30)." It appears as if this were Smith's way of staking out territory for further investigation, because he intended "to work up individuals who lived and worked after the Revolutionary War (30)."

Smith was enamored of another project as well, telling Browne, "For some reason I can't free myself from the idea that we ought to have a Journal devoted to the interests of the history of chemistry. This idea is not prompted by any idea on my part to become an editor or anything of that kind. You and Newell could do that work, but I believe that maybe I could collect money for such [from] a foundation. When you continue to think of it, there are a good many sides to the history of chemistry here in America that need to be brought to light (31, 32)." That was a mantra Smith would espouse to anyone who would listen—that the new Section should focus on the history of chemistry in America.

In October Browne informed Smith that Dr. Ralph McKee of Columbia University had recently "dug up" seven of the old photographic negatives, 8 x 8 inches, that were taken at the Priestley Memorial Celebration in Northumberland in 1874 (33)." McKee took the plates to a photographer, who pronounced them all "practically



Section of History of Chemistry

C. A. Browne, *Chairman*
Lyman C. Newell, *Secretary*

THURSDAY

1. Edgar F. Smith. Dr. Thomas Cooper—A Pioneer American Chemist.
2. C. A. Browne. Several Early References Pertaining to Chemical Warfare.
3. George L. Coyle. The Chemical and Scientific Achievements of Father Athanasius Kircher, S. J.
4. Ralph H. McKee. Some Photographic Reminiscences of the Priestley Centennial of 1874.
5. John N. Swan. A Book and a Battery.
6. J. A. Gunton. An Early Type of Chemical Slide-Rule.

Symposium on the History of Early Chemical Industries in America, More Particularly of Those in the South.

7. William McPherson. Reminiscences of Italian Chemists.
8. C. A. Browne. A Few Sources of Information upon Early Chemistry and Chemical Industries in America.
9. B. B. Ross. Some Facts Relating to Early Chemists and Chemical Industries in Alabama.
10. Elton R. Darling. History of the Early Salt Industry of the Ohio River and Kanawha Valley.
11. Eugene A. Smith. Some Early Southern Chemists and Their Work.

Several of the papers will be supplemented by exhibits of rare books, autograph letters, documents and apparatus.

***Figure 2**. Program of the first meeting of the Section of History of Chemistry, Birmingham AL, 1922. This is a photocopy of an original uncataloged program found in a closet at ACS headquarters by the author. Handwriting source is unknown but might be that of ACS Secretary Charles L. Parsons.*

as good as new" and was having prints made of them. Browne speculated that these old views might be of sufficient importance to interest many members of our Society. "I imagine that prints made from those plates could be sent to members who desire them at nominal cost (33, 34)."

Later that month Browne met with Arthur Lamb, editor of the *Journal of the American Chemical* Society, at the dedication of the new chemical laboratory at Dartmouth, discussing the possibility of "printing papers relating to historical chemistry in America. He believes very strongly that steps should be taken to do this in some way, either as monographs or possibly as journal articles (35)." Browne told the twenty-five chemistry professors at the dedication ceremonies about the wealth of historic materials relating to chemistry in this century, "and they were all anxious to have it studied and written up (35)." As a result of his conversation with Browne at Dartmouth, Lamb began taking an inventory of the early chemical apparatus at Harvard. Browne suggested to Smith that "the descriptions and photographs of early chemical apparatus in this country in college museums, in scientific institutions, and in private collections would make a very interesting monograph (36)."

***Figure 3**. Edgar Fahs Smith, University of Pennsylvania, Co-founder of HIST, at his desk with a portion of his collection in the history of chemistry in the background. Edgar Fahs Smith Collection, University of Pennsylvania Libraries*

Just six weeks before the Spring National ACS meeting in Birmingham, the first in which HIST would be on the formal program, Browne received a surprising letter from ACS Secretary Charles L. Parsons. As he related to Smith, "Dr. Parsons has just informed me, much to my surprise, of my appointment as chairman of the Section of Historical Chemistry (37). I regret greatly that you did [not] continue in this office, for without your fostering care this new section may not long survive (38)." Brief written accounts of the early days of HIST are not in agreement on this point, and the implication has always been that Browne was elected chairman at the New York meeting. This letter makes it clear that while it was decided to form a Section at the New York meeting, it was assumed Smith would be the chairman of the new group as he had chaired the informal meetings at Rochester and New York. Further, there was no election of Browne as chair as commonly assumed—he was appointed by Parsons many months after the New York meeting, certainly under Smith's direction as ACS president.

Having been ill with influenza, Browne now faced another dilemma, that of producing a program on such short notice. Complaining to Smith that "it is rather late in the day to begin on a program and as I am still very weak, it is not possible for me to do very much (38)." Nevertheless, Browne pledged "to do my best to assist Professor Newell in getting up some sort of a program (39)." Yet in the same letter he plunged ahead with his ideas. "It occurs to me that as we are meeting this time in Birmingham it might be well to have something on our program about the history of chemistry in the South (40). I might say something about John Clayton's old chemical tract on the "Observations of Virginia," written in 1688 to the Royal Society, in which there is much of historical interest. A brief history of the early indigo, turpentine, sugar, potash, salt and saltpeter industries of the South by various members of the Society might be given. A few remarks about old teachers of chemistry in the South might be interesting and in this connection I am wondering if you could talk about Dr. Thomas Cooper's relations with Southern villages, such as negotiations with Jefferson at the University of Virginia and his last years at Columbia in South Carolina (41). If you have any suggestions I would like to have them." Finally, Browne remembered that "some time ago Professor McKee told me he would like to speak of certain mementos of the Priestley Centennial in Northumberland at the next meeting of the historical section (38)."

In his reply Smith assured Browne that "nobody else was thought of for the Chairmanship of the Section on Chemical History than your good self (42)." In terms of the program, Smith counseled Browne, "Don't worry about papers. Ask McKee to present whatever

he wishes. I will have something on Dr. Cooper and some old books. You would do well if you would give a sketch of the earliest industries throughout the South, to which you have referred." Smith was also confident about the forthcoming Birmingham meeting, stating that "The Section is bound to go. There will be others there and I am sure we will have a very enjoyable and profitable meeting (42)."

The Chandler Medal

Prior to going to Birmingham, Browne attended the presentation of the Chandler Medal to Smith at the Faculty Club of Columbia University on the evening of March 3, 1922. While this was not a HIST event, the account of the affair Browne wrote in his journal is a fascinating snapshot of chemical history at several levels. (43)

> At the lecture room of Havemeyer, Smith delivered a most interesting address upon Dr. Samuel Latham Mitchell, who was Professor of Chemistry at Columbia from 1792 to 1831 (44). Dr. Smith spoke with his usual charming delivery and his address was warmly applauded. At the conclusion of his remarks the Chandler medal, which is presented each year to some recipient for worthy work in chemistry, was presented to Professor Smith by old Dr. Chandler himself (45). The picture of the aged scientist with his white hair and mustache, now in his 86th year, presenting the medal to Dr. Smith, who is in his 66th year, was a memorable one. They stood before the lecture room desk and after an impressive pause, Dr. Chandler said that he seemed almost an interloper on such an occasion as this.… Yet he rejoiced to hand the medal which bore his effigy to his old friend Dr. Smith and nothing gave him greater pleasure. Professor Smith in responding said that he and Dr. Chandler both studied under the same old master Wöhler in Göttingen, a name whom they both idolized and that to receive the medal from the hands of his old friend seemed the crowning event in their long friendship.

The Birmingham Meeting (Spring 1922)

The 63rd Annual Meeting of the ACS held in Birmingham on April 3–7, 1922, drew fewer than 400 registrants. The Divisional and Sectional meetings were planned to be held in the Sunday school rooms of the First Methodist Church, the first time a religious structure was used for a Society meeting. In an editorial in the *Journal of Industrial and Engineering Chemistry* it was noted that this arrangement was secured "after due consideration," but concluded that "the balance was swung in our favor by the fact that the church authorities recognize the efforts of chemists to ascertain the truth (46)."

For the first time the "History of Chemistry" Section was listed on the official program, along with nine divisions and three other sections (47). Browne and Newell put together a very respectable program of eleven papers, including four papers in the very first HIST symposium on the "History of Early Chemical Industries in America, More Particularly of Those in the South (48)." Over 100 people attended the session, which is quite remarkable since it accounts for more than twenty-five percent of the total registration, and it was scheduled for the last afternoon of the meeting (Thursday). It was probably one of the largest sessions of the entire meeting and a proud inaugural for a brand new section. Smith was serving his second consecutive year as ACS president and was still Chairman of CHED, whose members had met all day on Wednesday and Thursday morning. According to Browne's official reports (49, 50), Smith opened the session with "an entertaining address upon the life and work of Dr. Thomas Cooper." He was followed by Rev. George L. Coyle, who discussed the work of Father Athanasius Kircher, a seventeenth-century scientist noted for his opposition to alchemy. Ralph McKee described the photographs of the Priestley Centennial at Northumberland and Browne exhibited the photographs. John N. Swan displayed an early battery used by Sir Humphrey Davy and spoke about Davy's electrolysis experiments. He was followed by J. A. Gunton, who showed an early chemical slide rule and described its origin and use. The general papers concluded with William McPherson, who "spoke entertainingly upon reminiscences of celebrated Italian chemists."

Browne led off his little symposium with a paper on the sources of information of early chemistry and chemical industries in America. He mentioned that one of the first pieces of chemical work performed in America "was an assay of silver ores by Spanish explorers in Arizona in 1598." He was followed by B. B. Ross, who discussed the early indigo, sugar, and other industries in the South. He said that the first plant for artificial refrigeration in the U.S. "was built by Dr. John Gorrie of Apalachicola, Florida," who patented the process in 1850. Ross also described the work of Professor John Darby at East Alabama College and exhibited a Berzelius alcohol lamp that he used. Elton R. Darling's paper covered the early salt industry of the Ohio River and Kanawha Valley. The symposium concluded with the reading of a paper by Dr. Eugene A. Smith, which covered the work of many early Southern chemists. Smith summed up

the program by "making a strong plea for historical chemical research in America in the different sections of the United States." Continuing the tradition established at the previous informal meetings, there was "an exhibit of rare books, letters, photographs, and apparatus" which proved to be very popular with the attendees (49, 50).

Browne's Personal Account of Birmingham

Detailed accounts of personal experiences at ACS meetings are rare. Browne was very loquacious about the Birmingham meeting in his private journal, probably because it was an historic occasion and the official birth of HIST. Because Browne's notes are in unpublished typescript form, it is of interest to review the HIST session again, reproducing here much of what Browne said about the Birmingham meeting (43) in his own words. What follows is a much more colorful account of Birmingham than the terse, sanitized versions Browne wrote for the ACS (49).

Figure 4. *Charles A. Browne, Edgar Fahs Smith Collection, University of Pennsylvania Libraries*

After paying his registration fee of $3.00 and securing his badge at the Tutwiler Hotel (where rooms could be had for $2.50 to $8.00), Browne ran into Smith and they "had a long chat in the hotel lobby." Smith talked about Thomas Cooper and his recent visit to Cooper's grandson, "a man of very irritable temper, who remarked to Professor Smith that he inherited his grandfather's "cantankerous nature." Smith again brought up the idea of a Journal of Historical Chemistry, but Browne "did not think over one percent of the membership had an interest in the historical side of the subject." Smith "admitted that only a few chemists were interested in historical chemistry (51)." They talked briefly about the Priestley House (52) before moving on to a proposed bibliography "of all the early American text-books upon chemistry." Smith said that E. J. Crane was compiling such a bibliography (53). Browne mentioned an early book by Thomas Ewell of Virginia published in 1806 (54) "as one of the earliest such texts," and Smith responded that he was familiar with the book and that Ewell, a graduate of the University of Pennsylvania Medical School, "was quite a character, being a man of strong pugnacious disposition."

Then Smith "said that his researches in historical chemistry were confined mostly to the personalities of the men who influenced American chemistry in the early days. The history of early chemical industries in America and of other phases of the subject he was willing to leave to me and other investigators," effectively making it clear to Browne how the research territory should be divided. The discussion ended with a complaint by Smith that the flooding of his laboratory by a careless student who left water running destroyed many of his valuable tungstic acid samples but more importantly had damaged some of his rare books and prints, an incident "that disturbed Smith a great deal."

On Wednesday Browne found himself in more discussions with Smith, who related in great detail his oral examination by Wöhler, and Browne responded with his own experiences (55). They agreed that qualitative analysis was "the very best preparation for a beginner of chemistry. It gave the student a training in observation and logical deduction such as could be obtained in no other way." Smith related an amusing story about J. L. Smith, the second president of the American Chemical Society, who "was lecturing to his class upon nitrogen. A visiting professor asked how he prepared such large quantities of the gas. Smith…told his visitor that what he saw in the cylinders was not nitrogen at all but carbon dioxide. It answered the purposes of his demonstrations just as well and the students were none the wiser."

That evening Smith complained to Browne that "he had been bothered all the day and evening by long distance calls from politicians in Philadelphia who were urging him to accept the Republican nomination for the Governorship of Pennsylvania. The four factions of the Republican party could not come to an agreement but were willing to compromise upon him as a candidate." Smith rejected the offer as "he knew better than any one what a terrible life a Governor of Pennsylvania had to lead," having been "the close personal friend of six governors…while he was Provost of the University of Pennsylvania." Browne countered with the opinion that it seemed "a unique opportunity for an American chemist to accomplish something in the way of public service." The next day Browne asked what the final disposition was, and Smith "laughed and said that he telephoned… his refusal to accept the nomination…." Smith intended "to be true to chemistry last as well as first," to which

Browne replied, "I'm glad for Chemistry but sorry for Pennsylvania."

The day of the HIST session Browne met "John N. Swan of the University of Mississippi who asked that he be allowed to give his paper for the historical section in the morning session before the Educational Section, as he wished to send back the exhibits on an early train by an assistant. I consented to this and went to the Educational meeting to hear his paper (56). He exhibited an old battery which had formerly been part of a series of cells that belonged to Sir Humphry Davy at the Royal Institution. This cell came afterwards into the possession of J. [John] Millington, who brought it to this country with other apparatus in 1848 when he accepted a professorship at the University of Mississippi (57)."

Chairing the First HIST Meeting

"I dropped into the meeting of the sugar chemists for a short time and then returned to my room to arrange the material for the meeting of the historical section which I called at 2:10. Two rooms had been thrown together on the lower floor of the Sunday Schoo1 building at the left of the entrance. The room to my surprise was quickly filled and over 100 chemists were present.

After calling the attention of the section to two recent works upon the history of chemistry, viz. Gunther's *Early Chemistry at Oxford* (58) and Lippmann's *Chronological Tables on the History of Organic Chemistry* (59), I introduced Professor Smith who spoke for an hour upon Dr. Thomas Cooper and his work as a pioneer chemist in America. It was a most interesting address and was delivered with all that charm of manner which characterizes the public speaking of Professor Smith. He spoke without notes or manuscript, and could have held his audience for another hour without difficulty.

The next speaker was Father Coyle (60), who read an interesting paper upon the chemical and scientific work of Father Athanasius Kircher. I passed around my old copy of Father Kircher's "Magnes" for inspection during the reading (61). Attention was called to Father Kircher's opposition to alchemy and to his having hinted at the bacterial cause of diseases and many other later discoveries. In the absence of Professor McKee, who was to talk upon some photographic reminiscences of the Priestley Centennial of 1874, I exhibited my set of the Centennial photographs and asked if any could recognize some of those we had not identified, that the names be marked upon the key. I read a letter of Professor S. P. Sharples which was written immediately after the Centennial meeting (49).

Dr. J. A. Gunton next exhibited an early chemical slide rule, of which he gave an account and description of its use. The next speaker was Professor Wm. McPherson of Ohio State University. Professor McPherson said his subject of Italian chemists was so foreign to 'Chemistry in America,' the main theme of the meeting, that he thought it a pity to spoil the continuity of the program and offered to withdraw. I thanked him for the courtesy but remarked that a slight break in this continuity might be a welcome change and invited him to speak if only for 15 minutes. He thereupon gave a short delightful talk upon a few of the great Italians, such as Avogadro, Cannizzaro, Ciamician, and others who have influenced chemistry.

In opening the symposium on the history of early chemical industries in America, I remarked that while quantitative chemical control in American chemical industries did not begin until after the Civil War (the time when quantitative analysis first began to be taught in American colleges), yet there were many industries which we now call chemical that went back to the earliest colonial times. I then told of the work which the Spaniards did upon the assaying of silver ores in New Mexico and Arizona in 1598, according to the unpublished records in the Spanish archives of which I read the manuscript in the Library of Congress the previous Saturday. With this introduction I read my paper upon 'Early Chemistry and Chemical Industries in America,' which I supplemented with exhibits of books, photographs, Photostats, and old prints. At the conclusion of my paper President Smith spoke to the section upon the importance of investigating the early sources of information upon the history of chemistry in America. He alluded to my investigations upon the history of alchemy in America, which were presented at the New York meeting last September, and which he hoped might soon be published (62). He said this was work which every chemist of the country might undertake as chemistry in one form or another was pursued by the early colonists everywhere. President Smith made a warm plea upon the advantage of such historic studies and spoke of their importance in chemical education.

Professor B. B. Ross spoke next upon early chemists and chemical industries of the South. He spoke entertainingly upon the early sugar, turpentine, indigo, artificial ice, and other industries of the South; told of some early chemists such as Professor John Darby, and showed an alcohol Berzelius lamp which Professor Darby used, several scientific books which he wrote, and a bottle of

Prophylactic which he invented. The remarks of Professor Ross were listened to with great interest.

The final paper upon the program by Dr. Eugene A. Smith upon 'Some Early Southern Chemists and Their Work' was read in the absence of Dr. Smith by Professor Lloyd of the University of Alabama. It was now 6 o'clock and there being no further business the meeting adjourned. Everyone pronounced it one of the most interesting chemistry meetings which they had ever attended."

Birmingham Aftermath

At the banquet which followed at 7 P.M. the ACS Secretary, Dr. Charles Parsons, took some good-natured banter from different quarters, including Smith, who alluded to Parsons as our "great nitrate King." This came from the notoriety Parsons had acquired from newspaper accounts of his association with the Southern Nitrate Corporation. Smith had "applied this nickname to Dr. Parsons at the Council meeting, at the General meeting, and on other occasions, and when he sprang it again at the banquet Parsons manifested considerable displeasure. When he was later given the chance to defend himself, "Parsons proceeded to reproach President Smith for demoting him to the rank of a king. In the old days of his management of the office of Secretary of the Society he had been called a Czar and a Tyrant and now President Smith deliberately belittled him on every occasion with the common title of king."

A week after the Birmingham meeting Smith told Browne that the Section's meeting "was truly worthwhile" and asked if there would be anything in print from the session (63). Browne agreed that it was a "fine meeting" and ventured that "the side-line talks in the hotel lobby, the restaurants and in the excursions are in many ways the best part of these gatherings." Browne said he had submitted a brief write-up of the History Section to the *Journal of Industrial and Engineering Chemistry* (49) and was asked in return if any of the history papers might have a bearing on industrial chemistry. He thought Ross's paper on indigo was appropriate and that Ross had agreed to do it (64). Browne again followed Smith's train of thought, wondering "about the Journal of Historical Chemistry and wished some plan might be made to start such a publication (65)."

Editor Herty was very receptive to publishing HIST papers as Smith had earlier hoped. Two others from the session, one by Guyton (66) and the other by Browne (67), were subsequently published, an impressive four out of eleven papers given at the meeting.

Preparing for the Pittsburgh Meeting (Fall 1922)

In June Browne wrote to Smith that he had received an announcement from Charles Parsons that Smith had "reappointed me as Chairman of the Section." Browne continued, "I appreciate greatly the honor of the appointment and would proceed at once with Dr, Newell's help to solicit papers for our program except for the fact that I am so overcrowded with work at the laboratory (New York Sugar Trade Laboratory) this summer that it is very doubtful if I can do very much for the coming meeting or can even find it possible to attend. Mrs. Browne is also ill in the hospital and all my leisure time is spent with her. I think it would be better, therefore, under the circumstances, for someone else to be appointed chairman of the history section for the Pittsburgh meeting [which was only a few months away]. If I can attend the meeting I will do so and in case I find some time shall endeavor to prepare a paper (68)."

In Smith's reply he spent most of the letter expressing condolences and discussing gallstones. He did say that he would "get busy and write to some of our historical friends to see whether they will not be prepared with papers for the September meeting (69)." While the two continued corresponding through the rest of the summer to put together the Pittsburgh program, the subject of Browne's serving as chairman was never mentioned again.

Browne informed Smith in mid-July that Lyman Newell had suggested something on James C. Booth at the Pittsburgh meeting. Since Browne had recently visited J. E. Whitfield of "Booth, Garrett and Blair" in Philadelphia, he contacted Whitfield about giving a paper in Pittsburgh (70). Smith somewhat petulantly told Browne he had collected a lot of material on Booth and was going to be writing up his notes "in a day or two" but was going to contact Whitfield about his possible paper on Booth. "If he does not wish to do it, I can use my paper (71)." Smith was also contacting Frank Dains and Father Coyle, already HIST stalwarts, about presenting a paper, but obviously not giving them much time to prepare. A day later Smith wrote to express his frustration about dealing with Whitfield over the Booth matter and the refusal of a surviving daughter to meet with either of them (72). Browne, ever tactful, indicated he was happy to hear that Smith or Whitfield would talk about Booth (73). Browne noted how scarce information was about Booth and shared some information and sources with Smith. He then related an interesting story

told him by A. A. Breneman (74), whose laboratory was near Browne's on Water Street in New York (73):

> Dr. Booth was president of the American Chemical Society during the dark days of the eighties (75). The society had lost many members owing to the fact that the activities of the society were then too much localized in New York. Dr. Booth, although over 75 years old, made the trip to New York from Philadelphia to preside over the monthly meetings (unlike many of his predecessors). He usually came first to Breneman's laboratory where the chemists assembled. They would then go uptown to Siegortner's Restaurant in Lafayette Place for dinner and then walk across to Washington Square to the N. Y. University rooms for the meeting. I would give a great deal to have attended one of those meetings. I never saw Dr. Booth, but his picture hangs on my office wall.

Referring to a suggestion from Lyman Newell about HIST paying some attention to the history of metallurgy in America, Browne wrote to John A. Matthews, a metallurgist interested in history with an invitation to present at Pittsburgh. But Browne suggested caution to Smith, for "I think we ought to draw the industrial chemists into our section if possible, although I would not over-stress the industrial side (73)."

Figure 5. *Lyman C, Newell, Boston University, First Secretary of HIST. Edgar Fahs Smith Collection, University of Pennsylvania Libraries*

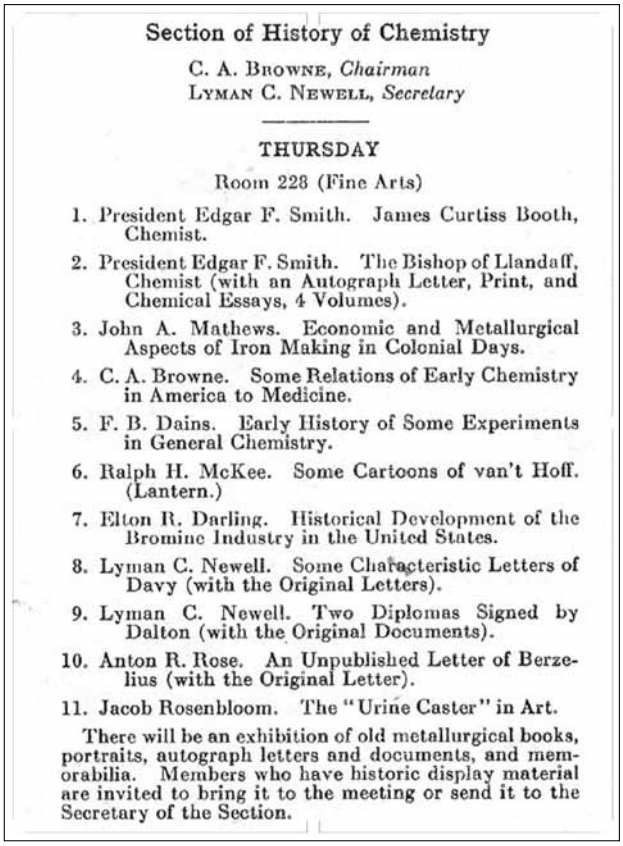
By the end of July Smith was optimistic "that it doesn't seem to me that there will be a dearth of papers. I imagine there will be some of the men from the south to talk to us. Each one of us can carry out to the meeting a book or some other historical object, so that the afternoon will be fully occupied (76)." Browne concurred, indicating that he had heard positively from several more speakers, and now that he had moved Mrs. Browne and their new daughter Caroline home from the hospital, "I shall have more leisure at evening" and promised a paper on the "Relations of early Chemistry in America to Medicine (77)." They were cutting it close: the Pittsburgh meeting was a little more than a month away.

The Pittsburgh Meeting (Fall 1922)

The 64th National Meeting of the ACS was held in Pittsburgh, PA, September 4–9, 1922, with general meetings held at the Carnegie Music Hall and the Divisional and Sectional Meetings at the Carnegie Institute of Technology. The meeting attracted more than 1,300 registrants with 453 papers given in 17 divisions and sections (78). (Among the highlights of the meeting was an all-day excursion to Donora, PA to view zinc roasting, the same process that killed 70 people in 1948 when an inversion layer trapped the smog from the smelters.)

It was stressed in an editorial in the *Journal of Industrial and Engineering Chemistry* that the "time has come when we must consider the desirability of establishing certain standards, for meeting papers, and make it something of an honor to be allowed to present a paper. Such a standardization will tend to reduce the number of papers presented, thus affording more time for discussion (79)." The ACS meeting stood in sharp contrast to European meetings, where each paper was followed by a "learned discussion…adding immensely to its interest and value (79)." Browne had lamented in his journal that he had no time for discussion at the Birmingham meeting.

As President of the Society, Smith gave his Presidential address at 9 P.M. on Wednesday evening, with an open invitation to the people of Pittsburgh to hear him talk about "Our Science." But it was Edwin E. Slossen, author of *Creative Chemistry*, whom Herty selected to reprint his address in the general session (80). Starting with noting that in 100 years chemistry had gone from being a toy to being a tool, Slosson proceeded to talk about "The Human Side of Chemistry." Just before the conclusion of his lengthy discourse Slosson remarked, "I am glad to see that you have already taken a step which will aid in the popularization of science by organizing a Section of the History of Chemistry." He



Section of History of Chemistry

C. A. Browne, *Chairman*
Lyman C. Newell, *Secretary*

THURSDAY

Room 228 (Fine Arts)

1. President Edgar F. Smith. James Curtiss Booth, Chemist.
2. President Edgar F. Smith. The Bishop of Llandaff, Chemist (with an Autograph Letter, Print, and Chemical Essays, 4 Volumes).
3. John A. Mathews. Economic and Metallurgical Aspects of Iron Making in Colonial Days.
4. C. A. Browne. Some Relations of Early Chemistry in America to Medicine.
5. F. B. Dains. Early History of Some Experiments in General Chemistry.
6. Ralph H. McKee. Some Cartoons of van't Hoff. (Lantern.)
7. Elton R. Darling. Historical Development of the Bromine Industry in the United States.
8. Lyman C. Newell. Some Characteristic Letters of Davy (with the Original Letters).
9. Lyman C. Newell. Two Diplomas Signed by Dalton (with the Original Documents).
10. Anton R. Rose. An Unpublished Letter of Berzelius (with the Original Letter).
11. Jacob Rosenbloom. The "Urine Caster" in Art.

There will be an exhibition of old metallurgical books, portraits, autograph letters and documents, and memorabilia. Members who have historic display material are invited to bring it to the meeting or send it to the Secretary of the Section.

Figure 6*. Program of the second meeting of the Section of History of Chemistry, Pittsburgh, PA, 1922. This is a photocopy of an original uncataloged program found in a closet at ACS headquarters by the author.*

also noted that in reducing science to a set of mathematical formulae and freeing it from all taint of time, place and personality, erratic history and "early gropings in the dark," one has eliminated the human element and thus eliminated the human interest.

HIST was again placed on the last day of the meeting and managed a full slate of eleven papers in spite of Browne's misgivings. In his journal entries for the meeting (81) Browne commented that on the opening day, Monday, September 4, "I met…Smith in the lobby of the…hotel [and] we retired to an obscure, quiet corner and had an hour's delightful chat upon our hobby, historical chemistry." They talked more about an historical journal which Smith was sure would happen with Browne as the editor. Browne demurred, claiming lack of "leisure time." The rest of the time was spent discussing the Spring 1923 National meeting at Yale, with Smith stressing the necessity of a strong HIST presence, especially because of Yale's chemical history and Benjamin Silliman's great influence on American chemistry.

On Thursday Browne and Smith took a cab to the Fine Arts Building, where "we went up to the third floor to our historical rooms and he placed his materials in the case with the other exhibits. He had a large mezzotint engraving of the Bishop of Llandaff, with an autograph letter of his and four volumes of his chemical essays (82). …. Professor Smith was much interested in our exhibit and thought that this feature should be continued at future meetings of the section (83). We talked over details of the exhibit and discussed historical chemistry until 9 o'clock, when the morning meetings began and Dr. Smith had to leave to conduct his educational section."

While secretary Newell provides a reasonably detailed account of the HIST session (Fig. 6) (84), it is again more instructive to see Browne's more personal account from his journal (81). "I called the meeting of the historical section to order at 2:05 P.M. President Smith spoke for 30 minutes upon the life and work of Dr. J. C. Booth (85) and for 15 minutes upon the life and work of the Bishop of Llandaff. After he finished he passed around a number of historical relics, among which was an old chemical manuscript recently discovered among some old papers in the library of the University of Pennsylvania. The manuscript seemed to be a source of lectures and contained many old chemical symbols, among which was that for phlogiston. It was probably written about 1780 or earlier.

"While President Smith was speaking, Dr. J. A. Mathews entered the room. I spoke with him for a minute. He said his paper was ready and he would speak next. He had not notified his local office that he was coming and they were, therefore, ignorant of his movements. Dr. Mathews spoke upon 'The Economic and Metallurgical Aspects of Iron Making in Colonial Days.' His address took 40 minutes and was warmly applauded. I expressed the hope that it would be printed in the Industrial Journal (86) .

"I followed with my paper upon 'Some Relations of Early Chemistry in America to Medicine,' which took 35 minutes. About 4 o'clock the room, which had been crowded with about 100 chemists with many standing outside, began to thin out. Some chemists had to catch trains, others wished to go to the afternoon lawn party and others to go to the lecture upon tomorrow's excursion. The excessive heat of the afternoon also caused many to leave. The next paper was a short 15-minute talk by Professor F. B. Dains upon the 'Early History of Some Experiments in General Chemistry.'

"At the end of Professor Dains' paper we moved our meeting to a room in the first floor which had just been vacated by the Educational Section, where there was a lantern. But before moving a gentleman from the University of Pittsburgh called our attention to a small exhibit of old books and documents which he had brought from the library.

"In our next meeting room Professor McKee showed us next some lantern views of some cartoons of Van 't Hoff which were greatly appreciated (87).

"Dr. Newell closed our program by showing us some interesting letters of Sir Humphry Davy and two diplomas signed by Dalton.

The other papers upon the list were presented briefly by abstract."

Pittsburgh Aftermath

"After finishing our program we held a short business meeting. Dr. C. L. Parsons, Secretary of the Society, thought the Educational and Historical Sections should hold joint meetings. I explained that this would mean the curtailment of the program as the Educational Section took usually four sessions to complete their work. Dr. Ellwood Hendrick was opposed to joint meetings and hoped the history section would continue as a separate organization. President Smith, Professor Coates, Dr, Newell, and others spoke to the same purpose. It was finally voted to meet as a separate section at the next New Haven meeting and our meeting adjourned at 5 o'clock (81)." The officers of the Section were reappointed and were already making arrangements for the New Haven meeting (84).

Newell's account (84) indicates all but one paper were given and omitted mention only of the last paper by Jacob Rosenbloom. But according to Browne, three papers by Darling, Rose, and Rosenbloom were read by abstract only (89). Browne seems to have had better control of the session than he did in Birmingham but still had to cut several papers (88). Yet by all accounts the meeting can be considered quite successful. It drew another large audience of more than 100 people in spite of the heat and a very poor place on the schedule. And it fended off an attempt to merge it with CHED by the powerful secretary of the society, which would have effectively put an end to HIST before it could ever mature (90).

As Herty remarked, "We all came away from the Pittsburgh Meeting impressed with the fact that the chemical profession is looking up, and confident that the American Chemical Society is able to undertake and carry through whatever is worthwhile for chemists and chemistry (79)." The officers of HIST, Charles A. Browne and Lyman C. Newell, under the watchful eye of Edgar Fahs Smith, enthusiastically said they were already preparing for the next meeting in New Haven.

HIST Meeting Number	ACS Meeting Number	Location	Date	Papers	Attendance	Comments
1	60	Chicago IL	6–10 Sept 1920	0	2	Informal meeting between Smith and Browne at Northwestern
2	61	Rochester NY	25–29 April 1921	16	20–50	"An informal section on the history of chemistry"
3	62	New York, NY	6–10 Sept 1921	10	>100	A "symposium" on the history of chemistry following the program of the Section of Chemical Education
4	63	Birmingham AL	3–7 April 1922	11	>100	First HIST meeting as a duly recognized Section of the History of Chemistry of the ACS
5	64	Pittsburgh PA	4–8 Sept 1022	11	>100	First use of lantern slides at a HIST meeting

Figure 7. Summary of the first three years of HIST Activity.

REFERENCES AND NOTES

1. Presented in part at the 198th national meeting of the American Chemical Society, Miami Beach, FL, September 1989, HIST 11.
2. For the previous paper in this series see J. J. Bohning, "Looking Back: Eighty-Five Years of Chemists and Their History," *Bull. Hist. Chem.,* **2007,** *32*, 66–81. This paper contains the details of the founding of HIST as well as a concise summary of HIST activities over the ensuing years.
3. See J. J. Bohning, "The Continental Chemical Society," *Bull. Hist. Chem.*, **1990**, *No. 6*, 15–21 for the compromise that saved the American Chemical Society from the formation of a rival organization and led to the concept of national meetings held outside New York City. See also J. J. Bohning, "Fighting City Hall: The Role of Washington Chemists in the Nationalization of the American Chemical Society," 220th national meeting of the American Chemical Society, Washington, DC, August 2000, HIST 06.
4. J. J. Bohning, "A Center of Crystallization in a Molecular Mélange: The 1893 World's Congress of Chemists," *Bull. Hist. Chem.,* **1989**, *No. 3*, 16–21.
5. See C. A. Browne and M. E. Weeks, "A History of the American Chemical Society: Seventy-Five Eventful Years," American Chemical Society, Washington DC, 1952, Ch. VI, 68ff and references therein.
6. A detailed account of this meeting with abstracts of many of the papers appears in *Science*, **1905**, *21*, 252–263.
7. See Ref. 5, Chapter VII, pp 81ff, for details of the first formation of ACS Divisions.
8. See Ref. 5, Ch. XVII, pp 264–265.
9. Browne's papers are at the Library of Congress, LC Control No. mm 78014134. The 36,000 items are only loosely catalogued. In his correspondence with Smith, Browne kept Smith's original plus a carbon of his reply, thus providing a reasonably complete picture of their exchange. All quotations of the Smith-Browne correspondence are taken from letters found in this collection. Smith's papers are at the University of Pennsylvania (see http://ead.library.upenn.edu/cgi/f/findaid/findaid-dx?type=simple;c=findaid;view=text;subview=fulltext;q1=annenberg%20rare%20book;id=PAURMsColl112, accessed 22 June 2010).
10. Smith to Browne, July 22, 1921 (9).
11. Smith to Browne, May 28, 1921 (9).
12. Browne to Smith, July 27, 1921 (9). It is unclear what "announcement" Browne is referring to.
13. The British Society of Chemical Industry was meeting first at McGill University before traveling to New York to have a joint meeting with the ACS.
14. Smith to Browne, August 6, 1921 (9).
15. Browne to Smith, August 9, 1921 (9).
16. Smith to Browne, August 10, 1921 (9).
17. Smith to Browne, August 19, 1921 (9).
18. Browne to Smith, August 22, 1921 (9).
19. Smith to Browne, August 23, 1921 (9).
20. E. F. Smith, *Chemistry in America*, D. Appleton & Co., Philadelphia, PA, 1914.
21. Browne to Smith, August 24, 1921 (9).
22. In the 1920s ACS meeting news was scattered in three publications: *Proceedings of the American Chemical Society*, *Journal of Industrial and Engineering Chemistry*, and *Science*. Smith's address on "The Progress of Chemistry" does not appear in any of them, although it was published as a separate offprint. A copy is available in the Lehigh library, Call Number SC Trx 2830AJ. Smith did mention Browne's work as promised.
23. Herty was the editor of the *Journal of Industrial and Engineering Chemistry*.
24. See "Program of Papers," *J. Ind. Eng. Chem.*, **1921,** *13*, 951–955 and "Reports of Meetings of Divisions and Sections," *J. Ind. Eng. Chem.*, **1921**, *13*, 956–960. For additional information about the meeting, see *J. Ind. Eng. Chem.*, **1921**, *13*, 667, 733–737, 750, 752, 844–848, 862–892.
25. A copy of the original is in the HIST archives at the Chemical Heritage Foundation.
26. For the events leading up to the formation of the Division of Chemical Education, see J. J. Bohning, "Crystallizing Classroom Chemists: From Isolated Disorder to Organized Interaction in the Teaching of Chemistry. A History of the Effort To Create a National Chemical Education Organization," *J. Chem. Educ.*, **2003**, *80*, 642–650.
27. J. C. Olsen, "The Meeting of the Section of Chemical Education," *J. Ind. Eng. Chem.*, **1921**, *13*, 1074–1076. A summary of the HIST session is given on p 1076.
28. L. C. Newell, "Historical Sketch of the Division of the History of Chemistry, American Chemical Society," *J. Chem. Educ.*, **1932**, *9*, 667–669.
29. Smith to Browne, September 14, 1921 (9).
30. Smith to Browne, September 21, 1921 (9).
31. Smith to Browne, September 16, 1921 (9).
32. Browne and Smith would continue to struggle with a mechanism for publishing historical chemistry for some time. For more details on the concept of a journal for the history of chemistry, see Ref. 2, pp 73-75.
33. Browne to Smith, October 21, 1921 (9).
34. Browne sent copies to Smith on November 2, 1921. Some of these pictures are also in the archives at The Pennsylvania State University. An article indicating the seven historic photographs were available for individual purchase appeared in *J. Ind. Eng. Chem.*, **1923**, *15*, 90–91. Three of these pictures were printed in Charles A. Browne, Ed., *A Half Century of Chemistry in America, 1876–1926*, as printed in a special issue of *J. Am. Chem. Soc.*, **1926**, *48*, 4,6,8.
35. Browne to Smith, November 2, 1921 (9).
36. Browne to Smith, November 10, 1921 (9).
37. Although Browne and Smith often use the term "Historical Chemistry," the official ACS name was "Section of the History of Chemistry."
38. Browne to Smith, February 25, 1922 (9).

39. Lyman Churchill Newell was a professor of organic chemistry at Boston University. Secretary of the Section, he was most likely appointed—not elected—by Parsons, as was Browne. For more on Newell, see W. D. Miles and R. F. Gould, *American Chemists and Chemical Engineers*, Gould Books, Guilford, CT, 1994, Vol. 2, 197 and references therein.
40. At least partly because of Browne's action, this concept of a regional chemical history based on the location of the national meeting would be a recurring theme for many HIST programs in the future.
41. Cooper was professor of chemistry and later president of the University of South Carolina in Columbia.
42. Smith to Browne, February 27, 1922 (9).
43. C. A. Browne, "Reminiscences of Professor Edgar Fahs Smith," original typescript in the Edgar Fahs Smith Collection, University of Pennsylvania Library, call number 540.92 Sm52B, 22–23,
44. The complete text of Smith's talk, "Samuel Latham Mitchell—A Father in American Chemistry," is in *J. Ind. Eng. Chem.*, **1922**, *14*, 556–559.
45. Smith was the sixth recipient of the Chandler Medal, which is still given by the Chemistry Department of Columbia University.
46. Details of the Birmingham meeting may be found in *J. Ind. Eng. Chem.*, **1922**, *14*, 83, 175, 238, 357–359, 449–460, and *Science*, **1922**, *56*, 21–30, 50–58. The printed 4 x 7.5 pocket-size program shows, however, that the meeting sessions were held at the Tutwiler Hotel and the Southern Club, contrary to the *Journal's* advance comments a month before the meeting about the Methodist church. Yet Browne's journal indicates the use of the Methodist church for the sessions (Ref. 45, p 28).
47. *J. Ind. Eng. Chem.*, **1922**, *14*, 450. The other probationary sections were Cellulose Chemistry, Chemical Education, and Petroleum Chemistry.
48. A searchable data base is being constructed that will contain every paper (and every symposium title) ever presented at a HIST Session, including the preliminary meetings at Rochester and New York in 1921. This is not a small undertaking and is being expanded as the various papers in this series on the history of HIST are written. There are currently 153 entries through 1927.
49. Browne's summary of the meeting is in *J. Ind. Eng. Chem.*, **1922**, *14*, 455, from which these quotes are taken. Although not on the program, Browne mentions that after McKee's presentation "a letter from S. P. Sharples was read describing the Centennial Meeting which resulted afterwards in the formation of the American Chemical Society." This is not an accurate statement, as shown in J. J. Bohning, "Opposition to the Formation of the American Chemical Society," *Bull. Hist. Chem.*, **2001**, *26*, 92–103 and **2002**, *27*, 46–47.
50. At this time abstracts of papers presented at ACS national meetings appeared in *Science*. Of all the speakers, only John A. Gunton submitted an abstract. See *Science*, **1922**, *56*, 52–53.
51. The full exchange between Browne and Smith on this matter is in C. A. Browne, "The Past and Future of the History of Chemistry Division," *J. Chem. Educ.*, **1937**, *14*, 461.
52. The relationship of Browne and Smith and HIST to the Priestley House is an interesting story, which would require a complete separate paper.
53. Crane was the editor of *Chemical Abstracts*. Crane and Austin M. Patterson published the first edition of *A Guide to the Literature of Chemistry* in 1927 (John Wiley and Sons, New York). Appendix 8, 353–411 is a select list of chemical books.
54. T. Ewell, *Plain Discourses on the Laws or Properties of Matter; Containing the Elements or Principles of Modern Chemistry*, Brisban and Brannan, New York, 1806. It did not appear in Crane and Patterson's list (Ref. 53).
55. The exchange is too lengthy to reproduce here but is interesting reading. See Ref. 45, pp 25–28. See also W. McPherson, "Some Experiences of Dr. Edgar Fahs Smith as a Student Under Wöhler," *J. Chem. Educ.*, **1928**, *5*, 1553–1557, based on a lengthy informal conversation between Smith and some HIST members in a hotel lobby at the ACS meeting in St. Louis in 1928.
56. The CHED session started at 9:30, and Swan was listed as the second speaker with the topic "Some Laboratory Helpers." It is assumed he replaced this with his HIST paper, "A Book and a Battery." In doing so, however, Swan deprived the 100 people at the HIST session from hearing his paper.
57. This equipment is still preserved in the Millington-Barnard Collection of Scientific Instruments in the University Museum at the University of Mississippi. Millington was hired in 1848, partly because of his equipment collection that could be used for instructional purposes. Most of the scientific apparatus was hidden from marauding Union forces during the Civil War and put back to use after the University reopened (Private Communication, University of Mississippi Museum). See http://www.olemiss.edu/depts/u_museum/Millington/index.htm (accessed June 25, 2010).
58. R. T. Gunther, *Early Science at Oxford*, Oxford University Press, London, 1920.
59. E. O. von Lippmann, *Zeittafeln Geschichte der organischen Chemie (Chronological Tables of the History of Organic Chemistry)*, Julius Springer, Berlin, 1921.
60. According to the official published program, Browne was scheduled to follow Smith with a paper on "Some Early References Pertaining to Chemical Warfare," but he makes no mention of it in his reports (49, 50). Browne admits that he did not have time for discussion after the papers (50), presumably because Smith rambled on for over an hour. (There are no starting times for the papers on the official program.) Trying to keep to some semblance of a schedule after Smith, Browne read his paper "by title" and moved on to the next paper by Coyle. The unread paper was quickly published in the July issue of

J. Ind. Eng. Chem., **1922**, *14*, 646. It was the first paper presented before HIST that was published.

61. A. Kircher, *Magnes sive, De arte magnetica opus tripartitum***,** Coloniae Agrippinae, Apud Jodocum Kalcoven, 1643.
62. Browne published two papers on alchemy in America, but neither is related to his presentation in New York. Instead, they were given at later HIST meetings in Baltimore (1925) and Milwaukee (1938).
63. Smith to Browne, April 15, 1922 (9).
64. B. B. Ross, "Some Early Notes on the Early Indigo Industry in the South," *J. Ind. Eng. Chem.*, **1922**, *14*, 1153–1154.
65. Browne to Smith, April 17, 1922 (9).
66. J, A, Gunton, "An Early type of Chemical Slide Rule," *J. Ind. Eng. Chem.*, **1923**, *15*, 747.
67. C. A. Browne, "Early Chemical Industry in America—A Few Comparisons of Past and Present Conditions," *J. Ind. Eng. Chem.*, 1**922**, *14*, 1066–1071.
68. Browne to Smith, June 21, 1922 (9).
69. Smith to Browne, July 13, 1922 (9).
70. Browne to Smith, July 15, 1922 (9),
71. Smith to Browne, July 17, 1922 (9).
72. Smith to Browne, July 18, 1922 (9).
73. Browne to Smith, July 19, 1922 (9).
74. Breneman was a consulting chemist with laboratories doing chemical analyses for profit. He had attended the meeting at the Priestley House in 1874 and was an editor of *J. Am. Chem. Soc.*, 1884–1893.
75. James Curtis Booth was president of the ACS in 1883, 1884, and 1885. He shared a common bond with Edgar Fahs Smith, who was the only other three-term president in 1895, 1921, and 1922.
76. Smith to Browne, July 21, 1922 (9).
77. Browne to Smith, July 25, 1922 (9).
78. Details of the Pittsburgh meeting may be found in *J. Ind. Eng. Chem.*, **1922**, *14*, 652–653, 742–743, 883, 885–893, 978–982 and *Science*, **1922**, *56*, 219, 138–140, 393–400.
79. Ref. 78, p 883.
80. Ref. 78, pp 887–893.
81. Ref. 45, pp 7–41.
82. R. Watson [the Bishop of Llandaff], *Chemical Essays*, London, Printed for J. Dodsley, et. al., 1782–1783, 4v, 2nd. ed., for example. There are multiple editions of this work, all of which are in the Smith Collection at the University of Pennsylvania, so it is impossible to tell which four volumes Smith brought with him to the meeting.
83. The practice of exhibits at HIST meetings continued for some time, then occurred very infrequently. Recent efforts to revive the exhibit concept have been unsuccessful.
84. Ref. 78, p 981.
85. Newell gives great detail of the contents of Smith's talk in Ref. 84.
86. There is no evidence this paper was published,
87. R. H. McKee, "Some Cartoons of van 't Hoff," *J. Ind. Eng. Chem.*, **1923,** *15*, 192–193.
88. No HIST abstracts were apparently published.
89. In these earlier ACS days programs were not nearly as rigorously scheduled as they currently are. No times were scheduled, and it was up to the chairman to keep things in order.
90. CHED and HIST have for the most part maintained a close relationship, in part because of the use of the history of chemistry in the teaching of chemistry (2). Joint sessions would indeed be held in the future, but HIST has always maintained its own identity.

ABOUT THE AUTHOR

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HENRY EYRING: QUANTUM CHEMISTRY, STATISTICAL MECHANICS, THEORY OF LIQUIDS, AND SIGNIFICANT STRUCTURE THEORY*

Douglas Henderson, Department of Chemistry and Biochemistry, Brigham Young University

Introduction

The author is pleased and honored to have a part in a symposium honoring Eyring that was part of an American Chemical Society Meeting in Salt Lake City in March, 2009. Earlier reminiscences and biographies, including one by Henry Eyring, the scientist, and one by his grandson, Henry J. Eyring, have been published earlier (1-6). Jan Hayes, the organizer of the symposium, pointed out that I am a coauthor of the last of Henry's publications. This is somewhat accidental as my book with him was the second edition of *Statistical Mechanics and Dynamics*, the first edition having appeared nearly twenty years earlier. Because of competing commitments, the production of the camera ready copy took five years. Had the preparation proceeded more quickly, I would not have occupied this position.

Recently, one of Henry's sons told me that Henry loved me. This is no great distinction as Henry thought positively of everyone. However, perhaps he loved some people more than others. He was a very warm and generous person. My parents were nervous when they were to meet such an eminent person. He immediately put them at ease. In any case, my truthful reply to his son was that I loved him. Henry treated me as an honorary son. The two scientists of whom I am most fond, Henry Eyring and John Barker, both treated me as an honorary family member. For this I am deeply grateful.

Early Years

Henry Eyring was grandson of Henry Eyring and Mary Brommeli, who came to America from Germany and Switzerland, respectively. His grandparents met as they traveled across the plains to Utah in 1860. They settled first in St. George in southern Utah and later were sent to northern Mexico to help establish a Mormon settlement. His grandfather was widely respected for his integrity. His grandmother spent some time in Berlin, where she

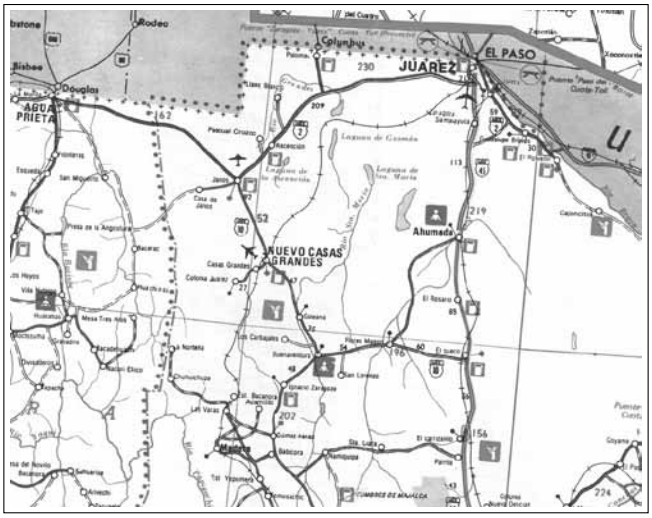

Figure 1. *Map of the region of Northern Mexico where Henry Eyring was born. Colonia Juarez is southwest of Nuevos Casas Grandes, at the end of a secondary road. Distances in Mexico are in kilometers.*

was jailed briefly because she refused to compromise her religious beliefs. His parents were Edward Eyring and Caroline Romney. Their son, Henry the scientist, was born in Colonia Juarez. Grandfather Henry Eyring owned a store, and his father, Edward Eyring, was a prosperous rancher with several hundred head of cattle. From this point, when I use the names, Henry Eyring and Henry, I refer to the grandson, the scientist.

Colonia Juarez is a small town located in the Mexican state of Chihuahua and is southwest of El Paso and southeast of the Arizona border crossings. A map of this region of Mexico is shown in Fig. 1. Several Mormon settlements were established in the late nineteenth century. Only two remain, Colonia Dublan and Colonia Juarez. The former does not appear on the map as it is now a suburb of Nuevos Casas Grandes.

The main industry of the region is fruit orchards. Today, Colonia Dublan / Nuevos Casas Grandes is the economic center of the region because there is more flat land and a railroad. However, Colonia Juarez is the religious/cultural center of the Mormon community and looks like a typical small town in Utah. The bilingual school, Academia Juarez, which Henry attended, is shown in Fig. 2 (a photograph taken by the author in 2007). It is in the foreground at the bottom of the hill. The building on the right dates back to Henry's time.

Henry lived in Colonia Juarez until 1912. Because of the turmoil of the Mexican Revolution, life became dangerous. The Eyring family and most, if not all, of the Mormons were evacuated by rail to El Paso. The expectation was that they would return soon, but the Eyring family decided not to return. The family settled in Arizona in considerably reduced circumstances. The family thought that Henry was an American by birth. It was not until the 1930s that he found that he was not. Thus, some of his most important and famous work was accomplished while he was a Mexican. It is reasonable to say that he is probably Mexico's most famous chemist.

Figure 2*. View from a hill overlooking Colonia Juarez*

Quantum Mechanics and Kinetics

Following the completion of B.S. and M.S. degrees at the University of Arizona and the Ph.D. at Berkeley in 1927, Henry spent two years engaged in teaching and research at the University of Wisconsin in Madison. In 1929 he was awarded a post doctoral fellowship to work at the Kaiser Wilhelm Institute in Dahlem in Berlin. Curiously, my parents lived in Dahlem for a time, as members of the diplomatic corps, while I was a doctoral student of Eyring. Eyring's original plan was to work with Bodenstein; but, perhaps fortunately, Bodenstein was away; and he collaborated with Michael Polanyi.

Quantum mechanics was in its infancy and there was much to be done. Quantum mechanics had not yet been applied to study reactions. Eyring and Polanyi (7) chose to study the simplest reaction, the replacement reaction, $H + H_2 \rightarrow H_2 + H$ by applying the Heitler-London method, including exchange. This was one of the first applications of quantum mechanics to obtain an energy surface for a reaction and, in my opinion, this was one of his most significant papers.

During his fifteen year tenure on the faculty at Princeton, where he stayed until 1946, Eyring produced many important results. He developed his famous reaction rate theory (8). A typical plot of the energy, say as calculated by the method of Eyring and Polanyi, that the reacting molecules must trace is plotted in Fig. 3. In this plot, the energy of the reactants is on the left and the energy of the products is on the right. As the incoming molecule approaches the molecule with which it will react, the energy increases. This energy barrier must be surmounted, rather like a hiker climbing up to and passing over a summit and then descending. The energy state of the products is on the right, and this energy state may be greater or lesser than or equal to that of the reactants. In Fig. 3, the products have a lower energy; this is irrelevant to our argument. The height of this barrier is $\Delta E^{\ddagger}$. As would a hiker, the constituents of the reaction may hesitate briefly at the pass. Eyring coined the name *activated complex* for this chemically unstable species at the top of the barrier.

The Boltzmann or Gibbs factor, $\exp(-E/RT)$, where R is the gas constant and T is the temperature, is

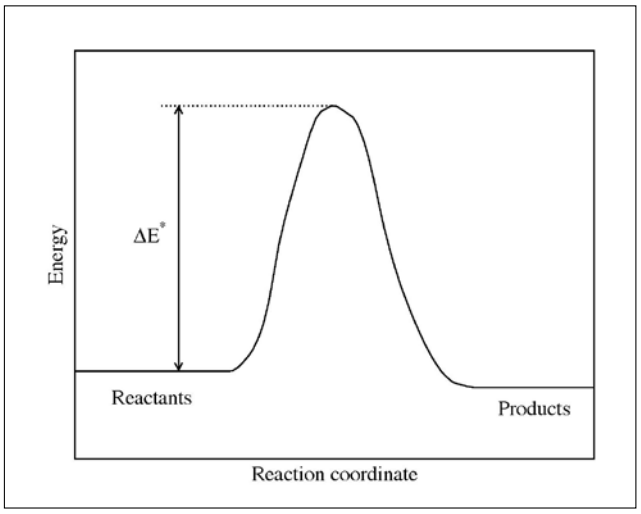

Figure 3*. The energy of a reaction along the reaction path. The zero point energy is included. The reactants are on the left and the products are on the right and are separated by an energy barrier of height* $\Delta E^{\ddagger}$ *. At the pass over which the reactants must traverse for the reaction to proceed, the reacting molecules form a transient complex that Eyring called an activated complex.*

fundamental in statistical mechanics. Thus, it is not surprising that such a factor is central in Eyring's famous rate equation. However, in the above form, the Boltzmann-Gibbs factor is appropriate for the canonical ensemble that is defined by volume and number of particles. In a reaction it is the pressure and chemical potential that are constant. Hence, it is the Gibbs free energy, G, rather than the energy, E, that should appear. The result that Eyring obtained for the reaction rate constant is

$$k' = \frac{kT}{h}\exp(-\Delta G^{\ddagger}/RT) \qquad (1)$$

where k is Boltzmann constant, the gas constant per molecule, and h is Planck's constant. The prefactor, kT/h, is formally the frequency of oscillation, v, of a soft spring that represents the mode of the activated complex that takes part in the reaction. This mode is soft, with a negative spring constant, because the activated complex is unstable. Using equipartition of energy, this frequency is given by $hv=kT$. A rigorous derivation of Eq. (1) is given in Laidler's text (9).

Of course, the reactants, on reaching the pass and forming an activated complex, may not cross the pass and form the products. They may fall back. Hence, it is often convenient to multiply the left hand side of Eq. (1) by a factor, k , that is called the transmission coefficient. Although there is no general method of calculating k, Eyring's rate theory has been very illuminating and has been used in a wide variety of chemical and biological applications. Eyring was awarded the National Medal of Science, the Berzelius Medal, the Wolf Prize, and many other prestigious awards for this work but, alas, not a Nobel Prize.

At Princeton, he started writing his famous book, *Quantum Chemistry* (10). This may have been the first book in English with this title. The writing took a decade. Eyring told me that Kimball and Walter never met. In any case, the book became a standard text and was translated into several languages. It was the book from which I first studied quantum mechanics. Of course, I had encountered quantum mechanics but not as the exclusive subject of a course. Not only is quantum mechanics covered in this book, but it is an excellent reference for special functions and group theory.

Theory of Liquids; Significant Structure Theory

In 1946, with his wife's encouragement, he accepted the position of Dean of the Graduate School at the University of Utah. The University of Utah, a long established institution, planned to inaugurate a doctoral program; Henry found the chance to help build this program an irresistible temptation. In this he was highly successful. The University of Utah has a very prestigious graduate program.

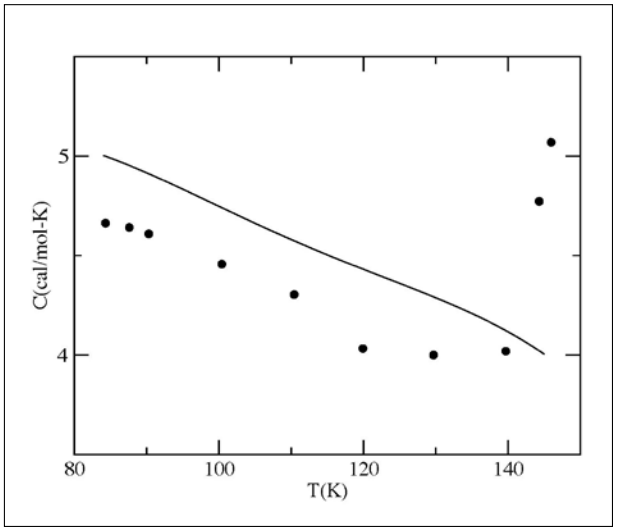

Figure 4*. Heat capacity of argon, as obtained from Eq. (3), compared with experiment.*

Earlier he had developed an interest in the theory of liquids. This, I assume, resulted from a desire to extend reaction rate theory from gas phase reactions to reactions in condensed phases. At the time it was thought that in contrast to gases and solids, there was no satisfactory theory of the liquid state. It is interesting that this is not true. The van der Waals theory did provide the basis of a satisfactory theory of liquids, but this was not understood until recently. In any case, until the 1960s the thinking was, since the density of a liquid is not too different from that of a solid, a theory of the solid state would be a promising starting point. Eyring, and others, developed the cell or lattice theory of liquids.

In reality this is a classical (as opposed to quantum) theory of a solid, due to the higher temperatures of most liquids. Eyring, and probably others, realized that the entropy of the cell theory lacked a factor of *Nk*. Eyring coined the term, *communal entropy*, and added the missing entropy arbitrarily. Although arbitrary, this is preferable to ignoring the issue and does give a liquid a different free energy from that of a solid. He went one step further and developed the idea that when a molecule evaporated, it left a hole or vacancy in the quasi-lattice of the liquid. Thus, for every molecule in the vapor phase, there would be a vacancy in the liquid that mirrored the gas molecule. If this were literally true the sum of the densities of the liquid and vapor would be a constant, equal to twice the critical density. This is not quite correct. The average density of the two phases is a linear function of the temperature but is not a constant and decreases somewhat as the temperature increases. Nonetheless, this reasoning provides a simple qualitative explanation of the law of rectilinear diameters.

He 'formalized' his reasoning into the *significant structure 'theory'* (11, 12) at Utah. Using the idea that a liquid is a mixture of molecules and vacancies that mimic the vapor molecules, the partition function, *Z*, could be written as

$$Z = Z_s^{V_s/V} Z_g^{(V-V_s)/V} \qquad (2)$$

where Z_s and Z_g are the partition functions of the solid and vapor phases, respectively, and V and V_s are the volumes of the liquid and solid phases, respectively. Eyring used the Einstein theory and ideal gas theory for Z_s and Z_g. The Einstein parameter, θ_E , and V_s are taken from experiment. The significant structure theory is a description rather than a theory. Conventionally, a theory in statistical mechanics relates the properties of a system to the forces between the molecules, whereas Eyring's description relates the properties of the liquid to those of the solid and vapor without obtaining either from the intermolecular forces. This said, Eyring by focusing on the volume as the important variable was on the right track and anticipated later developments, such as perturbation theory of liquids.

One consequence of Eq. (2) is that the heat capacity, *C*, of monatomic liquid, such as argon becomes

$$\frac{C}{Nk} = 3\frac{V_s}{V} + \frac{3}{2}\frac{V - V_s}{V}. \qquad (3)$$

since, for argon, *T* greatly exceeds θ_E. As is seen in Fig. 4, Eq. (3) gives a reasonably good description of the heat capacity. The heat capacity is a second derivative of the free energy and is difficult to obtain accurately from theory. The experimental heat capacity becomes infinite at the critical point. Equation (3) does not predict this. Much has been made of this failure. However, it should be kept in mind that no simple theory predicts the singularity of the heat capacity at the critical point. Some are less successful than Eq. (3). For example, the augmented van der Waals theory (a widely accepted theory) gives the prediction $C = 3Nk/2$ Later Eyring grafted the renormalization group approach onto Eq. (2) to obtain the singularity. However, I find this artificial.

I collaborated with him in his study of liquids by applying the significant structure theory to liquid hydrogen. I also assisted in the writing of the book, *Statistical Mechanics and Dynamics* by Eyring, myself, Betsy Stover, and Ted Eyring (13). This book was an outgrowth of the lecture notes prepared by one of his first students at Utah, Marilyn Alder. These notes were mimeographed and bound with a yellow cover and referred to by students as the *yellow peril*. The book was rather unusual in that the first chapter covered the field in an informal way, and then the material was repeated more formally in the subsequent chapters. Needless to say, significant structure theory was included in one of the chapters. This book was moderately successful. With Jost, he and I collaborated on a multi-volume treatise on physical chemistry.

During his final years, he became interested in cancer both because of his wife's illness and because of the cancer that ultimately took his own life. Betsy Stover came to him with the observation that the mortality curves of the experimental animals that had been exposed to radiation that caused them to die of bone cancer were strikingly similar to a Fermi-Dirac distri-

bution. This suggested to Eyring that this was similar to saturation in adsorption and the rate of mutation that was responsible for the cancer was proportional to the product of the fraction of normal cells multiplied by the fraction of mutated cells. He and Stover wrote several papers under the general title of the *Dynamics of Life*, based on this idea.

Summary

As I have mentioned Henry had a warm personality. At times, he became annoyed with someone (including me) but never held a grudge. Despite his accomplishments, he never felt he was better than someone else. I found him to be very kind.

Many people have conjectured about why he never won a Nobel Prize. Henry J. Eyring (Ref. 5) wonders whether it was because he left Princeton for Utah. Certainly his cheering section of prominent people would have been greater had he stayed at Princeton. However, one person at the University of Utah has won a Nobel Prize, so it is not impossible to win that distinction at a 'provincial' university. Others have wondered whether the fact that Henry was religious played a role. Perhaps it was due to Henry's intuitive style of research that was more fashionable in the 1930s than later. Peter Debye called Henry's style, "the inductive-deductive method." Henry's description was that his method of finding the path through the forest was first to cut down all the trees in the forest. My feeling is that his not being awarded a Nobel Prize is part of the uncertainties of life. He won many prizes. He would not have won them if the above considerations were a factor. The other prizes are equally important. In any case, he was beloved by all who knew him.

At Henry's funeral, Neal Maxwell, a friend and neighbor, former university colleague, and church leader, said that Henry taught us how to live well and how to die well—not a bad epitaph.

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ABOUT THE AUTHOR

Douglas Henderson obtained his Ph. D. at the University of Utah, under the direction of Henry Eyring, in 1961. He collaborated with Eyring on the writing of a book on statistical mechanics and in the editing of several other books. The bulk of his career was spent at the IBM Almaden Research Laboratory in San Jose, CA. Since 1995 he has been with the Department of Chemistry and Biochemistry of Brigham Young University, Provo, UT 84602, from which he retired in 2005. Email: *doug@chem.byu.edu*. In 1967 he helped develop the well-known perturbation theory of liquids. Subsequently, he worked on the theory of charged ions near charged electrodes and in physiological channels.

FINDING EKA-IODINE: DISCOVERY PRIORITY IN MODERN TIMES*

Brett F. Thornton, Department of Applied Environmental Science (ITM), Stockholm University, and Shawn C. Burdette, Department of Chemistry, University of Connecticut

Missing Members of the Periodic Table and the Discovery of the Heaviest Halogen

The International Union of Pure and Applied Chemistry (IUPAC) currently recognizes 111 elements for the modern periodic table (1). The discovery timeline for most of these elements can be traced clearly to a specific person or group; however, many elements discovered in modern times have a more nuanced history. Over fifty elements were discovered in the 19th century as advances in technology allowed many of Mendeleev's predictions to be proven, but the unexpected discovery of the noble gases and the difficulty placing the large numbers of rare earth elements on the periodic table cast doubt on periodic table dogma. This changed when H. G. J. Moseley's (1887-1915) measurements established that only seven elements—43, 61, 72, 75, 85, 87, 91—between hydrogen and uranium remained unknown at the start of the 20th century (2, 3). With few unknown elements remaining, the probability of discovering and naming a new member of the periodic table dropped drastically. Competing discoveries appeared for all of Moseley's "missing" elements, and the validity of some claims remained controversial for decades. The race to characterize element 85 provides perspective on how history often influences the course of and credit for scientific discovery.

Element 85, eka-iodine in Mendeleev's terminology, was chemically characterized in 1940 by postdoctoral researcher Dale R. Corson (b. 1914), graduate student Kenneth R. MacKenzie (1912-2002), and Emilio Gino Segrè (1905-1989). The three Lawrence Berkeley Laboratory (LBL) workers reported the results of bombarding a sample of bismuth (^{209}Bi) with 32 MeV α particles in the newly completed 60-inch cyclotron in Berkeley (4-7). Under these conditions, a radioactive sample with a half-life of 7.5 hours was formed, a phenomenon they attributed to ^{211}85. Unlike many reports of element discovery in the early 20th century, the LBL researchers were able to perform chemical analyses on and to track the radioactivity of the samples during the treatments (6). While Corson, MacKenzie, and Segrè are widely recognized as the discoverers of element 85 (8), through the 1920s several discoveries of eka-iodine were claimed, disputed, and refuted—some proclaimed that eka-iodine could not even exist. (Table 1).

Searching in Sand: Alabamine and Dekhine

Because families of elements possess similar physical properties, early investigators assumed that eka-iodine would have a low melting point, be diatomic in its elemental state, and form salts with metals. Since elements at heavier periods often resemble their n+1 and n-1 neighbors more than their lighter congeners, eka-iodine also was expected to be radioactive and metallic like polonium. Searching for eka-iodine in substances that contained other halogens was deemed a reasonable strategy for finding the missing element by early researchers.

Table 1: Reports on the Existence of Element 85

Researchers	Country	Date	Isotope	Technology	Source	Proposed Name	Name Derivation
Loring (58, 59)	UK	1922	None[a, b]	Numeric analysis	NA	-	-
Loring (60, 61)	UK	1925	NIS[b]	Cathodic X-ray determination	Pyrolusite	-	-
Hahn (62)	Germany	1926	None[b]	Chemical separation	^{228}Ra	-	-
Friend (63)	UK	1926	NIS[b]	Chemical separation & cathodic X-rays	Dead Sea water	-	-
Allison (11)	USA	1931	NIS	Magneto-optic[c]	Brazilian monazite and sea water	Alabamine	Alabama
Toshniwal (64)	British India	1933	NIS[b]	UV spectra	Iodine	-	-
De (16)	British India	1937	NIS	Chemical separation[d]	Travancore monazite	Dakin	Dacca
Anderson (65)	Denmark	1938	NIS	Chemical separation[e]	Various	-	-
Hulubei & Cachois (22, 23)	France	1936 1939	218	Decay X-rays	^{222}Rn	Dor	world peace
Loring (66)	UK	1939	None[a, b]	Numeric analysis	NA	-	-
Minder (34)	Switzerland	1940	218	α-particle detection[f]	^{222}Rn	Helvetium	Switzerland
Corson, Mackenzie & Segrè (5)	USA	1940	211	Cyclotron & α-particle detection	^{209}Bi + a	Astatine	Unstable
Valadares (30)	Portugal	1941	218	Decay X-rays	^{222}Rn	-	-
Minder & Leigh-Smith (35)	Switzerland & UK	1942	216	α-particle detection[g]	^{220}Rn	Anglo-helvetium	England & Switzerland
Karlik & Bernert (33)	Austria	1942	218	α-particle detection	^{222}Rn	Viennium	Vienna
Karlik & Bernert (36)	Austria	1943	216	α-particle detection[h]	^{220}Rn	Viennium	Vienna
Karlik & Bernert (38)	Austria	1943	215	α-particle detection	^{219}Rn	Viennium	Vienna
De (17)	British India	1947	NIS	Chemical separation[d]	Travancore monazite	Dekhine	Dakin & eka-iodine

NIS – no isotope specified

a. Authors claimed element 85 could not exist
b. Authors report not being able to isolate element 85
c. Magneto optical method was later discredited (12, 13).
d. Element 85 instability inconsistent with reported properties.
e. Assumption that element 85 would separate chemically like iodine was disproven by chemical tests on synthetic samples from Berkeley (5).
f. Disproved by Karlik and Bernert (32, 33).
g. Disproved by Karlik and Bernert (40, 67).
h. Disproved by Seaborg (68).

The first widely popularized claim of the existence of eka-iodine was reported by Fred Allison (1882-1974) at the Alabama Polytechnic Institute. Allison had developed a new method of analyzing materials, which he called the magneto-optic method (9). The technique relied on a time delay in the Faraday Effect, the rotation of plane-polarized light or other electromagnetic radiation passing through certain substances by an applied magnetic field. By rapidly switching the field on and off, he suggested that systematic patterns were observed because the time delay changed the position of the light passing through the analyte. Such a phenomenon would result in related substances giving a series of patterns that could be delineated even when contained in a single matrix. Allison examined typical halogen-containing compounds including sea water, hydrohalic acids, apatite, and Brazilian monazite sand, a source of rare earth minerals. In 1931, Allison's first paper describing eka-iodine was followed by a second article in 1932, where he suggested the name alabamine (Ab), derived from Alabama, for the new halogen (10, 11). He also described chemical tests on the alabamine, but its presence was determined exclusively by the magneto-optic effect. There is no time delay in the Faraday effect however (12), and in 1935, MacPherson demonstrated that Allison's observations were due to imperfections in the machine (13). So alabamine ceased to exist except on periodic tables and textbooks, where it remained well into the 1940s.

Rajendralal De, a little known Indian chemist working in Dacca (now Bangladesh, then British India), read about Allison's results prior to the revelation about the flawed methodology. De studied at the Kaiser Wilhelm Institute in Germany with Otto Hahn and Lise Meitner in the 1920s, when they had unsuccessfully looked for missing elements. Monazite sand such as Allison used in his research can be found in numerous locations around the world. The sand is occasionally found on beaches, such as in the Brazilian monazite which was used by Allison, or as Travancore monazite from the Travancore state in southwestern British India, which was studied by De. Like Allison, De believed monazite sand would contain substantial quantities of eka-iodine. He subjected the sand to a battery of chemical treatments and found a black, sublimable substance (14), which he identified as eka-iodine and named dakin (15, 16). Without access to an original copy of the 1937 pamphlet, De's reasoning for the name dakin cannot be deduced; however, it is probably named for Dacca, which sometimes is spelled Dhaka.

De published an update on his work in 1947 (17) and a review of his studies in 1962 (18). In his 1947 pamphlet, De proposed a revision to his original name. He recommended the name dekhine instead of his original suggestion of dakin. He argued that dekhine is evocative in sound to both dakin and eka-iodine. In his article, De describes in detail his method of purifying element 85 from Travancore monazite sand. De's description of eka-iodine is inconsistent with its chemical properties reported by the LBL group in 1940. Although he reports isolating milligram quantities, the intense radioactivity of even the longest-lived, 8-hours isotope of eka-iodine would have precluded De from safely handling the material. No other papers appear to cite De's 1947 pamphlet, and the only reference connecting De's 1947 pamphlet to any source is to Allison's discredited work.

Measuring X-rays Disrupted by Worldwide Conflict

World War I had ended before the search for element 85 commenced in earnest, but both World Wars had a significant influence on research efforts and the people intertwined in its discovery. When Romania entered World War I on the side of the Allies in 1916, a young Romanian, Horia Hulubei (1896-1972, Fig. 1) was selected to go to France and join the Aéronautique Militaire. Hulubei had studied physics and chemistry at the University of Jassy (Romania) until his country entered the war. Moving to France would have a profound impact on Hulubei's life and career. After the war Hulubei returned to Romania but was unable to continue his education until 1922 (19). After graduating from the University of Jassy in

Fiure 1. *Horia Hulubei*

1926, Hulubei returned to France to work for Nobel laureate Jean Baptiste Perrin (1870-1942). There they built a new X-ray laboratory at the Sorbonne (now University Paris VI). In 1928, Yvette Cauchois (1908-1999), who had recently graduated from the Sorbonne, began working in the same group (Fig. 2). As part of her 1933 doctoral thesis work, she constructed a new X-ray spectrograph. The instrument incorporated a curved crystal for splitting the high energy X-rays into a spectrum, which was then recorded on a photographic plate (20). This curved-crystal arrangement greatly improved the resolution of heavy-element spectra and reduced the energy losses in the spectrometer. The unique arrangement was later called the Cauchois spectrometer. The Cauchois arrangement allowed significantly weaker spectra to be studied, and Hulubei and Cauchois first used it to examine noble gases, which had previously eluded X-ray characterization. The Cauchois arrangement is still used for studying the hard X-ray and gamma regions.

Figure 2. *Yvette Cauchois*

In 1925 Rutherford and Wooster had demonstrated that a radioactive isotope of lead, then known as radium B (^{214}Pb), when not excited by an external source of electrons, produced the X-ray spectrum of bismuth (21). According to Rutherford, the X-ray emission occurs because the spontaneous transformation of ^{214}Pb into ^{214}Bi causes "a reorganisation of the external electrons," which is a similar effect to bombarding the sample with electrons. Rutherford and Wooster were able to show that ^{214}Bi produced the observed X-rays, not the parent isotope. With their improved spectrometer, Hulubei and Cauchois hoped to locate the emission lines of elements like eka-iodine that might be produced during the radioactive decay of radon, which resides in the adjacent slot of the periodic table.

Rather than follow the standard method of exciting a sample placed on the anode of a cathode ray tube, Hulubei and Cauchois placed a radon sample tube in the spectrometer and measured the characteristic X-rays produced when radon daughter elements formed via radioactive decay. In 1934 they described a study in a paper entitled "Nouvelle technique dans la spectrographie cristalline des rayons γ" (New techniques in the crystal spectrography with gamma rays) (22). In this article, which Perrin presented in October, 1934, Hulubei and Cauchois described the multiline spectra obtained from a ~150-250 mCi (millicurie) sample of radon after 12 hours of exposure. Although eka-iodine is not mentioned in the paper, Hulubei would later cite this publication as the first time they saw its spectral lines. In 1936, Hulubei and Cauchois reported observing a line at 151 X-units (or siegbahn, a unit equal to ~1.0021×10-13 meters) where the $K_{\alpha 1}$ line for eka-iodine should appear (23-26). These results convinced Hulubei that they might indeed be able to identify more elements produced during the decay of radon. Shortly after publication of the results, their work was delayed partly due to a temporary lack of radon sources. The rationale for finding eka-iodine in a tube filled with ^{222}Rn was based on nuclear decay to ^{218}Po, which had long been known to α-decay to ^{214}Pb, but the β-decay to eka-iodine was uncertain. Hulubei also considered ^{222}Rn β-decaying to ^{222}Fr, which might α-decay to ^{218}85.

Prior to the escalation of hostilities, prompted by Germany's invasion of Poland in September, 1939, Hulubei and Cauchois had reported observing X-ray wavelengths for three spectral lines of eka-iodine, $K_{\alpha 1}$, $L_{\alpha 1}$, and $L_{\beta 1}$ (Table 2), which closely correlated with Moseley's predicted positions (27). They used the technique they described in 1934, but started looking for new elements in the spectra and repeated the experiments with the spectrometer from Cauchois' thesis research that had a 40-cm radius curved mica crystal reflecting on the mica 201 plane. In addition the length of the exposure was increased to 24 hours to reveal more spectral lines. The radiation emitted by the radon source included lines of Po—and apparently 85—on the top part of the plate. The emission lines of Pb, Bi, and Po also were produced in the X-ray tube and appeared on the bottom of the plate; these lines were used as an internal standard (28).

Although Hulubei's and Cauchois' work would soon be disrupted by the war, Manuel Valadares (1904-1982), who was a student at the Sorbonne with Cauchois, performed some related studies on X-ray spectra of ^{222}Rn at the University of Lisbon in Portugal (29). Valadares had the advantage of a stronger source than his predecessors—600 mCi instead of ~100-200 mCi. Because

he worked in a slightly more limited wavelength range (700-1200 X-units, about 70-120 pm), he could not see the $K_{\alpha 1}$ line. He published his results in 1941, noting that they were suggestive of eka-iodine (30). During the war there was often little communication between scientists, and Hulubei only learned of Valadares' work when he visited Portugal in 1942.

Investigating α-Particles in an Occupied Country

In 1938 Germany annexed Austria, forcing many prominent Austrian scientists to flee the country; however, physicists Berta Karlik and Traude Bernert remained in Vienna to work at the Institute for Radium Research. Karlik (1904-1990) had obtained her Ph.D. from the University of Vienna in 1928; Bernert began working as a volunteer at the institute in the early 1940s (31). In early 1942, Karlik and Bernert (Fig. 3) reported detection of α particles in samples of ^{222}Rn, which they attributed to ^{218}85 because the energies they observed were in agreement with those predicted by the Geiger-Nuttall Rule, about 5.53 cm (32, 33). Karlik and Bernert, who began their studies during the war, were unaware of the creation of artificial eka-iodine in Berkeley when they published their first reports. They demonstrated that measurements of α-particles from ^{222}Rn by the Swiss physicist Walter Minder (1905-1992) and Alice Leigh-Smith, attributed to eka-iodine (34, 35), were likely in error because of contamination.

Figure 3. *Berta Karlik (right) and Traude Bernert.*

In 1943 and 1944 Karlik and Bernert, unaware of the ongoing work outside of German territory, were convinced they had identified an isotope of a new element (36-40). They next attempted to detect it in the radioactive decay of ^{220}Rn and ^{219}Rn. It was not until their later papers that they became aware of the Berkeley work (41). Nonetheless, the identification of eka-iodine within the natural decay series was a major goal, independent of the Berkeley group's synthesis of the element. Karlik and Bernert continued studying the formation of element 85 in the decay series, showing that the β-branching of radon to element 87, then α-decaying to 85, was at least a million times less common than α-decay of radon (40).

Geopolitics, Scientific Discovery, Resolution, and Nomenclature

All of the investigators involved in the search for eka-iodine were impacted by world politics and war. Segrè, who previously isolated element 43 with Carlo Perrier from cyclotron-exposed molybdenum (42), was forced to leave Italy because of anti-Semitic government policies and move permanently to Berkeley. Despite leaving his homeland, Segrè was fortunate to join the LBL, which was at the vanguard of nuclear chemistry in the 1940s. When Germany invaded France in 1940, Perrin, Hulubei's mentor and supporter, also was forced to leave France for the United States. In contrast, Cauchois, Hulubei, Karlick, and Bernert all remained in Europe. While Cauchois stayed in Paris during the occupation, Hulubei returned to the University of Bucharest, where he was named rector in 1941. Unfortunately, Hulubei's return to Romania created political problems for him in the immediate postwar years (19). After the Soviet Union occupation of Romania, Hulubei's earlier advancement at the University of Bucharest while Romania was a German ally led to accusations that he supported the Germany-allied Romanian government during the war. The intervention of French Nobel Laureate Jean-Frédéric Joliot-Curie was needed to clear his name (43).

In a 1944 article, Hulubei reported the April destruction of his laboratory from an American bombardment, but also provided a detailed summary of his X-ray studies and other researchers' work on eka-iodine (44). In the summary of his work with Cauchois, combined with Valadares' studies, Hulubei described six lines attributable to element 85, believed to be formed by the β-decay of ^{218}Po that appeared exactly where theory predicted (Table 2). He believed Karlik's work on α particles provided the strong corroborating evidence. In his review, Hulubei suggested the name dor for the new halogen, presumably derived from the Romanian word for "longing," as in longing for peace. He dedicated the work to Perrin, who died in exile in the United States two years earlier. Hulubei was writing in French, which does not include the "-ine" suffix, so the name presumably would have become dorine in English. The name

Table 2: X-ray Spectral Lines for Element 85 Observed by Hulubei, Cauchois, and Valadares

Spectral Line[a,b]	Observed (x units)	Observation Accuracy[c]	Observed (eV)	Calculated Value (eV)[d]	Possible Interferences[e]
$K_{\alpha 1}$	151	0.33%	81935.8	81520.0	-
$L_{\alpha 1}$	1082.6	0.05%	11428.3	11426.8	-
$L_{\beta 1}$	892	0.06%	13870.3	13876.0	Pt
$L_{\beta 3}$	917	0.05%	13492.2	13474.4	Br
$L_{\beta 4}$	880	0.06%	14059.5	14058.4	-
$L_{\beta 5}$	875	0.06%	14139.8	14164.4	Hg, Sr

a. Valadares' line designations are based on extrapolations from the Bearden compilation (69).

b. Hulubei and Cauchois reported the $K_{\alpha 1}$ line in 1936 (23, 24), and additionally the $L_{\alpha 1}$ and $L_{\beta 1}$ lines in 1939 (27). The other 3 lines were reported by Valadares in 1941 (30).

c. The error in the original data is based on Hulubei and Cauchois' reported ± 0.5 X-units. Note that the error is larger for shorter wavelengths.

d. $K_{\alpha 1}$, $L_{\alpha 1}$, $L_{\alpha 1}$ are calculated values from (69). The last 3 lines were extrapolated because values are not listed for these lines. We calculated the values by obtaining a linear fit to the reported values for Pb, Bi, and Po, and extrapolating a value for element 85. Interpolation would require using Po and Th, which may be less accurate than the extrapolation because of the large gap between values.

e. Interferences are lines of other elements, which would fall within the reported experimental error. Interferences would be more likely in studies using an external X-ray source and not when observing X-rays created by radioactive ay processes.

dor is also significant because it signaled a shift away from nationalistic names of elements, which had been popular since the late 1800s. The names of elements discovered since Mendeleev's predictions were rife with nationalistic pride: (e.g. gallium, germanium, rhenium, polonium, lutecium, and hafnium).

When World War II ended in Europe in 1945, questions began to emerge in the chemistry community about new elements. Some of the discoveries associated with the Manhattan Project, such as the indisputable existence of plutonium and other transuranium elements, presented the questions: were man-made elements comparable to classical elements, and was synthesizing an element equivalent to discovering an element in nature? The debate on these questions was particularly relevant to the question of discovery priority and the eventual sanctioning of a name for eka-iodine.

At a 1946 conference in Nice, Hulubei presented a summary of his work on element 85 as well as the work of others (45). When the paper was published the following year, Hulubei included a detailed discussion on the detection limits of the technique he and Cauchois had employed. He claimed that they could detect as few as 1,000-10,000 atoms of element 85, based on their experience with detecting ^{214}Bi in a matrix produced from ^{222}Rn. He contrasted their ability to do such sensitive qualitative detection with quantitative analysis techniques that required ~2.5 x 1011 atoms of heavy elements to reach the sensitivity limits of standard cathode ray tube X-ray techniques.

Friedrich Adolph Paneth (1887-1958), a respected Austrian chemist working in the United Kingdom after being forced to leave Austria, helped establish a new order in chemical nomenclature. In the early 20th century, many isotopes were given element-like names, and statements were often encountered stating that two "elements" were chemically inseparable. This practice was gradually abandoned, but the chemistry world was now confronted with the existence of man-made elements. On January 4, 1947, Paneth published an editorial on the process of naming new elements in *Nature* (46). In the article he described a procedure for deciding the names of elements in situations where more than one name had been proposed. He suggested that the first group to characterize the element reproducibly should be granted naming privileges. So masurium, the originally suggested name for element 43, was dismissed because of irreproducibility. Paneth insisted Segrè and Perrier were the rightful discoverers of element 43, and that the discovery of element 85 should be credited to the LBL group. He invited those groups and the group that found element 61 to propose names. In response to Paneth's request, a letter was published in the same issue of *Nature* proposing the name astatine for element 85, from the Greek word for unstable astatos (αστατος) (47). Unlike earlier reports of discovery, the LBL group had not suggested a name for the element in their previous papers because they were cognizant of

the failed alabamine claim. The lingering prominence of alabamine made them hesitant to suggest a name until the discovery was accepted (48).

Paneth noted that after the Berkeley group produced element 85 in the cyclotron in 1940, Karlik and Bernert showed that it exists in natural sources (46). He went on to state that "former claims were open to grave objections and were experimentally disproved by very careful work by the Vienna physicists." Although Paneth did not identify the specific former claims, those of Minder and Leigh-Smith were the only ones that Karlik and Bernert had disproved since they measured α particles and not X-rays in their studies (49). They had pointed out errors in Minder's work, but they had not reported any issues with Hulubei's and Cauchois' studies. Paneth had worked at Vienna before leaving Austria, and his polite words regarding Karlik and Bernert, who stayed behind, may have been due to his knowledge that Karlik strongly disliked German war policies. Paneth did not have a personal knowledge of Hulubei and Cauchois politics, so their residency and advancement in occupied Europe may have influenced his judgment. Paneth was influential in the discovery disputes with other elements (50). He supported fellow Austrian Auer von Welsbach's claim to have first obtained element 71 over Georges Urbain's claim, although today Urbain and von Welsbach are given credit for its discovery simultaneously. Lutetium, a modification of Urbain's suggestion, is the adopted name.

The statement that his work was disproved coupled with the simultaneous publication of a proposed name upset Hulubei. His 1946 presentation was not published yet, but he arranged to have a short appendix added before publication (45). In the appendix he indicated the oversight and politely attributed Paneth's omission of his X-ray work on element 85 to the difficulties caused by the war, a diplomatic statement since both Karlik and the Berkeley researchers cited Hulubei and Cauchois. He noted that Karlik had not refuted his work "contrary to what one would think after reading the exposé of Mr. Paneth." Hulubei and Cauchois appeared to have been slighted unjustly since Karlik had not conducted any X-ray studies, but Paneth's phrasing and lack of citations made it appear that Hulubei and Cauchois' work was definitively erroneous. Shortly after Paneth and Hulubei's papers were published, Karlik suggested in a summary paper that Hulubei and Cauchois' work was insufficient, due to the small amount of element 85 in their sample. Karlik estimated 6 x 10-16 g, or ~1,670,000 atoms in Hulubei's samples and suggested the possibility of interferences in the X-ray data (51); however she only cited one paper, and the criticism seems to be based on the detection limits of traditional cathode ray tube X-ray spectrometry, not the technique pioneered by Rutherford and Wooster (21). In 1949 at its meeting in Amsterdam, the International Union of Chemistry sanctioned the name astatine for element 85 (52). Paneth, who was the committee's chair, was able to convince the committee to adopt his previously outlined nomenclature practices. Statements released after the meeting detailed that certain names had been chosen over others; for instance, that the name astatine was preferred over alabamine, but none of the other suggested names for element 85 was mentioned.

After the apparent resolution of element 85's discovery, Hulubei went on to a distinguished career and helped to rebuild the post-war Romanian physics community. In 1949 the Institute of Physics of the Romanian Academy was established, Hulubei being named its first director. In 1956 the Institute was split, and Hulubei led the Institute of Atomic Physics until 1968. In 1996 the Institute of Physics and Nuclear Engineering (IFIN) was renamed the Horia Hulubei Institute of Physics and Nuclear Engineering (IFIN-HH), 24 years after his death. Cauchois remained active in the X-ray spectroscopy field throughout her career. From 1953 until her retirement in 1978, she directed the Laboratoire de Chemie Physique at the Sorbonne. She received numerous awards for her work during her career. Karlik also had a successful career in Austria, where she worked at the University of Vienna the rest of her life, leading the Radium Institute for almost 30 years. The Austrian Academy of Sciences awarded her its Haltinger prize in 1947 for discovering element 85 in the natural decay series, and in 1967 the Erwin Schrödinger Prize, partly for her work on element 85. She became the first female member of the Austrian Academy of Science in 1973. After leaving Berkeley, Dale Corson joined the faculty of Cornell University as a professor of physics and later served as the president and chancellor of the university. After working on the Manhattan Project in the 1940s, Emilio Segrè became a professor of physics at the University of California, Berkeley, where he remained until 1972. He returned to Italy in 1974 as professor of nuclear physics at the University of Rome, where he had started his career 40 years previously.

Epilogue: Ambiguity of Discovery

Corson, MacKenzie, and Segrè are recognized as the first to prove the existence of astatine, but can the early element hunters like Hulubei and Cauchois claim some

credit for the discovery of the element before 1940? Although the X-ray determination of elements was popular early in the 20th century, the minute quantities of the new elements produced in particle accelerators, nuclear reactors, and small tubes of radon gas during and after World War II were not amenable to detection with this technique. The studies conducted on astatine after the war utilized almost exclusively the characteristic α-particle radiations of the common artificial isotope ^{211}At, a variation on the technique of Karlik and the Berkeley group. Although Hulubei had claimed his technique could detect as few as 1,000-10,000 atoms of astatine and that he had ^{218}At, Paneth's unilateral dismissal of competing discoveries discouraged further inquiries.

From the reported activity of the Hulubei and Cauchois samples, a ^{222}Rn source would produce ^{218}Po with a half-life of 3.11 min, and ^{218}Po rapidly decays to ^{218}At or ^{214}Pb. Only 0.0202 % of the ^{218}Po decays into ^{218}At, which has a half-life of less than 2 seconds. So, within a few minutes of obtaining a sample of ^{222}Rn, steady-state conditions, with stable concentrations of ^{218}At and ^{218}Po, are reached. Hulubei and Cauchois had a ^{222}Rn sample with 200 mCi activity, which corresponds to 7.4×109 becquerels (^{222}Rn decays per second) or 7.4×109 ^{218}Po atoms produced each second. After ^{218}Po enters steady-state, a 0.0202 % conversion to ^{218}At corresponds to 1,500,000 astatine atoms being produced each second. With a 2-second half-life, ~3 million astatine atoms would be present at any one time. Standard cathode ray tube X-ray studies, requiring at the time at least 0.1 nanogram of sample material, meant the amount of astatine in the sample tube was below the detection limit. Hulubei and Cauchois, however, relied on the radiation from the decaying atoms, so the instantaneous astatine concentration is not important, but rather the total number formed during the measurement. Over a one-hour spectrum, about 5.25 billion astatine atoms would briefly appear and then decay away in Hulubei and Cauchois' sample, emitting their characteristic X-rays before vanishing, a number far above Hulubei's claimed limit of detection. Additionally, they were able to see clearly the $L_{\alpha 7}$ line of polonium, which has approximately a 500-fold lower transition probability than the observed astatine $L_{\alpha 1}$ and $L_{\beta 1}$ lines, suggesting that the astatine lines would be visible to Hulubei and Cauchois (28). These numbers would be approximately tripled in Valadares' samples, because he had a 600 mCi ^{222}Rn source.

Corson, MacKenzie, and Segrè definitively produced synthetic astatine in 1940 and were able to perform chemical tests on the element, something that Hulubei and Cauchois could not claim. Hulubei recognized this deficiency in his work, which perhaps explains his lack of significant protests after 1947. There were numerous erroneous element discoveries based on X-ray studies in the 20th century, where lines were observed in the correct positions but the element was not present. Without a very high precision spectrometer, nearby lines of other elements may masquerade as the searched-for element. Hulubei and Caucois encountered this issue in their studies of element 87 (53); yet their observed lines for element 85 were actually fairly interference-free (Table 2). Unlike other flawed studies with X-ray spectroscopy, Hulubei and Cauchois indisputably had astatine in their samples. The only uncertainty is whether their instrument was sensitive enough to distinguish the spectral lines of element 85.

The criteria for discovering an element have changed with technology. Old techniques have been replaced with new ones, but occasionally the trends reverse. In the early 20th century an X-ray spectrum was necessary to convince the scientific community a new element had been found; but for Hulubei's and Cauchois' work, it was deemed insufficient because they lacked chemical proof. By the 1940s, α-particle studies were necessary to verify the discovery of radioactive elements. Karlik and others provided these measurements for naturally occurring astatine, as did several other investigators, but as the quest for new elements reached past Z=100, some felt α-particle studies were no longer enough (54). Throughout history, the only constant for being credited with element discovery has been the ability to convince your scientific peers of your success. In some eras, Hulubei's and Cauchois' work might have been accepted, but at the time they reported their data their methods were not accepted widely. Convincing scientific peers of an experiment's validity is often easier with an influential scientist as an advocate. Although Hulubei and Cauchois were respected in the scientific community, Nobelist Jean Baptiste Perrin, who was the most ardent supporter of their claim of discovering element 85, had died in 1942.

There were three defendable "discoveries" of element 85. The first may have occurred in 1934 or 1939 when Hulubei and Cauchois reported X-ray emission lines corresponding to element 85 in a sample that contained ^{218}85. The second came in 1940, when the Berkeley group produced ^{211}85 in a cyclotron, and chemically characterized their newly created element and detected its characteristic α particles. The third occurred in 1942, when Karlik and Bernert detected the characteristic α

particles of naturally occurring ^{218}85. At various times in history, any of these groups might have been regarded as the discoverers.

Hulubei, Cauchois, Valadares, Karlik, and Bernert all published their work on element 85 in non-English journals, which may account for their lack of familiarity to English readers. To complicate matters, the mistranslation into English by several reviewers of astatine chemistry of some of the early European articles led to perpetuation of erroneous analysis of the research (55-57). In most modern English-language sources, Corson, Segrè, and MacKenzie are credited exclusively as the discoverers of astatine. German language texts tend to credit both the LBL group with discovery and mention that Karlik found astatine in natural sources in 1942. Authors from France and Eastern Europe often recognize the contributions of Hulubei and Cauchois to the discovery of element 85. Unfortunately, this inconsistency detracts from the contributions these scientists made not only to the search for missing elements, but also to other areas. This ambiguity has also led to an occasional misconception that astatine is a completely artificial element. Neither natural nor artificial astatine is available in substantial quantities; all studies must be done on miniscule amounts of the element. Whether Hulubei and Cauchois were able to detect the X-ray radiation from the astatine formed, and whether that detection, without chemical characterization, constituted 'discovery' as Hulubei believed, is an interesting question that can be left to debate if and when the experiments are ever revisited.

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14. De dissolved monazite sand in concentrated sulfuric acid. The residue isolated was heated to a white heat with fusion mixture (an analytical flux of sodium carbonate and potassium nitrate). After cooling, water was added and hydrogen sulfide was passed through the aqueous solution, which produced a gelatinous precipitate. When dried, the precipitate became a white chalk-like mass. The water-insoluble portion of the fusion mixture was treated with glacial acetic acid and heated to remove the acetic acid. The resulting material was treated with dilute nitric acid, neutralized with ammonia, and treated with hydrogen sulfide to remove calcium and magnesium. The precipitate was washed and dissolved in a solution containing HCl, effecting the removal of sulfur as hydrogen sulfide. Nitric acid was added, and the solution was allowed to evaporate to oxidize the precipitate. The solution was neutralized and made slightly basic with ammonia to yield a clear precipitate. When treated with an excess of ammonium hydroxide, a second gelatinous precipitate was obtained (which was insoluble and rather inert); but the first, clear precipitate yielded fibrous crystals that would sublime when heated. This material was recrystallized and converted to a sodium salt by addition

of sodium hydroxide. The sodium salt did not evaporate on heating, nor was it changed by addition of sulfuric acid and heating; however, adding hydrobromic or hydriodic acid caused the formation of a volatile substance (assumed to be element 85), and the sodium salt could be converted to sodium sulfate by addition of sulfuric acid (to the acid-treated material). De used the stoichiometry of sulfate metathesis to determination the approximate atomic mass for element 85 (211).

15. De's work was reported in three self-published pamphlets, which appeared in 1937, 1947, and 1962, all of which are very rare. De's work may have gone unnoticed except for a citation in a review of astatine chemistry by Soviet chemists in 1968 (Ref. 56); however, the format of their bibliography suggests that they may not have had access to the original pamphlet. The lack of access to these pamphlets has led to numerous inconsistencies when subsequent writers have cited De's work.
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AURORAL CHEMISTRY: THE RIDDLE OF THE GREEN LINE

Helge Kragh, University of Aarhus, Denmark

Introduction

The aurora borealis, also known as the northern light, rarely appears in works on the history of chemistry. The phenomenon is located in the upper atmosphere and is caused by streams of electrical particles originating from the sun. Hence the history of the subject may seem to belong to either the history of meteorology or astronomy; or, as far as the mechanisms are concerned, to the history of physics. Indeed, these three subdisciplines of history of science have their important share of the story of how the aurora became understood scientifically. What is missing from the picture, I suggest, is that chemistry, too, was significantly involved in the process. To my knowledge "auroral chemistry" has never been examined by historians of science, and yet even a cursory view at the development shows that problems of a chemical nature were an important part of the history that led to an understanding of the northern light. First and foremost, this was the case in the difficult problem of establishing the nature of the substances from which the colors of the aurora arose, which is largely the same as the problem of interpreting the auroral spectrum in terms of chemical elements.

The complex problem only received a satisfactory explanation in the 1920s, after more than 50 years of research. This essay examines the early phase of the development, up to about 1913, focusing on the problem of identifying the chemical nature of the elements responsible for the northern light. Emphasis focuses on the uncertainty and many unfruitful hypotheses that characterized the development. It was a period of great change in the relationship between chemistry and physics, including a new definition of chemical elements and a greater understanding of the periodic system in terms of atomic theory. Attempts to find the origin of the spectral lines continued and eventually succeeded, in part because of more advanced experiments and their interpretations in terms of quantum theory (1).

The Green line and Astrospectroscopy

The general idea that the fascinating colors of the aurora are due to chemical elements in the higher atmospheric regions was expressed even before the invention of spectroscopy proper. Observing by means of a prism the colors produced by various elements subjected to electric sparks, an American researcher noted (2):

> The colors also, observed in the aurora borealis, probably indicate the elements involved in that phenomenon. The prism may also detect the elements in shooting stars, or luminous meteors.

These were prophetic words, but they could only be turned into a scientific research program, chemical astrospectroscopy, after the invention of the spectroscope in 1860.

What was probably the first spectroscopic observation ever of the aurora was announced in 1868 by the

Swedish physicist Anders Jonas Ångström (3), who found a bright greenish line of wavelength 5567 in the units named after him (1 Å = 1 Ångström = 0.1 nm). Ångström's observations gave rise to a great deal of activity and many measurements of the spectrum of the aurora borealis. Observing an aurora visible in the Boston area in October, 1870, Alvan Clark and Edward Pickering suggested that two of the lines could be ascribed to hydrogen and one to the hypothetical substance assumed to make up the solar corona (4). Henry Procter of the Royal College of Chemistry, London, disagreed, arguing that some of the auroral lines could be produced in discharge tubes at low pressure. He thought that the green line had its origin in oxygen (5).

Another early auroral researcher was the Kiel astronomer and astrospectroscopist Hermann Carl Vogel, who in 1872 made a careful examination of the spectra of atmospheric gases and compared them with those of the aurora borealis (6). He suggested that some of the lines, possibly including the bright green line, were due to nitrogen and in general that the auroral spectrum was a modification of the spectra of the gases in the atmosphere—modified because of very different pressure and temperature conditions. However, he was unable to obtain a precise match between the green line and the lines produced in the laboratory. Vogel's research was followed up by John Rand Capron, an English businessman and accomplished amateur scientist. In a comprehensive monograph of 1879, he reported an extensive series of experiments on the spectra of gases in discharge tubes, but without being able to identify the green line (7). (Figure 1).

During the 1870s many researchers were busy with studying the auroral spectrum. Among the chemists who took an early interest in the field were John Newlands and Arthur H. Church of the Royal Agricultural College (8). This kind of work resulted in more precise wavelength determinations and an extension of the number of lines, but not in a satisfactory understanding of the chemical nature of the substances responsible for the lines. By the late 1870s it was often assumed that the green line was due either to nitrogen or oxygen which, at the low pressure and temperature of the upper atmosphere, was excited by electrical actions coming from the sun. However, in spite of many attempts no one succeeded in reproducing the green line in the laboratory and thus its nature remained an unsolved problem.

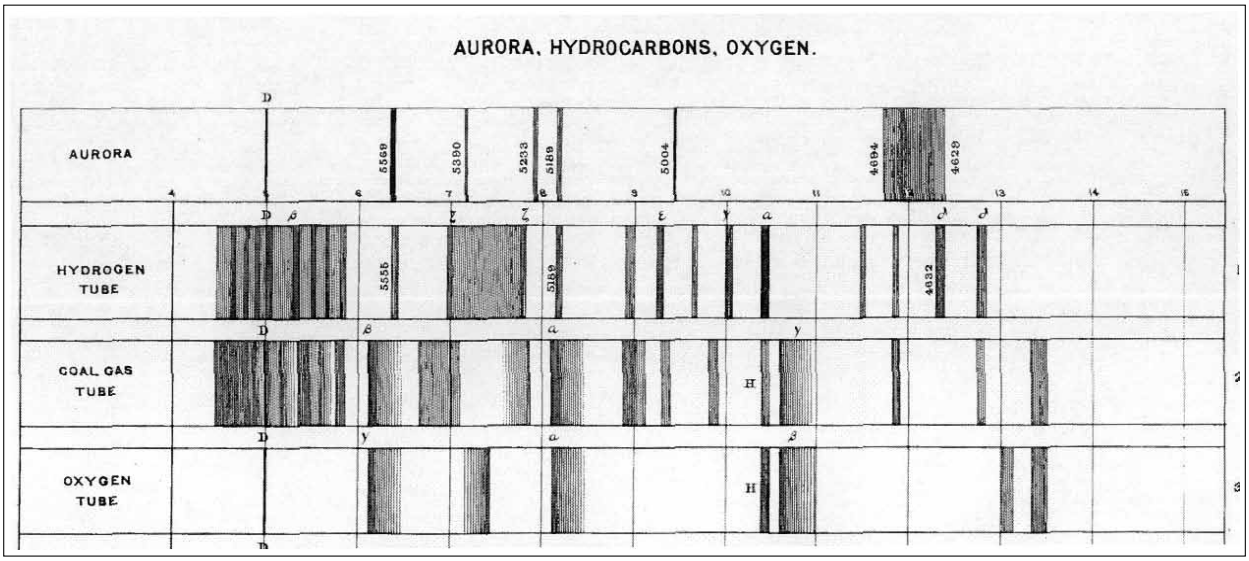

Figure 1. *Rand Capron's comparison of the spectrum of the aurora with other spectra (Ref. 6).*

Hypotheses and Blind Alleys

Most suggestions related to gas molecules, but alternative explanations were discussed as well. One of them was that the green line had its origin in iron dust particles in the atmosphere of the earth, supposed to come from the combustion of meteorites, such as proposed by John Newlands, an industrial chemist who is better known as one of the precursors of the periodic system (8). Although the iron hypothesis was supported by a few researchers, it was never a serious candidate. Given the great number of iron spectral lines, the approximate coincidence with several auroral lines would be almost inevitable and hence of no real significance. A somewhat similar idea was

entertained by J. Norman Lockyer, according to whom the green line might be due to meteoritic manganese (9). However, neither did this hypothesis survive for long.

On a Danish expedition to Iceland 1899-1900, the meteorologist Adam Paulsen and his team succeeded in obtaining good photographs of the auroral spectrum, including 23 lines of which 12 were new and mainly located in the ultraviolet region. Paulsen reported on this work to the international congress of physics in Paris in 1900, leaving the origin of the lines unexplained. Based on Paulsen's Icelandic data and subsequent experiments with discharge tubes made in Copenhagen (10), the Potsdam astrophysicist Julius Scheiner concluded that "the auroral spectrum is absolutely identical with the cathode spectrum of nitrogen" (11). The Swedish physical chemist Svante Arrhenius agreed, stating that "the spectrum of the northern light is nothing but the spectrum of air which has been made luminous in the vicinity of a cathode" (12). However, the identity did not cover the characteristic green line, which resisted showing up in the laboratory experiments of Paulsen, Arrhenius, and other researchers. For example, experimenting with discharge tubes with air at very low pressure, S. D. Liveing and James Dewar found several of the auroral lines but no trace of the green one supposed to be the defining line of the polar light (13).

The state of art in auroral spectroscopy in the early twentieth century may be inferred from a detailed article on the aurora polaris in the 1911 edition of *Encyclopedia Britannica*. According to this article, written by the British geophysicist Charles Cree, the most complete record of the spectrum was obtained by Swedish scientists on Spitsbergen, who found no fewer than 158 auroral lines. By far most of these had wavelengths between 3684 Å and 5205 Å, many of them coinciding with oxygen and nitrogen lines (14). However, measurements were ambiguous and interpretations even more so. At about the same time the spectroscopic expert Heinrich Kayser, professor at Bonn University, concluded that "We know nothing at all about the chemical origin of the lines of the polar light" (15).

In the early part of the twentieth century the recently discovered gas krypton appeared to be a good candidate for several of the auroral lines. This possibility was first suggested by Arthur Schuster, who noted that the green line coincided with an intense krypton line. Determining the wavelength of the krypton line to 5570.4 Å, the German physicist Carl Runge agreed that the match with the auroral line of λ = 5571.0 Å was sufficiently close to make the identification convincing (16). W. Marshall Watts, an English meteorologist, was even more confident; in 1907 he concluded (17):

> There seems now little doubt that the chief line of the aurora, i.e., Ångström's green line, must be assigned to krypton,.

The optimism, however, was premature as well as problematic. For one thing, krypton was known to be a very rare constituent of air and it was difficult to imagine why such a relatively heavy gas (atomic weight 83.80 u) should appear in the upper atmosphere; for another thing, not all of its bright lines could be found in the spectrum of the aurora. Although provisionally assuming the identity of the green line with the krypton 5570 line, William Ramsay, the discoverer of krypton, cautiously concluded that the question remained undecided (18).

Peirce's Auroral Element

Given the many unsatisfactory attempts to identify the green line with known substances, it was natural to look at another possibility, namely that the green line and perhaps also some of the other auroral lines were due to an element unknown to the chemists. Having reviewed the various ideas of the origin of the green line, Scheiner suggested as much (19):

> It appears more plausible to ascribe the existence of the green northern light line to an unknown gas which, perhaps because of its small specific weight, only turns up in the high regions of our atmosphere.

This may seem to be a far-fetched hypothesis, but it made sense at the time and fitted well with contemporary developments in astrospectroscopy and speculative chemistry. The early examinations of the auroral spectrum coincided with Mendeleev's introduction of the periodic system; yet this system in no way precluded the existence of new elements that only existed in the heavens. By accident, Ångström's discovery of the green line occurred at the same time as Lockyer detected a yellow line, denoted D_3, in the chromosphere of the sun. Lockyer, as well as a few other scientists, believed that the line had its origin in a new element, soon known as helium, that existed only in the sun and possibly had an atomic weight smaller than that of hydrogen (20). If helium were accepted as real, why not an auroral element?

Helium was not the only hypothetical element ushered into the Victorian era as a result of astrospectrography. In investigations of the sun's corona, the American astronomer Charles Young found in 1870 a green line of

wavelength 5316 Å, which he suggested might be due to a rare gaseous element, generally known as "coronium." Young speculated that the hypothetical element "must be something with a vapor density below that of hydrogen itself" (21). Although coronium never became part of chemistry, it found its way to at least one version of the periodic system, proposed by Benjamin Emerson (22). In 1919 two American chemists even thought they had found traces of it in a helium gas well (23). Because of the apparent similarity between the aurora and the rarefied solar corona, the two phenomena were often thought to be related.

The first suggestion of a distinct auroral element came from an unlikely source, the later eminently famous American philosopher and logician, Charles Sanders Peirce. As a young man Peirce worked as an assistant at the Harvard College Observatory (1868-1875), just at the time when spectroscopy began to transform astronomy in a more physical and chemical direction. He had at that time considerable interest and competence in chemistry, witnessed by a brief paper published anonymously in the *Chemical News* of 1869, dealing with the classification of the elements according to their atomic weights and chemical characters (24). In this little known paper he presented a table with 50 elements ordered in two series, which he called "artiads" and "perissads." As he pointed out, there was a close correspondence between elements belonging to the two series. In fact, the correspondence amounted to a classification of groups of elements which in some cases were the same as those proposed by Mendeleev the same year. Although Peirce's "pairing" scheme of elements has not attracted attention among historians of chemistry, it clearly has a place in the history of the periodic system.

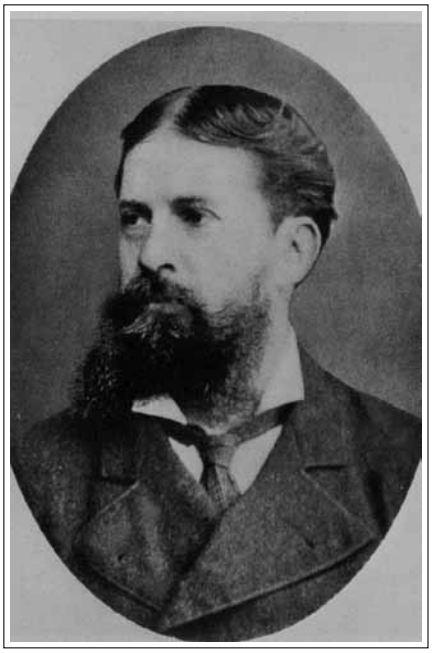

Figure 2. *Charles Sanders Peirce*

Of greater importance in the present context is that Peirce made spectroscopic observations and, as early as April 1869, studied the auroral light. According to the *Annals* of the Harvard College Observatory (25):

> On April 15, 1869, the positions of seven bright lines were measured in the spectrum of the remarkable aurora seen that evening; the observer being Mr. C. S. Peirce.

The same year, Peirce wrote an insightful review of the eminent English chemist Henry Roscoe's *Spectrum Analysis*, a subject with which he was thoroughly familiar, both with regard to its astronomical and chemical aspects. Peirce's comments on the use of the spectroscope in auroral research are not well known and they deserve to be quoted at some length (26):

> The spectrum of the aurora, as usually seen, consists of a single yellowish-green line, which belongs to no substance with which we are acquainted. As the aurora is held to be above the ordinary atmosphere (and this is confirmed by its showing no nitrogen lines), it follows that there is some unknown gas reaching above the other constituents of the atmosphere. According to the laws of gravity and diffusion of gases, this substance must extend down to the surface of the earth. Why, then, have not chemists discovered it? It must be a very light elastic gas to reach so high. Now, the atomic weights of elementary gases are proportional to their density. It must, then, have a very small atomic weight. It *may* be as much lighter than hydrogen as hydrogen is than air. In that case, its atomic weight would be so small that, supposing it to have an oxide of the type of water, this oxide would contain less than one per cent of it, and in general it would enter into its compounds in such small proportions as almost infallibly to escape detection.

As an example Peirce suggested that the auroral gas might have an atomic weight of 0.07 u. If it were divalent and combined with oxygen as X_2O, it would make up only 0.87% of the compound.

This was the first suggestion that the green auroral line might be due to an unknown chemical gas with atomic weight smaller than that of hydrogen. Although an interesting speculation, it attracted very little attention, which is scarcely surprising in view of the fact that it was published as an unsigned review in an obscure American journal. Peirce did not himself return to the hypothesis, but a few other scientists toyed with the idea of "aurorium," an appropriate name for Peirce's element but not one he used. The spurious element "aurorium" only appeared in the chemical literature in 1923, when it was mentioned by B. Smith Hopkins, a chemistry professor at the University of Illinois (27).

Wegener's Geocoronium

With the gradual completion of the periodic system, and especially after the incorporation of the new group of inert gases, it appeared increasingly difficult to find a place for new gaseous elements. However, there still remained the possibility of subhydrogenic elements, such as proposed by Peirce. Indeed, in his revised system of 1903 Mendeleev considered the existence of two such elements, one of which he thought might be identical with coronium, and the other, even lighter element, to be the same as the physicists' world ether (28). Among his inspirations was an address to the British Association for the Advancement of Science, in which Dewar had suggested that some of the auroral lines "may perhaps be due to some volatile element which may yet be discovered in our atmosphere" (29). According to Mendeleev (30):

> This is only a few steps from the yet more distant regions of space, and from the necessity of recognizing the existence of a still lighter gas capable of permeating and filling space and thus giving a tangible reality to the conception of the ether.

That is, the Russian chemist entertained the idea of a very light auroral element in the form of an intermediate between the ether and ordinary gases.

The hypothesis of an auroral element was also suggested by Alfred Wegener of drifting continents fame. Primarily a meteorologist and astronomer, Wegener had a strong interest in the composition of the upper atmosphere, including its chemical and physical aspects (31). Measurements showed that the intensity of the unknown 5570 line increased with the height of the aurora and completely dominated the high-altitude steady arcs, which Wegener took as evidence that the line originated in a light gas only found in the uppermost regions of the atmosphere. He first made the suggestion in a paper of 1910, where he speculated that the gas might be lighter than hydrogen and be analogous to the substance of the solar corona (32). The following year he went a step further, suggesting that the hypothetical gas was a new chemical element.

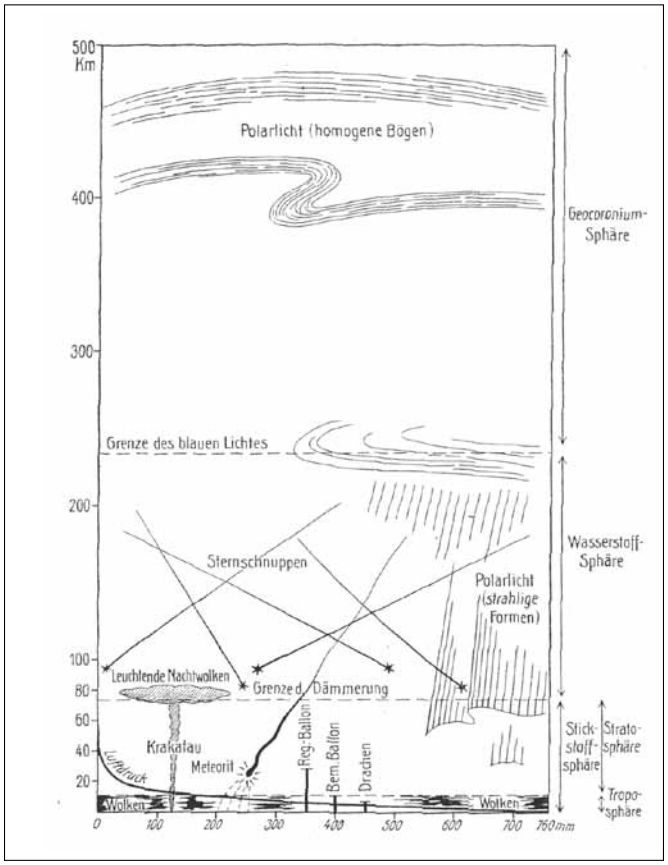

***Figure 3**. Wegener's picture of the atmosphere, as reproduced in his textbook of 1911 (Ref. 33).*

According to Wegener, whereas the atmosphere consisted of a nitrogen-oxygen mixture up to about 80 km, at very high altitudes it was quite differently composed. Hydrogen would be abundant but mixed with the new gas which he proposed to call "geocoronium" (33). Wegener calculated that at a height of 200 km the atmosphere would consist of equal amounts of hydrogen and geocoronium, whereas at a height of 500 km the distribution would be 93% geocoronium and 7% hydrogen. In a paper published in the *Zeitschrift für anorganische Chemie*, he expressed the belief that "in this way it is possible, for the first time, to establish some order in the confusing chaos of contradictory observations and opinions" (34). (Figure 3).

Wegener was aware of Mendeleev's earlier speculations, which he considered to provide support for his hypothesis. Assuming geocoronium to be monoatomic, with an atomic weight of 0.4 u (a value he took from Mendeleev), and with a partial pressure at height 200 km equal to that of hydrogen, he found that the atmosphere at sea level should include 0.00058% geocoronium according to volume. This was a small amount indeed, but not very much smaller than the amount of hydrogen. "A direct detection cannot be ruled out," he commented (35). As to the nature of the new gaseous envelope of the earth, he thought it might be similar to or perhaps identical with the solar coronium. Although the bright aurora line did not coincide with the coronium

line, he argued that the difference might be ascribed to different excitation mechanisms in the solar and terrestrial coronas. He therefore concluded that the two gases were very likely identical.

Published in a monograph and in two of the leading journals of physics and chemistry, the geocoronium hypothesis was noticed by contemporary scientists. However, it was coolly received. Among the few supporters of the hypothesis was the German geophysicist Gustav Angenheister, according to whom the lower auroral region consisted of about 64% hydrogen, 33% geocoronium, and 3% helium (36). Most chemists were unwilling to consider new elements of the kind proposed by Mendeleev and Wegener, and meteorologists and other specialists in the aurora thought that the green line could be explained without the drastic assumption of a new gas enveloping the earth (37). There was no independent evidence for geocoronium, and so the hypothesis might seem to be based on a circular argument. The Norwegian pioneer in auroral research, Kristian Birkeland, found Wegener's hypothesis interesting, but his former assistant Lars Vegard rejected it as speculative and unnecessary (38).

At the time Wegener proposed the geocoronium hypothesis, other scientists suggested that the new and exciting phenomenon of radioactivity might throw a much needed new light on the aurora and its spectrum. For example, Vegard suggested a detailed theory of the aurora borealis according to which the characteristic drapery bands were caused by alpha rays emitted from the sun. Although he expressed great confidence in the new theory, he had to admit that it failed to offer an explanation of the green line. Forty-four years after Ångström had pioneered auroral spectroscopy, "the origin of the most conspicious line with a wave-length $\lambda = 5570$ is still unknown" (39).

The Green Line Identified

From about 1920, Vegard, the period's foremost authority in auroral spectroscopy, started a series of systematic investigations in order to establish the origin of the green line. He had at the time become convinced that the green line belonged to an unusual form of nitrogen, possibly in the form of crystalline dust. To vindicate the hypothesis, he made a series of low-temperature experiments with solid nitrogen exposed to cathode rays which made him conclude that the puzzle of the green line had finally been solved (40). However (and to make a long story short), Vegard's discovery claim was disputed by similar experiments made in Toronto by John McLennan and Gordon Shrum in 1925 (41). The Canadians demonstrated that the green line did not have its origin in solid nitrogen, but that it was due to a "forbidden" transition in atomic oxygen. This has remained the accepted explanation.

Although Vegard failed to explain the green line, his extensive work in auroral spectroscopy was not wasted. Vegard did his first scientific work in physical chemistry (42) and kept an interest in borderline problems between physics, chemistry, and meteorology. He published a couple of important papers on X-ray spectroscopy in the *Journal of the Chemical Society*. While a professor of physics in Oslo he was primarily occupied with the aurora, but he also did much work on the structure of crystals of alums and other compounds. As a consequence of his failed interpretation of the green line, he extended this work to the crystal structure of solid nitrogen and other gases in the solid state (43). This line of work, mostly published in the *Zeitschrift für Kristallographie*, was important to the new field of solid state chemistry.

With respect to the green auroral line ("aurorium"), there is a noteworthy analogy to three other elements, only one of which is real: helium, coronium, and nebulium. The evidence for these hypothetical elements was unidentified spectral lines in the heavens, either from the sun or from the distant nebulae. The status of helium changed drastically in 1895, when the gas was found in terrestrial sources. No such change occurred in the cases of coronium and nebulium. While the main coronium line was eventually identified as due to iron in a highly ionized state (Fe^{13+}), the nebulium lines were explained in a way similar to the green auroral line, namely as transitions between metastable states in doubly ionized oxygen. The resolution of the nebulium puzzle dates from 1927, two years after the green line had been understood, whereas the coronium puzzle was delayed until the late 1930s before it was resolved (44). Of course, in this period no one seriously believed in the existence of new gaseous elements of low atomic weight.

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To the Editor:

I enjoyed John Plater's article in the most recent issue of the *Bulletin* (**2010**, *35(1)*, 40-45) on serendipity. Though, in his discussion of the use of lithium salts to retreat mania, he mentioned several mineral waters, such as Perrier and Vichy, which naturally contain small concentrations of lithium ion, he failed to mention one of the more famous commercial soft drinks that tried to cash in on the original lithium craze – 7 Up. First created by Charles Leiper Grigg of St. Louis in 1920 under the name of "Bib-Label Lithiated Lemon-Lime Soda," it was originally formulated with lithium citrate as one of its active ingredients. Since Grigg was a professional designer of soda flavors rather than a pharmacist, it is unclear from the accounts I have read just what the original motive was for adding the lithium salt, nor is it obvious whether the current soda still contains any lithium citrate, since apparently the brand has been sold and resold several times to various companies and has also been reformulated in the process. But of greater interest is the name "7 Up" which rapidly displaced Grigg's original tongue twister. I have never come across an explanation of its origins but have always wondered whether "Up" was a references to the idea that lithium could act as a pick-me-up and that 7 was a reference to the atomic weight of Li. Perhaps this explanation is too cleverly chemical to be true. Nevertheless, I would be interested in knowing whether the readers of the *Bulletin* might have some insights into this question.

William B. Jensen, Oesper Professor of the History of Chemistry, University of Cincinnati

THE DEVELOPMENT OF THE MERCURY LAMP

Mordecai B. Rubin, Technion, Haifa, Israel

Introduction

The mercury (vapor) lamp (1) is an evacuated tube, usually of quartz, with electrodes sealed in at the ends and containing a quantity of liquid mercury. Variation of size, shape, amount of mercury, and electrical system can produce a small, low intensity lamp suitable for detecting spots on a thin layer chromatogram (2) or a lamp of output in the hundreds of watts appropriate for outdoor lighting. These are but two of the great variety of uses of such lamps. Their long history began with Humphrey Davy, 19 years after he had discovered the carbon arc lamp (3). Described here is the early development of the mercury lamp .

Humphry Davy: The Discovery

The first connection of electricity to mercury was reported to the Royal Society of London by Davy in 1821 (4). Earlier workers had argued that electricity could not be transmitted through a vacuum, the "ether" being required as a medium. Davy was interested in testing the validity of this hypothesis. He chose to use mercury as an electrode material, apparently on a suggestion of Berzelius. Fig. 1 is a reproduction of the simple apparatus he constructed as described in his 1822 paper: a bent tube containing an amount of mercury with an electrode cemented in at one end and a stopcock at the other. The lamp was filled to any desired level with mercury and degassed by evacuation with an air pump followed by repeated boiling of the mercury.

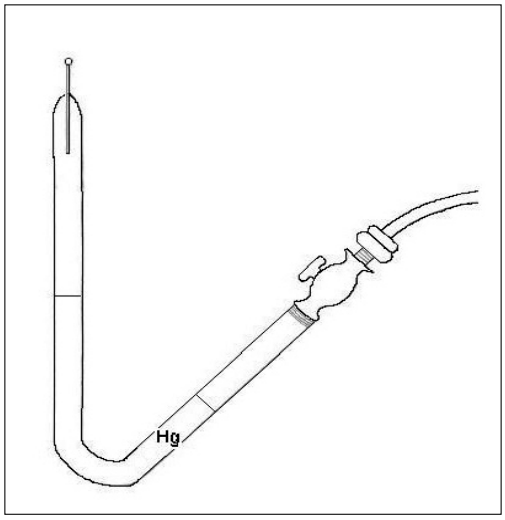

Figure 1*. Sir Humphry Davy's Mercury Lamp*

A remarkably bright light was observed when the electric current from a battery was applied. Davy investigated various effects, such as temperature, on the behavior of the system. Satisfied that he had established the fact that current could be transmitted through a vacuum, he turned his attention in other directions.

Three scientific papers using mercury light sources for study of the emission spectrum of mercury vapor appeared during the remainder of the 19th century until the report of Arons in 1892 (see below) when the study of mercury lamps returned to the realm of science. The first of these in 1835 was due to Wheatstone (5), who obtained emission spectra of mercury and of the molten metals zinc, cadmium, tin, bismuth, and lead. The action of an electric spark on mercury gave "seven definite rays separated

from one other by dark intervals." Emission spectra were also obtained by the same procedure from the metals listed above. "The appearances are so different that, by this mode of examination, the metals may be readily distinguished from each other"(5). This was suggested as a superior method for analysis, but Wheatstone's interests lay in other very productive directions involving mainly electrical apparatus. He did no further work nor did he evince any interest in application of mercury lamps for illumination. He did anticipate the work of Bunsen and Kirchoff over a decade later.

Ångstrom (6) reported an extensive study of emission spectra of many substances in 1855. He used Geissler (7) tubes to obtain the emitted light and included mercury among the substances investigated. This was followed by a study of mercury by Gladstone, who used a lamp he obtained from Way (8) (see below). There was good agreement between the results of the latter two investigators.

Wiedemann, using Geissler tubes, studied emissions of mercury with a variety of other substances also (9). Fig. 2 presents an idealized emission spectrum of mercury vapor. As will be discussed, the relative intensities vary with the pressure of mercury. To be noted is the large number of well-spaced emission lines.

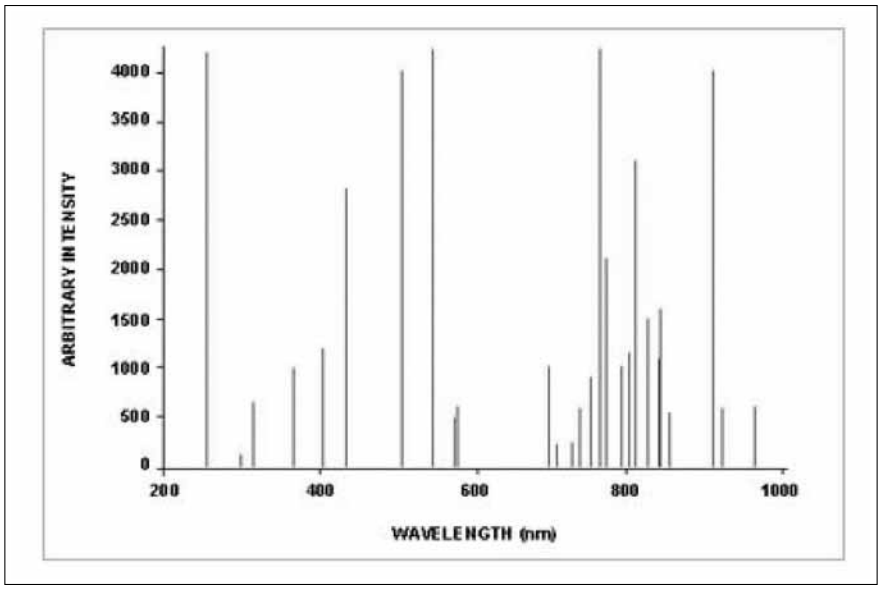

***Figure 2**. Idealized Version of Mercury Emission Spectrum*

19th-Century Patents

Except for work relating to the emission spectrum of mercury described above, activity in the area of mercury lamps was concentrated exclusively in the field of patents for lighting applications until Arons' paper (see below) in 1892. A few of those patents, listed below, were discussed and summarized by Recklinghausen (10) and by Perkin (11). There are undoubtedly more; the middle of the 19th century was a time when street lighting came into popular use.

1852. E. H. Jackson of Soho patented a lamp based on carbon electrodes, one electrode with a recess containing a quantity of mercury.

1857. J. T. Way Brit. Pat. No. 1258, 4 May 1857, "Improvements in Obtaining Light by Electricity, and in Employing light so Obtained for lighthouses and for Giving Signals," No. 2841m, 10 Nov., 1857, "Improvements in Obtaining Light by Electricity." For details see below.

1857 Charles W. Harrison patented a lamp with a carbon rod suspended over a cup of mercury.

1867. Sir W. Siemens (UK) developed a lamp with a vibrating electrode dipping into a mercury cup which gave intermittent light. Proposed for lighting buoys at sea.

1879. J. Rapieff, Brit. Pat.. 211, 18 Jan., 1879, "Producing and Applying Electric Currents for Lighting &c". Two mercury poles in U-tube, started by shaking or tilting the U tube, either *in vacuo* or air.

1887. Rudolph Langhans, German Pat. 45880, 24 Nov. 1887, Klasse 21, described a U-tube filled with metal or metalloid.

1889. Rizet French Pat. 132426, 27 Aug., 1889, similar to that of Rapieff but filled with nitrogen.

These devices quietly faded into obscurity, but the lamp of J. T. Way caused much excitement in its time. A long article in the London *Times* of Aug. 3, 1860 (12) ecstatically described a night time boat trip in the English channel illuminated by a Way lamp and including a run by the Queen's channel residence (Osborne House), so that she could see the new marvel. This was also

reported in other publications (13). Quoting the *Times*: "The strongest and purest light in the known world, and the nearest approach to sunlight…"

For a discussion of the ignition of Way's lamp, see the later section on lamp ignition. The lamp itself was not closed to the atmosphere; and Monasch reported (14) that because of the exposure to mercury vapor, Way paid with his life for the experiments with his lamp. This was an exaggeration, since he continued an active career in agricultural and environmental science into his later years and died in 1883 at age 63. In any event, nothing was heard of his lamp after 1860; nor was it mentioned in his obituary (15) in the *Journal of the Chemical Society*.

Arons' Lamp

The development of the mercury lamp began in earnest with the work of Arons published in 1892 (16); he is sometimes given credit (17) for its invention, although he cites the work of Way in the first footnote to his second paper (18) and the use of Geissler tubes by Wiedemann (9) to obtain the mercury spectrum. His lamp design follows that of Rapieff by using a U-tube.

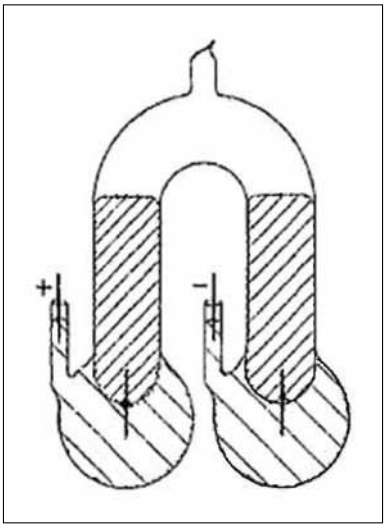

***Figure 3**. Aron's Mercury Lamp*

The simple construction of Arons' lamp is shown in Fig. 3. It consisted of an inverted U-tube (2-cm diameter tubing) with 6-cm arms and a side tube at the top for connection to a vacuum pump, etc. Platinum electrodes were sealed into the closed ends of the two arms with cement, and the whole apparatus filled with mercury nearly up to the bend, exhaustively evacuated, and sealed off. The apparatus shown in the figure is a modification with additional mercury reservoirs at the bottom for dissipation of the heat; these could be further cooled in water. Exhaustive evacuation and good sealing were key elements in successful lamp preparation. Current for the lamp was provided by a battery or by the municipal electrical supply (105-110 v DC) with suitable regulator. The lamp was ignited by connecting the current supply followed by tapping or tilting to create a temporary metallic circuit. This led to the vaporization of some mercury; and after a very short interval the lamp, returned to the vertical position, ignited to give a remarkably intense, stable, grayish-white light.

The Table gives the current-voltage relationships Arons found. At currents of 1.4 amp or less, ignition was not possible. It was necessary to ignite the lamp at a higher current and then reduce it to the desired value. In contrast to the carbon arc, the cathode of the mercury lamp was appreciably hotter than the anode. Arons, using a grating apparatus, observed 33 lines in the emission spectrum of his lamp. It should be noted that ordinary glass was used, for lack of an alternative, eliminating emission below about 300 nm.

Table. Current-voltage relationships in Arons' mercury lamp

Amp	11	9	7	5.5	3	2	1.4	0.8	0.5
Volt	17.5	17	16.5	16	15.3	14	20	28	40

The considerable amount of heat generated was the major problem with Arons' design, affecting the seals and resulting in deposition of mercury on cooler walls of the apparatus.

Detailed studies of the inverted U-tube lamp including results with a variety of amalgams were reported by Arons in 1896 (18). Major factors in the construction of stable, long-lived lamps were temperature control, high vacuum, and good quality sealing of the electrodes. A modified lamp housing which allowed more efficient utilization of the light produced by avoiding condensation of mercury drops on the light-transmitting part of the apparatus was described by Lummer (19), who arranged for commercial production of this lamp with a water-cooled housing, as illustrated in

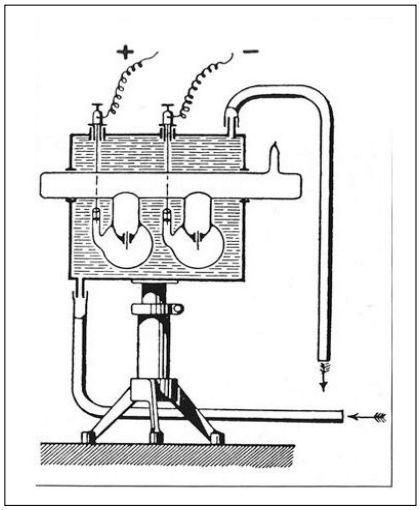

***Figure 4**. Lummer's Commercial Water-Cooled Mercury Lamp*

Fig. 4. The mercury lamp was on its way to becoming an important tool in science. For example, Fischer and Braehmer (20) in 1905 used a home made mercury lamp for a detailed study of the photochemical formation of ozone from oxygen.

Cooper Hewitt's Street Lamp

The first practical mercury lamp was developed by Peter Cooper Hewitt. Cooper Hewitt made a detailed study of the factors involved in operation of a lamp, such as geometry, electrical characteristics, amount of mercury, etc. A simplified drawing from his 1901 patent (21) is shown in Fig. 5. The bulb at the top of the lamp was introduced to optimize the cooling of the lamp; similar bulbs grace many mercury lamps produced over 100 years later. Ignition was achieved by a solenoid arrangement, which tilted the lamp so as to close a circuit and vaporize some mercury, whereupon the lamp was returned to the vertical position (22). Recklinghausen (10) has discussed Cooper Hewitt's design in some detail.

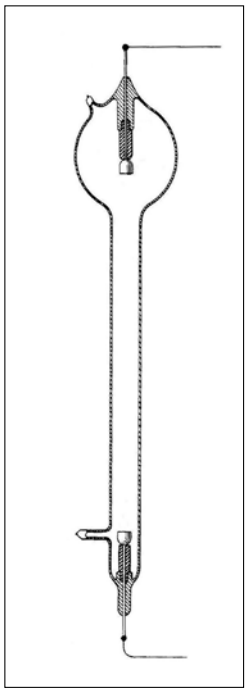

Figure 5. *Cooper Hewitt's Gas-Vapor Lamp*

Cooper Hewitt's lamp had a long lifetime and a light output far in excess of tungsten lamps of comparable wattage. Its main drawback was the light itself, which made objects appear an unnatural chalky color. This did not interfere with some uses such as outdoor lighting or use as a projection lamp. Much work was done to improve the quality of the light. Cooper Hewitt and George Westinghouse established a company to market the lamps; this was taken over by Westinghouse Electric in 1902 and changed to a joint arrangement with General Electric (GE) in 1913. Westinghouse subsidiaries in a number of European countries marketed the lamp in Europe (23). GE took over the lamp operation upon George Westinghouse's death in 1914. The Cooper Hewitt lamp served as a model for lamps produced by other companies.

Quartz Lamps.

The next advance in mercury lamps was the result of developments in quartz technology, which came at the beginning of the 20th century (24). The lamps described earlier were all constructed from ordinary glass. The development of quartz with high transparency in the ultraviolet allowed construction of lamps with improved optical properties and much greater heat resistance (24). The higher temperatures that could be tolerated by quartz resulted in higher efficiency of the lamps.

It should be noted that the much improved ultraviolet transparency requires great care in avoiding exposure of skin and particularly eyes to the light produced. In 1905 Schott (25) described a commercial lamp, called the Uviol lamp, which transmitted light down to 253 nm. He stated that Heraeus quartz was transparent to 220 nm. The efficiency of the mercury lamp improved sufficiently at higher pressure, so that it was economical to construct lamps for street lighting of quartz and enclose them in an envelope of ordinary glass for protection of passers-by.

Ignition

If the usual working current is applied to a cold mercury lamp, nothing will normally happen. The early workers with U-tubes found that their lamps would ignite if a temporary circuit were closed by tilting or tapping the mercury. After brief flow of current, the lamp would ignite as soon as the circuit was interrupted. It was assumed that this was necessary because of the low vapor pressure of mercury at ambient temperature. Weintraub speculated that formation of ions or local arcs was necessary for ignition. As noted above, temporary tilting was an integral part of Cooper Hewitt's and the Uviol lamps. Way (26) had an ingenious method for ignition using flowing streams of mercury to close the circuit; ignition occurred when the flow was interrupted. Intermittent flashing light could be generated by adjusting flows to have periodic breaks. With systems under high vacuum, ignition could also be initiated by an external Tesla coil.

A simple, practical solution to the ignition problem was discovered by Weintraub (27), who introduced a third, metallic electrode close to the cathode. Initial application of current between the two proximate electrodes led to some activity at the main cathode, and this in turn initiated interaction between the two main electrodes. Many present day commercial mercury lamps incorporate Cooper Hewitt's bulb and Weintraub's third electrode.

Final Remarks

An idealized emission spectrum of the mercury lamp is shown in Fig 2, where it can be seen to consist of a

series of lines covering the range from 187-254 nm and through the UV and the visible spectrum. Individual lines or narrow groups of lines can be isolated with commercially available filters, making the lamps particularly useful for photochemical studies. They became available at a time when much attention was being paid to photochemical reactions because of the Einstein postulate relating the number of photons absorbed to the number of molecules absorbing. Mercury lamps continue to be extremely valuable in photochemical investigations up to the present day.

The output of mercury lamps is partly dependent on the operating conditions of the lamp. When the amount of mercury involved is very small, the emission spectrum of the resulting low pressure lamp is concentrated in the ultraviolet (on the order of 90% at 187 and 254 nm). This wavelength range was shown to be very efficient in destroying undesirable bacteria, and sterilization lamps were available commercially before 1911. The fluorescent lamp, developed in the 1930s (28), is also a low pressure mercury lamp contained in a tube which has an inner coating of a material that absorbs the short wavelengths and emits in a useful region of the spectrum.

Increasing the amount of mercury in the lamp leads to medium-, high-, and superpressure lamps. Self absorption by excess mercury vapor present results in disappearance of the 254-nm emission in higher pressure lamps and some broadening of the remaining emissions. By the time of these developments, progress in mercury lamps had been largely concentrated in the hands of the industrial producers of lamps, so that much of the information is proprietary or in the form of patents. Almost anywhere light is required, the mercury lamp can be found in the appropriate configuration. High and super-pressure lamps (1-2 mm i.d., 2 cm length) can approximate point sources and be used in optical systems.

Mercury sensitization is a special case in which a solution containing traces of dissolved mercury is irradiated with a mercury lamp. The resulting excited mercury may transfer its energy by collision with other molecules present, resulting in reaction of the excited state which is formed.

Present demands for nonpolluting, high-efficiency light sources promise an interesting period in lamp development in the near future. Minimum efficiency for ordinary domestic lamps has been legislated in various parts of the world, including the U. S. The leading candidate at the time of preparing this article is the "long life" compact fluorescent lamp, another mercury-derived lamp. Vigorous research is in progress to improve the efficiency of the classic tungsten lamp as well as development of new types of lamps such as the sulfur lamp.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. The term mercury lamp and mercury vapor lamp are often used interchangeably, but they may be indexed separately. The correct usage (IUPAC) is mercury lamp, deuterium lamp, hydrogen lamp, etc.
2. An extremely useful technique for analysis and separation of mixtures. The most convenient method for visualizing the separated materials after migration of a solvent on an adsorbent layer is shining light from a mercury lamp on the dried plate.
3. An anonymous referee, whose erudition we admire and to whom our thanks are due, has brought to our attention the "barometric light" discovered by Picard in 1675 and reported in detail by Francis Hauksbee in 1709. When a tube containing mercury under a modest vacuum is shaken, a glow is observed, presumably the effect of static electricity on the mercury. See Wikipedia or any edition of the *Encyclopedia Brittanica* under the heading barometric light.
4. H. Davy, "On the Electrical Phenomena Exhibited in Vacuo," Abstracts of the Papers Printed in *Philos. Trans. R. Soc.*, London, **1821**, *2*, 159; H. Davy, "On the Electrical Phenomena Exhibited in Vacuo," *Philos. Trans. R. Soc., London,* **1822**, *112*, 64-7.
5. C. Wheatstone, "On the Prismatic Decomposition of Electric Light," *Philos. Mag.* Ser. 4, **1835**, *9*, 32. Sir Charles Wheatstone, 1802-1875; originally worked with musical instruments. Prof. Kings College, 1834. Made important contributions to electrical apparatus. His name has been perpetuated by the Wheatstone Bridge for measuring resistance, invented by S. H. Christie but developed by Wheatstone. .

6. A. J. Ångström, "Optical Researches, " *Philos. Mag.,* **1855**, Ser. 4. *9*, 327-342. Anders Jonas Ångström, 1814-1874. D. Phil., Uppsala, 1839. Priv.-Doc in Physics Uppsala, 1839. Traveled 1843-44 in Germany, France, and England. From 1858 Prof. of Physics in Uppsala; made a detailed study of emission spectra of many substances.
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ABOUT THE AUTHOR

Mordecai B. Rubin (chrubin@tx.technion.ac.il) has been emeritus professor of chemistry, Schulich Faculty of Chemistry Technion since 1994. It has become difficult to remember when he was not retired. This work on the mercury lamp originated from investigation of the early photochemistry of ozone, where mercury lamps played an important role— thus showing that his historical research is still dominated by the history of ozone.

CARL BOSCH AND HIS MUSEUM

Fathi Habashi, Laval University

Carl Bosch (1874-1940) (Fig. 1) was born in Cologne, studied metallurgy and mechanical engineering at the Technische Hochschule in Berlin (1894-96), then chemistry at Leipzig University, graduating in 1898. In 1899 he entered the employ of the Badische Anilin- und Sodafabrik in Ludwigshafen (Fig. 2) and participated in the development of the then new industry of synthetic indigo.

Figure 1. *Carl Bosch (1874-1940)*

When in 1908 the Badische acquired the process of high-pressure synthesis of ammonia, which had been developed by Fritz Haber (1868-1934) at the Technische Hochschule in Karlsruhe, Bosch was given the task of developing this process on an industrial scale. This involved the construction of plant and apparatus which would stand up to working at high gas pressure and high-reaction temperatures. Haber's catalysts, osmium and uranium, had to be replaced by another which would be both cheaper and more easily available.

Bosch and his collaborators solved the catalyst problem by using pure iron with certain additives. Bosch´s success was based on the cooperation of many collaborators. One of his closest co-workers was Alwin Mittasch (1869-1953) (Fig. 3), who was responsible for the development of the catalysts. Further problems which had to be solved were the construction of safe high-pressurized reactors and a cheap way of producing and cleaning the gases necessary for the synthesis of ammonia. Step by step Bosch went on to using increasingly larger manufacturing units. In order to solve the growing problems posed by materials and related safety problems, BASF set up the chemical industry's first Materials Testing Laboratory in 1912 to identify and control problems in materials for instrumentation and process engineering.

The plant in Oppau for the production of ammonia and nitrogen fertilizers was opened in 1913. Bosch wanted fertilizers to be tested thoroughly, so that customers were to be given proper instructions for their use. This meant extensive trials to determine the effect of fertilizers on soil and on plants. The result was the opening in 1914 of the Agricultural Research Station in Limburgerhof, near Ludwigshafen.

When World War I began in 1914, Germany poured its resources into the war effort. Synthetic ammonia was converted into nitric acid at the Oppau plant and then delivered to the explosives industry. Chlorine and

Figure 2*. BASF in 1881*

phosgene, important intermediates used to manufacture dyes and drugs among other things, were used as poison gas by the German army. After several expansions of the Oppau ammonia facilities, the government ordered the construction of a second major production plant. A plant in eastern Germany, away from the danger of air raids, was commissioned and started operation in 1917 at Leuna near Merseburg. At the end of the war in 1918, the situation in Germany was alarming. The Kaiser had abdicated; reparations, the dismantling of factories, a scarcity of coal, and inflation prevented economic recovery. BASF was occupied by French troops, and German dye manufacturers lost their leading position on world markets. Production facilities, subsidiaries, associated companies, and sales companies abroad were confiscated, as were the patents registered abroad. Reparations imposed by the victors hampered economic recovery.

In 1919 Bosch was appointed Managing Director. On September 21, 1921 Oppau was rocked by a huge explosion. This accident, which occurred during blasts carried out to loosen ammonium fertilizer stored in a warehouse, claimed more than 500 lives and caused considerable damage to the site and the neighboring community,

In 1923 BASF had to merge with five other companies to form Interessengemeinschaft für Farbenindustrie AG, abbreviated IG Farben. The economic crisis in Germany in the 1920s shattered the political structure of the Weimar Republic. This was accompanied by mass unemployment and economic hardship and the rise of the Nazi party. Adolf Hitler, appointed chancellor in 1933, took control of the socio-political and ideological aspects of the individual operating units of IG Farben. The national socialist ideology also shaped day-to-day operations at the Ludwigshafen and Oppau plants. The local newspaper reorganized, labor unions were banned, and IG Farben gradually became enmeshed in the Nazi system.

In 1932, Allgemein Elektrizität Gesellschaft abbreviated AEG and IG Farben collaborated in the development of a magnetic recording device. A year later, the first "magnetophones" were presented to the public at the 1935 Radio Fair in Berlin. In 1936, the Guest House in Ludwigshafen hosted a special concert, recorded on magnetic tape, with Sir Thomas Beecham conducting the London Philharmonic Orchestra. By that time Bosch had been appointed Chairman of the Board of Directors of the I.G. Farbenindustrie A.G.

Figure 3. *Alwin Mittasch (1869-1953)*

The outbreak of World War II in September 1939 forced IG Farben to switch production to the war effort. Many male employees were called up and replaced by women conscripts, prisoners of war, and forced laborers from the occupied countries of Eastern Europe. Concentration camp inmates were put to work at IG Farben's Buna factory in Auschwitz, commissioned on the orders of the German army high command in 1940. Massive air raids were launched on Ludwigshafen in 1943/44. Production dropped drastically and came to a standstill by the end of 1944. By the end of the war in 1945, the extent of the damage was

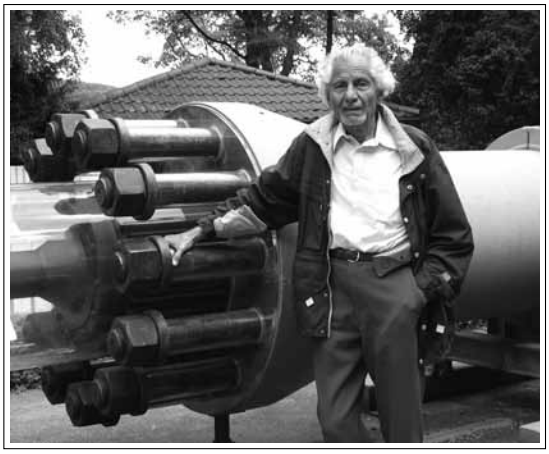

Figure 4. *Example of high-pressure reactors (with author); photo by Nadia Habashi*

enormous. Economic recovery was hindered by continuous political unrest, reparations obligations, the dismantling of factories, lack of coal, transportation problems, and the French occupation of the west bank of the Rhine. In November, 1945 the Allied Control Council ordered the dissolution of IG Farben. Little by little, a starving, freezing, and war-weary population began to rebuild the site, and production was resumed.

Among Bosch's many honors, he was awarded the Nobel Prize for Chemistry, jointly with Friedrich Bergius, in 1931 for their contributions to the invention and development of chemical high-pressure methods. Bosch received this honor for converting a laboratory procedure into a large-scale industrial process. He became President of the Kaiser Wilhelm Gesellschaft in 1937.

Carl Bosch Museum

The Carl Bosch Museum was inaugurated in May, 1998. It is located in Heidelberg near the castle in a villa built by BASF as a residence for its Chief Executive Officer, at 46 Schloβ-Wolfsbrunnenweg. The museum shows the most interesting highlights of the life of Bosch. The display covers IG Farben's role during the Third Reich and the development of high-pressure technology from its beginnings in the laboratory to the creation of gigantic industrial complexes. The Museum portrays both Bosch's private life and his professional career. Even as a boy he gained some technical experience in his father's plumbing workshop. Because of his studies in mechanical engineering he was rather skilled in being a process technician. Another section is dedicated to Bosch's activities as founder of the ammonia synthesis plants at Oppau and at Leuna-Merseburg. The original incentive for ammonia synthesis was the enhancement of crop yields, but this changed during World War I.

Additional features in the Museum include the knowledge of materials, safety standards at work, a competent process control, and the advent of a new profession: the chemical technician. The "high-pressure workshop," equipped with a lathe, tools, fittings, and high-pressure pipes, illustrates the new dimension an industrial technician was confronted with in those days.

The devastating explosion of the Oppau plant in 1921 did not deter industry from going ahead with the technology. The construction and manipulation of high-pressure reactors required new empirical and theoretical knowledge, as well as new approaches to education and training. The construction of the most important elements of an ammonia producing plant, like the inner part of the reactor, the ammonia separator, and the mole-pump gives the visitor an impressive idea of this new industrial technology.

Figure 5. *Example of high-pressure reactors (with author); photo by Nadia Habashi*

Bosch's technical and scientific achievements are well documented by his honors and distinctions and by his 1931 Nobel Prize. Documents of his active struggle against National Socialist anti-Semitic policy are preserved there. Bosch devoted much spare time to various scientific hobbies. His crystal and insect collections became so large that he bought a nearby house and converted it into the "House of Collections." As an amateur astronomer, he built a small observatory in his house. A unique part of the museum is the large high-pressure equipment displayed in the open air outside the building (Fig. 4 and 5).

Figure 6. *Some equipment on display at the* German Chemistry Museum *in Merseburg*

German Chemistry Museum

Closely related to the Bosch Museum is the Deutsches Chemie-Museum in Merseburg not far from Leipzig, located on the campus of the University of Applied Science. This Museum contains a unique collection of original chemical plants and apparatus used in the chemical industry of the 20th century. Set up in 1993, it has been developing ever since. It is composed of two parts: The Technical Park displaying the high-pressure equipment used in ammonia synthesis in 1925; and The Pupils' Lab, meant to acquaint the young generation with science. About 500 experiments related to chemistry and the physical sciences are set up for the young people to carry out. A view of some of the equipment on display is shown in Fig. 6.

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FEUDING RULE MAKERS: ALEKSANDR MIKHAILOVICH ZAITSEV (1841-1910) AND VLADIMIR VASIL'EVICH MARKOVNIKOV (1838-1904). A COMMENTARY ON THE ORIGINS OF ZAITSEV'S RULE

David E. Lewis, University of Wisconsin, Eau Claire

Two of the most widely known examples of empirical rules for predicting the outcomes of organic reactions are named for the Russian* chemists Aleksandr Mikhailovich Zaitsev (1841-1910) (1) and Vladimir Vasil'evich Markovnikov (1838-1904) (2). Today most students in organic chemistry are familiar with the empirical rules devised by these two chemists: Zaitsev's (Saytzeff's) Rule for predicting the regiochemistry of base-promoted β-elimination from alkyl halides (3) and Markovnikov's (Markownikoff's) Rule for predicting the regiochemistry of the addition of unsymmetrical electrophiles to unsymmetrical olefins (4). Indeed, Markovnikov's name (though not, generally speaking, his rule) is one of the few remembered by students in organic chemistry years after they have completed the course. What is less well known is the fact that these two chemists were well acquainted with each other, having been students at Kazan' University, a frontier outpost that developed into one of Russia's finest universities with the pre-eminent chemistry school in the nation (5), and that they carried on a long standing feud that lasted their entire careers.

Zinin

As students at Kazan', Markovnikov and Zaitsev were the recipients of a chemical education that was one of the best in Europe at the time. During the middle third of the nineteenth century, Kazan' University boasted some of the most productive, perceptive, and creative organic chemists practising the science, as well as some of the most enlightened administration of the time. The mathematician Nikolai Ivanovich Lobachevskii (1792-1856), developer of non-Euclidean geometry, served as rector from 1827-1846. During 1834-1837, Lobachevskii supervised the construction of a new science building, with the chemistry floor modeled on the Giessen laboratory (6).

The rise to eminence of the chemistry school at Kazan' is usually traced to Nikolai Nikolaevich Zinin (1812-1880) (7), although his colleague at Kazan', Karl Karlovich Klaus (1796-1864) (8) may well have played an equally important part in its development. The organic chemist Zinin actually spent a relatively short time at Kazan', but Russian historians, in particular,

cite his contributions as the catalyst forming the "Kazan' School" of chemistry. After graduating with a degree in physics and mathematics, Zinin was appointed as adjunct in those disciplines. However, the Ministry of Education had other plans for the young man and, despite his lack of knowledge in chemistry, he was appointed to teach chemistry after the dismissal of the "undistinguished" (5a) professor of chemistry Dunaev. It was common practice at this time for professors to be appointed with a view to the students receiving lectures in the requisite subjects without necessarily considering the qualifications of the instructor in the subject (5b). As part of his training for the professoriate, Zinin was sent on a *komandirovka* (study leave abroad) to attend lectures by eminent western chemists. This was not intended as a research trip, but Zinin nevertheless spent time in the Giessen laboratory of Justus von Liebig, where he discovered the benzoin condensation (9). How this reaction was discovered is not known, but the condensation of benzaldehyde to benzoin is catalyzed by cyanide anion, and it is also known that Zinin was in Liebig's laboratory during the period when Liebig and Wöhler were carrying out their seminal researches on benzoyl compounds. The synthesis of mandelonitrile (benzaldehyde cynohydrin) by addition of hydrogen cyanide to benzaldehyde fails to give the desired product if the cyanide salt is added too slowly. So, under conditions where, for example, the cyanide salt is added to the aldehyde too slowly or insufficient cyanide is used, the product isolated from the reaction becomes benzoin. Is it possible that Zinin's experimental technique was very tentative because of a lack of experience, and that this then led to the discovery of a new reaction? My experience in organic synthesis leads me to believe so, but this cannot be proven beyond doubt. On his return to Kazan' in 1841, Zinin was appointed to the Chair of Technology (Klaus had been appointed to the Chair of Chemistry during Zinin's absence), and he began the studies with nitroaromatic compounds that led to the monumental discovery of the reduction of nitroaromatic compounds to anilines (10) and to the synthesis of azobenzene, azoxybenzene, and benzidine (11). In 1847 Zinin left Kazan' to take up the Chair of Chemistry at the Medical-Surgical Kazan' University of the University of St. Petersburg, where he later became mentor to the chemist-composer Aleksandr Porfir'evich Borodin (1834-1887).

Klaus

In contrast to his colleague, Klaus' contributions are frequently overlooked by historians of organic chemistry because of his general preference for work in pharmacy. After he had obtained his master's degree in chemistry from Dorpat University (now Tartu, in Estonia), he applied for the vacant chair in pharmacy at Kazan' but received, instead, an appointment in chemistry. On graduating with his doctoral degree in pharmacy in 1839, he was promoted to Extraordinary Professor of Chemistry, and, in 1844 (the same year as his discovery of ruthenium), he was promoted to Ordinary Professor. When he left Kazan' in 1852, it was to take up the newly-created Chair of Pharmacy at his alma mater.

Klaus' predilection towards pharmacy and his conservative chemical views (he was an adherent of the dualistic theories of Berzelius) may have deterred later biographers from recognizing his real impact on the careers of chemists who studied under him. Oddly enough, his place in history is not as a pharmacist, but as the discoverer of ruthenium, a result of work begun in the chemistry of the platinum metals at the instigation of a friend who worked at the mint (Russia used platinum as a coinage metal in addition to silver and gold). Klaus' discovery of ruthenium capped an impressive body of work in the chemistry of the platinum metals, and he also directed research students in the chemistry of these metals. Butlerov studied the chemistry of osmium under Klaus. An objective examination of Klaus' research record would suggest that his contributions to the development of the science itself, as well as his effects on the subsequent career choices of his students, were more important than is usually allowed by more chemistry- (and especially organic chemistry-) oriented biographers.

Between them, Zinin and Klaus were responsible for the chemical education of the man who was to become the most influential Russian organic chemist of his day: Aleksandr Mikhailovich Butlerov (1828-1886) (12), after whom the Butlerov Prize is named.

Butlerov's entry into chemistry was hardly auspicious: he was apparently electrified by the lectures of Zinin, but after Zinin's departure for St. Petersburg, Butlerov chose to remain in Kazan'. Here he continued his study of chemistry under Klaus, becoming the first person to observe the oxidation of organic compounds by osmic acid (osmium tetroxide) (13). Nevertheless, the young Butlerov was not as enamored with chemistry as one might have expected, given his enormous impact on the later development of the science in Russia. In fact, he wrote his *kandidat* dissertation on the diurnal butterflies of the Volga region (14)! Furthermore, his master's and doctoral dissertations (15) were largely reviews of known chemistry, with little evidence of the piercing intellect and creativity that he would later display. Despite his apparent lack of interest in and commitment to chemistry, it was to Butlerov that the University entrusted the teaching of chemistry following the departure of Zinin to St. Petersburg and Klaus to Dorpat.

Butlerov

One of the first things the University did was to send Butlerov abroad on a *komandirovka* to study chemistry, and Butlerov made the most of his opportunity. The timing of the trip could hardly have been more auspicious: the year 1858 was a nexus in the development of organic chemistry, with the new ideas of organic structure and reactivity being developed by the younger generation of chemists exemplified by Kekulé and Erlenmeyer in the face of (often vitriolic) opposition by the conservative Kolbe and his adherents (16). During his trip, Butlerov generally associated with the younger, more progressive chemists. He met Kekulé, who became a life-long friend, and he spent close to a year in Paris in the laboratories of Charles Adolphe Wurtz, where he almost certainly had the opportunity to meet and interact with Archibald Scott Couper. By the end of his trip, Butlerov had been inculcated with the views of the modernists. One of the first to appreciate the true power of the new structural theory of organic chemistry, he was one of the first to use it in the classroom and to predict the existence of new organic compounds. By 1860, Butlerov had incorporated his own version into his lectures and had become one of its most influential and ardent advocates. Butlerov's contributions have only recently been given their due place in discussions of the development of organic chemistry by western scientists, and he is now accorded a place alongside Kekulé and Couper as one of the important founders of the structural theory of organic chemistry. Over the next quarter century, Butlerov was to become one of the most influential Russian chemists of all time. It is rather ironic that Butlerov, a strong proponent of structural theory at this pivotal time in its development, sent two of his brightest students to study with Hermann Kolbe—its most resolute opponent—when they left Kazan'.

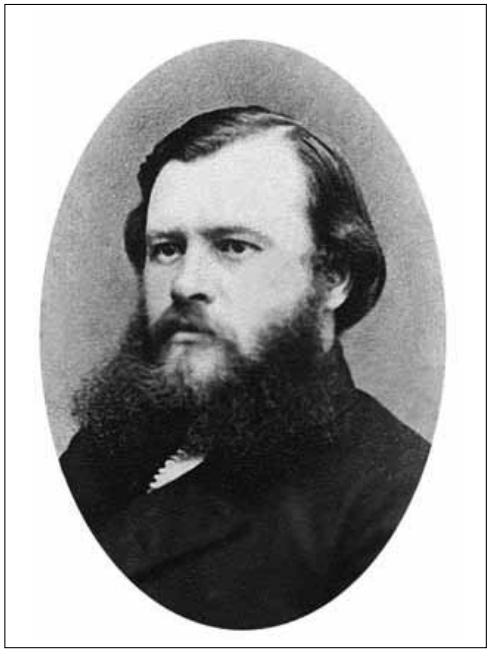
The subjects of this paper, Zaitsev and Markovnikov, had both entered Kazan' University as students in economics—*cameralisty*—and both came under the influence of Butlerov, who inspired them to become chemists. Unlike Zaitsev's student, E. E. Vagner (1849-1903), both students remained *cameralisty* through graduation. Of the two young chemists, it appears that Markovnikov, the older of the two, may have been the more theoretically inclined; certainly, it was Markovnikov who continued his mentor's work in structural theory as part of his master's degree. In contrast, Zaitsev appears to have been much more at home in the role of an experimentalist, and this is the nature of most of his contributions to organic chemistry.

One might have expected that being students of the great Butlerov, at the very time when he was making seminal contributions to the development of organic structural theory, would have cemented a friendship between the two young chemists. It actually appears that nothing could be further from the truth, and it is fascinating to speculate on the origins of this animosity, as well as on its importance in the development of organic chemistry as a whole.

Markovnikov graduated with a degree in economics in 1859. Following his graduation, Markovnikov began studies with Butlerov and wrote both *kandidat* (1860) and Master's (1865) dissertations under his direction. His *Magistr Khimii* (M. Chem.) dissertation, "On the Isomerism of Organic Compounds" (17), gave an incisive analysis of the state of organic structural theory and its

development, and was critical of Kekulé's overweening claims for his version of the theory and priority in its development. His doctoral dissertation, "On the Reciprocal Influences of Atoms in Chemical Compounds" (18), submitted four years later, was a brilliant theoretical exposition on the influence of structure on chemical reactivity. What we now know as Markovnikov's Rule—that the addition of hydrogen halides to unsymmetrical alkenes proceeds such that the major product obtained has the hydrogen bonded to the less substituted carbon atom—came out of this dissertation. The rule was published in both German (4a) and French (4b); but despite Butlerov's urgings that he publish the findings of his dissertation in German, it appeared as a complete entity only in Russian.

In the dissertation, Markovnikov not only gave a rationale of the regiochemistry of addition, but he went so far as to suggest that one should be able to predict the major product of an elimination, since this reaction would simply be the reverse of the addition reaction leading to it. In some ways, this prediction foreshadowed what we now know as the Principle of Microscopic Reversibility. Regardless, the application of this principle, as defined by Markovnikov, leads to the conclusion that since hydrogen iodide adds to 1-butene to give 2-iodobutane as the major product, elimination of hydrogen iodide from 2-iodobutane should give 1-butene as the major product.



Markovnikov

Markovnikov was an intuitively brilliant chemist whose theoretical insights earned him a place as one of the few Russian chemists to attain eminence outside Russia during his lifetime. However, he was also a prickly individual: a stubborn idealist whose character is perhaps best defined as a mix of jingoistic Russian, modernist rebel, and political *naïf*. Thus, despite the higher visibility and better reputation of the German journals, Markovnikov published some of his most important work only in Russian journals, in an attempt (ultimately futile) to raise western consciousness of Russian chemistry. At the same time, this loyal subject of the Tsar appears to have had a healthy disrespect for authority in all its personifications—except, of course, for his revered Butlerov. And finally, he seldom appears to have tempered his willingness to take a stand on controversial issues with a real appreciation of the potential consequences of doing so. Certainly, scientific eminence abroad and at home did not protect Markovnikov from his political enemies as it had protected Mendeleev.

This rather incongruous mix of characteristics, which resulted in Markovnikov's inspiring both fanatical loyalty and equally committed enmity, may explain some of his checkered career, which is illustrated by the mechanism of his removal from his Chair at Moscow. In 1881 the freedom that had been enjoyed by universities under the reforms of Aleksandr II were severely curtailed, and professors could, by vote of the faculty, be forcibly retired 25 years after their first appointment to an academic position. Markovnikov's appointment as Extraordinary Professor at Kazan' occurred in 1868. Thus, in 1893, his political opponents were able to use the arcane regulations of the Ministry of Education to orchestrate his ouster from the Chair of organic chemistry while Markovnikov and his supporters were absent from the University; and he was forced to turn over his chair to Nikolai Dmitrievich Zelinskii (1861-1953). The supervision of his doctoral student, Aleksei Evgen'evich Chichibabin (1871-1945), was left to his assistant, Konovalov, since Zelinskii did not want anything to do with the students of his predecessor.

After his graduation, Markovnikov took a *komandirovka* in western Europe, spending 1865 and 1866 with Kolbe in Leipzig. It is interesting to note that Markovnikov, the older student, actually followed the younger, Zaitsev, into Kolbe's laboratory. Markovnikov's adherence to the modern structural ideas of Butlerov led to more than one interesting discussion with Kolbe, who eschewed the term, "chemical structure," in favor of the term, "rational constitution," even though his theory was much closer to the more modern view held by Butlerov and Erlenmeyer than he would like to admit. Despite their occasional scientific differences, it is clear that Markovnikov both liked and respected his German mentor.

On his return to Russia, Markovnikov became *docent* at Kazan' University; and, thanks to the efforts of Butlerov, he was appointed as Extraordinary Professor (Associate Professor) of Chemistry. This is a critical

example of how Butlerov, who had already served two terms as Rector of the University, promoted his students by making the case that students in the cameral sciences at Kazan' were well prepared for careers as *scientists*, not just as members of the government bureaucracy. Butlerov's support—and his vigorous championing of students in cameral science as being as well qualified for careers in science as students in the Mathematical-Physical Faculty—was critical in the careers of Markovnikov and Zaitsev, both of whom had graduated in cameral science. Markovnikov was promoted to Ordinary (Full) Professor of Chemistry at Kazan' in 1869, succeeding his mentor. In 1871 he left the University and took up the post of Professor of Chemistry at Odessa; two years later, he took up his final position as Professor of Chemistry at the University of Moscow.

In contrast to his older contemporary, Zaitsev appears to have been much more astute politically. The son of a tea merchant, Mikhail Savvich Zaitsev, Aleksandr Zaitsev had—with the help of his uncle, the astronomer, Lyapunov—persuaded his father to allow him to study at Kazan' University, although his father imposed the condition that he study economics as a prelude to entering business. The death of his father shortly before his graduation and the sale of the family business and distribution of the proceeds among the sons immediately thereafter freed Zaitsev from the specter of a life spent in the mercantile guilds and eliminated his financial worries for a while.

While a student in economics at Kazan', Zaitsev had also fallen under the spell of Butlerov, and he had begun to work with him. While the Russian biographical literature, at least, implies that Butlerov claimed Zaitsev as a disciple from the beginning of their relationship, a reviewer has suggested that it is not really legitimate to call Zaitsev a disciple of Butlerov at this time, at least not in the reciprocal sense. He maintains that it should be stressed, instead, that while Zaitsev might have considered himself a Butlerov disciple, he was not close enough to Butlerov at this time to be counted as one of his disciples.

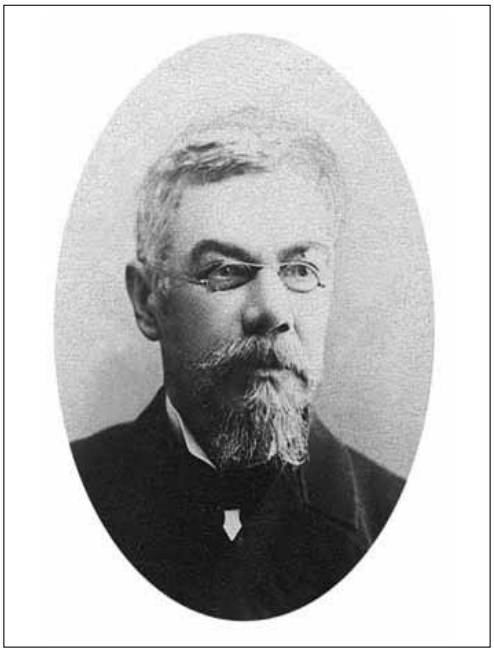
The removal of his financial worries (for a while, at least) and the elimination of his father's control over his future allowed Zaitsev to take the very risky and unconventional step of leaving Russia, as soon as he had graduated with his *Diplom*, to study in Western Europe with Kolbe, then the most influential organic chemist in western Europe. In studying with Kolbe, Zaitsev may have been influenced by his older brother, Konstantin Mikhailovich, who, in 1862, had become the first of a series of Kazan' students to study at Marburg. Rocke (19) has suggested that the steady stream of students from Kazan' to Marburg may have been at Butlerov's instigation, which would mean that Zaitsev's choice may still have been influenced by Butlerov.

While studying in Kolbe's laboratory, Zaitsev probably had time to consider the potentially serious consequences of his actions in leaving Kazan' before obtaining the degree of *kandidat*. At that time, the degree of *kandidat* was the minimum required qualification to be appointed to a salaried position as a laboratory assistant in Russian universities; and Zaitsev may have realized that his rather precipitous departure might have compromised his future. Thus, in 1863, after his first year with Kolbe, Zaitsev submitted a 76-page hand-written dissertation, "The Theoretical Views of Kolbe on the Rational Constitution of Organic Compounds and their Relationship with Inorganic Compounds" (20), for the degree of *kandidat*. The move could hardly have been more ill-considered. Not only did this dissertation expound favorably on the views of Kolbe, structural theory's most ardent opponent, but it was examined by Butlerov, structural theory's most ardent champion. Butlerov's evaluation of this dissertation was unusually acerbic. At one point he characterizes it as "a poor rendering of the German" and in other places mercilessly criticizes lapses in logic. Needless to say, the degree was not awarded.

Zaitsev remained abroad until his money was nearly depleted; and then, lacking the funds to follow Kolbe to Leipzig, he returned to Russia to seek a position. Now surfaced the first of his problems: without the *kandidat* degree, he was not qualified for a salaried position as a laboratory assistant. What he did to overcome this problem was characteristic of the man: he realized that there was but one individual who could restore him to the good graces of the administration of Kazan' University: Butlerov. So he offered him his services as an unpaid assistant. Why Butlerov bothered to help Zaitsev is something of a puzzle, since he had no compelling reason to do so. At Mendeleev's urging, Butlerov was already in negotiation with St. Petersburg University for the chair of Chemistry, and he had more than enough students wanting to work with him. But, by this time, Zaitsev's record in the laboratory of Kolbe, where he discovered the sulfoxides and the sulfonium salts (21), and his work with Wurtz, which had led to a series of five publications on the reactions of carboxylic acid derivatives (22), had marked him as a gifted experimentalist. Zaitsev's level of productivity in his three years abroad was clearly appreciated by Butlerov, whose actions permit one to

deduce that he recognized his skill and determined to preserve it for Russian chemistry (23). The impressive body of synthetic chemistry centered around zinc alkyls—notoriously air-sensitive and difficult reagents to work with—developed by Zaitsev and his students over the next three decades tends to affirm Butlerov's wisdom in helping Zaitsev re-enter the academic mainstream in Russia.

Immediately on his return to Russia, Zaitsev was shepherded by Butlerov through the process of writing his *kandidat* dissertation, describing the work he had done while a student in Wurtz' laboratory in Paris (24). As soon as he had obtained his degree, Zaitsev was appointed laboratory assistant in agronomy, and the direction of the agronomy laboratories was given over to him. At this stage, Zaitsev had re-entered the career mainstream. However, he had his sights set on a professorship in chemistry, and the only way to obtain a professorship was by holding the degree of Master of Chemistry or Doctor of Chemistry.



Zaitsev

This time it was not entirely Zaitsev's fault that his career nearly ended in ruins. His *kandidat* degree was in *cameral* science, and this meant that he was not formally eligible to receive the degree of *Magistr* in the Mathematical-Physical Faculty. Even here, his response to the problem was typical of the man: instead of waiting for his mentor Butlerov to plead his case, as he had done for Markovnikov before him, Zaitsev sought his own—legalistic—solution. Finding that a doctoral degree from a foreign university would satisfy the requirements, Zaitsev submitted a dissertation for the doctoral degree in chemistry to Kolbe at Leipzig (25). There, thanks to the influence of his former mentor (which suggests that Kolbe had fond memories of his Russian student), he was awarded the degree of D. Phil. in 1866 *in absentia*. Even with this degree in hand, however, there were some who were opposed to granting the exception that would allow him to submit for the master of Chemistry degree, and it was Butlerov who, again, came to the aid of his student by making the case very strongly for this graduate in cameral science.

At Butlerov's suggestion, Zaitsev submitted the work detailing his discovery of the sulfoxides at Marburg, for the degree of Master of Chemistry at Kazan' in 1867 (26). In 1870 he defended his doctoral dissertation, a two-part study entitled, "A New Method for Converting a Fatty Acid into its Corresponding Alcohol. Normal Butyl Alcohol (Propyl Carbinol) and its Conversion to Secondary Butyl Alcohol (Methyl Ethyl Carbinol)" (27).

With Butlerov's impending departure for St. Petersburg, Markovnikov was the obvious choice for his replacement, having substituted for him while Butlerov was abroad in the west making his case for priority in the development of the structural theory of organic chemistry. However, Markovnikov's temperament was such that the University administration was determined that he would not occupy the chair alone; unlike Butlerov, who was universally loved and admired, Markovnikov as the sole occupant of the chair in chemistry raised a specter that the University administration did not want to face. Another Butlerov student, Aleksandr Nikolaevich Popov (1840-1881), who had written a brilliant master's dissertation on structural theory under Markovnikov, was the first choice to occupy the second chair at Kazan'. However, before he could be formally offered that chair, he accepted the invitation of the chair of chemistry at Warsaw University and departed for Bonn to study under Kekulé prior to taking his new appointment. This left Zaitsev as the logical choice for the vacant chair at Kazan'.

Markovnikov's disdain for Zaitsev was very poorly disguised, and Zaitsev's appointment as Extraordinary Professor in May, 1869, left Markovnikov so chagrined that he wrote in a letter to Butlerov in October, 1869 (28):

> With the departure of Popov I am determined to speak to nobody. I see Zaitsev only before his lectures...

Further evidence of Markovnikov's contempt for his new colleague arose when Zaitsev submitted his doctoral dissertation. Markovnikov, appointed as the primary examiner of the dissertation, wrote an overtly positive review that was filled with negative innuendo. This attempt to derail Zaitsev's promotion to Ordinary Professor

failed because Butlerov and the university faculty were well aware of Markovnikov's personal animus towards Zaitsev; and so, on the strength of Butlerov's positive recommendation, he was awarded his doctoral degree and promoted to Ordinary Professor by a 19-12 split vote in November, 1871. Although the primary reason for Markovnikov's rancorous departure for Odessa is universally accepted as the dismissal of the popular Rector, Pyotr Frantsevich Lesgaft (1837-1909), Zaitsev's appointment as Ordinary Professor must have been a factor. Markovnikov left less than six weeks after Zaitsev's election.

The origins of the bad blood between Zaitsev and Markovnikov are not known explicitly, so some degree of inference (even speculation) is required to provide a plausible reason for their mutual antipathy. There are two plausible causes for the mutual dislike, and while the evidence for each individually is not especially strong, I submit that the combination of the two provides a reasonable rationale for the origins of the feud.

The first potential cause of the feud is Zaitsev's failed *kandidat* dissertation. At the time that Zaitsev submitted the dissertation, Markovnikov was completing his master's degree with Butlerov at Kazan'. Given that Butlerov later recommended Markovnikov as one of the formal opponents (i.e. examiners) of Zaitsev's doctoral dissertation, I suggest that Butlerov might also have shared this early dissertation with Markovnikov, especially in light of the latter's work with structural theory. Were this to be the case, the apparent apostasy of Zaitsev, another student who had received instruction from his revered Butlerov, would undoubtedly have been viewed by the very nationalistic Markovnikov as nothing less than an idealogical betrayal of Russia and Russian chemistry.

The second potential cause may be Kolbe himself, who may have (unwittingly) negatively affected the relationship between his two young Russian students. To what extent he compared the gifted theoretician Markovnikov with the talented experimentalist Zaitsev is not clear. However, given his practical turn of mind and the evidence of his support for Zaitsev's doctoral dissertation *in absentia*, it is probable that Kolbe had fond memories of Mr. Zaitsev. Consequently, Markovnikov may have occasionally found himself compared to his younger colleague by the Herr Dr. Professor. Such comparisons would have prompted a terrible dilemma for Markovnikov, given that any praise of Zaitsev by Kolbe would, of necessity, have meant praise for a Russian chemist trained by Butlerov …but at the price of having been compared to an apostate who had flouted Russian customs.

Unlike that of his demonstrative colleague, Zaitsev's career was not colored by outbursts that provide a window into his character, which means that one must use inference to divine his opinions. His career, as we have already pointed out, suggests that Zaitsev was far from being a political *naïf*, although, as a young man, he did suffer from an impetuousness and lack of foresight that almost derailed his career before it had begun. But Zaitsev always seemed to know how to fix the problems caused by his impatience: he appreciated who it was he needed to cultivate, and when. He seems to have been aware of Butlerov's feelings about building a Russian professoriate in Russian universities, and his appeal to Butlerov as an unpaid assistant to allow his return to Russia was a masterful political stroke.

By 1875 Markovnikov had left Odessa, where he had served as Professor of Chemistry from 1871-1873, and had become established in the Chair at Moscow University, where he was working diligently to upgrade the laboratory. Zaitsev, likewise, had settled into what was to become a productive, 40-year career at Kazan'. Insofar as I have been able to determine, the interaction between the two by this time was minimal, at best.

Markovnikov's international reputation had been established by his report of what we now call Markovnikov's Rule for addition, which appeared first in the *Annalen der Chemie und Pharmazie* in 1870 (4a). Zaitsev's paper, in which he set out what is now known as Zaitsev's Rule, appeared in 1875 (29). The paper, which was largely a literature review and contained results from his students Grabovskii and Vagner, appeared right after Markovnikov had begun publishing his series of three papers in the *Comptes Rendues* detailing his empirical rule for addition (4b). Zaitsev's was not the first report of regioselectivity in an elimination reaction, however. Some three years earlier, Popov had speculated on the regiochemistry of dehydration reactions in a letter to Butlerov, describing his oxidation work with chromic acid (30), and in a paper in 1873, where he speculated on the regiochemistry of dehydration during the oxidation of 3-methyl-2-butanol to acetone and acetic acid (31). In a paper presented at a conference in Kazan', Popov, speculating again on the regiochemistry of dehydration reactions during oxidation, suggested that this idea might be extended to dehydrohalogenation reactions (32). Zaitsev would certainly have been aware of Popov's papers but did not acknowledge his work in the 1875

paper; it is not clear why Popov's work was not cited or acknowledged.

What follows is, admittedly, speculative because we cannot know the extent to which the clash of personalities contributed to Zaitsev's decision to pursue this line of research, and, more importantly, to the timing of its publication. As implied above, Zaitsev's temperament is not illuminated by his actions nearly as much as is Markovnikov's. Nevertheless, it seems reasonable that there is enough circumstantial evidence to suggest that Zaitsev's Rule, at least, may ultimately be a result of a desire to get back at the one person who held him in contempt: Markovnikov. This, of course, leads to an ultimate irony, that these two rules of regiochemistry in organic reactions stand side by side in the sophomore organic chemistry curriculum, as neither of their protagonists would in life.

REFERENCES AND NOTES

* The names of the principal subjects of this paper will be transliterated from the Cyrillic as Zaitsev and Markovnikov throughout the body of this manuscript; in literature citations this spelling will be used in reference to articles in Russian. In the references to journal articles in German and French, their names will be spelled exactly as they appear in the journal (e.g. Saytzeff and Markownikoff). The same treatment has been applied to the journal articles of other Russian chemists (e.g. Butlerov).

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BOOK REVIEWS

Rediscovery of the Elements. James I. and Virginia R. Marshall. JMC Services, Denton TX. DVD, Web Page Format, accessible by web browsers and current programs on PC and Macintosh, 2010, ISBN 978-0-615-30793-0. jmarshall@jennymarshall.com $60.00 ($50.00 for nonprofit organizations {schools}, $40.00 at workshops.)

Before the launching of this review it needs to be stated that DVDs are not viewable unless your computer is equipped with a DVD reader. I own a 2002 Microsoft Word XP computer, but it failed. I learned that I needed a piece of hardware, a DVD reader. It can be installed inside the computer or attached externally. The former is cheaper, in fact quite inexpensive, unless you have to pay for the installation. Fortunately, a friend did this for me.

The first printing of *Rediscovery* is in process as I write, to be available in time for the BCCE (Biennial Conference of Chemical Education), which will be held in August, 2010 in Denton, TX, the authors' home campus. I am looking at a preliminary version, but I hold a complete list of the few significant changes and some corrections.

Clicking anywhere on the cover picture propels us to the opening statement and table of contents. During the last eleven years the authors personally visited every site where a chemical element was discovered. And opening any of the links reveals the extraordinary achievement this DVD represents, based on prodigious labors.

Here you can find mini-biographies of scientists, detailed geographic routes to each of the element discovery sites, cities connected to discoveries, maps (354 of them) and photos (6,500 from a base of 25,000), a time line of discoveries, 33 background articles published by the authors in *The Hexagon*, and finally a link to "Tables and Text Files," a compilation probably containing more information than all the rest of the DVD. I will discuss this later, except for one file in it: "Background and Scope." Here the authors point out that the whole project of visiting the sources, mines, quarries, museums, laboratories connected with each element, only became possible very recently. Four recent developments opened the door: first, the fall of the Iron Curtain allowing easy access to Eastern Europe including Russia; second, the universality of email and internet communication; third, digital cameras; and fourth, GPS navigation.

Being something of an historian, I tend to skim lists of names, and I was surprised to discover Liebig among the 217 names for whom the authors supply thumbnail biographies and explanatory background pictures. What did Liebig have to do with the elements? Well, I learned he had a sample of bromine before Balard had identified the element. However, Liebig had thought it was iodine chloride and labeled it as such. After Balard made his announcement, Liebig moved the bottle to his cupboard of "Mistakes." So I had to look up bromine in the list of elements, as well as Balard and Liebig among the scientists.

Do you want to know where bromine was discovered? Join Jim and Jenny Marshall as they travel to

bromine's place of discovery. And thanks to the magic of clickable DVDs, you can catch the travelers and they will show you. Look up bromine in the list of elements and you learn that it was identified as an element at the school of pharmacy in Montpellier, France by Balard, who treated local brines with chlorine. Under bromine you also learn of bromine's crustal abundance, and you see a rare solid mineral that contains silver bromide. The formula of the ancient Phoenicians' Royal Purple (dibromoindigo) is given, as well as a picture of a murex seashell from which the dye was extracted. Under the Liebig biography you are asked to go to Montpellier. Why? You view numerous views of the city and of the school of pharmacy, but one panel is marked LIEBIG and tells of the latter's misidentification of the element—in French.

Shown a map of Montpellier, you can find a map directing you also to every other location where an element was discovered. And at those locations you will find photographs taken by the Marshalls showing the major sites, buildings, science-related institutions, and the ores and rocks where the element is most often found.

Those 217 names do not include duplications. You will find Andrada both under A and under D because his fuller last name was de Andrada, but he is not counted twice.

The elements are listed alphabetically for easy location, but where it says "next element" you might fear that you will be taken to the next element alphabetically. The authors, however, know their chemistry and they know what chemists and chemistry teachers are looking for. The next element refers to the one coming next in the periodic table, the one with one extra proton in the nucleus, the one with the next higher atomic number.

In preparation for their Magnum Opus the Marshalls published 33 articles in *The Hexagon*, the journal of Alpha Chi Sigma. You are linked to these and can read them whenever you want to, because they are part of the DVD. They include one mysterious title *Phosphoro de Bologna*, which makes you guess it is about phosphorus but you are mistaken. It is about phosphorescent substances such as barium and calcium sulfide. This and the other *Hexagon* articles contain detailed references to the primary or secondary literature, Lavoisier's treatise, and Partington—also to Oliver Sacks, who discusses phosphorescent materials on pages 226-7 of his memoir *Uncle Tungsten*. (Sacks made a special trip to Denton, TX to visit the authors and see their collection of elements and ores. In New York, Sacks has his own collection of elements, each sample in its proper place in an elaborate periodic table.) Three *Hexagon* articles focus on vanadium because it was first discovered by del Rio in Mexico. The information and samples were brought by von Humboldt to Europe, where it was not believed because of typical Eurocentric prejudices; it was then rediscovered in Swedish ores, and Wöhler gave convincing proof that the Swedish and Mexican elements were the same. This leads to a general discussion of Wöhler's life and work, including his artificial creation of urea in 1828 for which the original publication is given in *Ann. Phys. Chem.*

Another link takes you to biographical information about the authors. There you learn that James Marshall obtained his doctorate in organic chemistry at Ohio State University and ever since has taught and done research at the University of North Texas, while Virginia (Jenny) is a computer expert and has taught the subject in schools and to yearbook staffs. She is responsible for much of the helpful computer wizardry in this DVD that makes it such a pleasure to use.

On their opening page the authors announce that this DVD was designed for students, teachers, and interested laymen. However, historians of chemistry and of the chemical elements should not, because of this disclaimer, pass it by. There is much here that may be helpful: the maps, the new photographs, and the links that may take the scholar to new sources and new locations.

You may find some typographical or substantive errors. Having been an editor (mostly part-time) for over two decades, I know that no matter how hard one tries, an error-free document is practically impossible. And authors greatly appreciate learning of errors and problems because corrections can be made for a new printing, even for a DVD, long before a new edition is contemplated.

Focusing now on the link entitled "Tables and Text Files," it contains seven sections of which the first is "Acknowledgments," five and a half pages, single spaced, of 194 individuals who were "direct contributors" to the *Rediscovery* project. Most were visited where they worked, in their museums, laboratories, university departments; and a few are well known in the history of chemistry community: Günther Beer of Göttingen; William Brock of Leicester (on Crookes); Norman Craig, Oberlin (Aluminum); Roald Hoffmann, Cornell; George Kauffman (on Döbereiner); Peter Morris, Science Museum, London; Alan Rocke; Oliver Sacks.

In one section called "Additional Explanatory Notes" the authors mainly discuss GPS geographical data, compass orientations, and latitude and longitude given with a precision of 0.01 minutes of ark. "Background and Scope," partially discussed above, is a fascinating account of all that went into the creation of *Rediscovery*. We also learn that multi-volume background print sets have been deposited in the Library of Congress and a few other sites. There follow a historical sketch of discoveries, from the ancients and alchemists to our time, covering over a hundred pages; Tables of Auxiliary Sites, comprising a list of statues, monuments, each with GPS specifications (134 entries); then a table of museums; a table of "primary discovery sites"—element discovery events, GPS etc. (398 entries), with ratings: b++ = building still exists, or lab still functional, q- = quarry filled in; 65 pages including specifications for every element.

Thinking back to my boring high school exposure to the elements (I only chose chemistry because of a "sixth form" exposure to organic compounds), I am certain this DVD would have transformed the experience: allowing faculty and students to view the elements on the screen, search for the elements' origins, meet with the discoverers, and pursue student questions probably towards convincing answers. This DVD is a monumental achievement. *Theodor Benfey, Greensboro, NC*.

The Age of Wonder: How the Romantic Generation Discovered the Beauty and Terror of Science. Richard Holmes, Vintage Books, New York, NY, 2008, xxi + 552 pp, ISBN 978-1-4000-3187-0. $17.95

The phrase "Romantic Science" sounds like either the caption of a lobby poster for the 1940s movie about Marie Curie or else perhaps an oxymoron. The late 18th century movement called Romanticism emphasized imagination and emotions rather than the rationality usually associated with science; surely it is a mistake to conflate these two very different ideas. On the contrary, Richard Holmes argues that there was a tremendous overlap between these two concepts, both in terms of the people involved as well as the way the world was being viewed. Romanticism was an attempt to focus more directly on the study of nature, and the scientific advances of the early part of the 19th century were just as much a part of that change as were the books and poems that are now identified as Romantic.

The Age of Wonder is literally bookended by voyages of discovery. It begins in 1768 with Joseph Banks, setting sail with James Cook as a botanist on the HM Bark *Endeavour* and ends with Darwin's voyage on the *Beagle*, which began in 1831. Banks' activities provide continuity throughout the rest of the book, first with his adventures, both scientific and amorous, in the South Seas, and then as the long-time President of the Royal Society, where he often played a key role in the development of science policy. However, Holmes places two men at the center of his narrative: the astronomer William Herschel and the chemist Humphry Davy. Two chapters deal with Herschel who discovered the planet Uranus, and his sister Caroline, who made significant astronomical contributions. Together, they changed the way humans looked at space and time. If any scientist ever reached the sublime that was so longed for by the Romantics, it was Herschel, with his new visions of the heavens gained from the powerful telescopes he produced.

Sir Humphrey Davy is the name that is most likely to catch the eye of historians of chemistry. Holmes discusses Davy's personal relations with many of the most important personalities of the Romantic period, like Coleridge, Shelley, and Southey, and quotes extensively from Davy's own poetry. It should not be surprising to hear Davy called a Romantic scientist. As early as 1812 Thomas Young, who was Davy's colleague at the Royal Institute, wrote, "Davy was born a poet and has only become a chemist by accident." (1) Fullmer points out that Wilhelm Ostwald labeled Davy as a "romantic" scientific personality as early as 1907, and this label has been reasserted several times since then (2). David Knight's biography of Davy was notable for describing not only Davy's scientific work but also his poetry and his relations with the major figures of the Romantic movement (3).

Holmes brings an unusual perspective to this work, since he is best known for his prize-winning studies of the Romantic poets, like Percy Bysshe Shelley and Samuel Taylor Coleridge. Holmes' work on Coleridge led him to recognize how active Coleridge was in the science of his time and also the friendship that existed between the English Romantics and those, like Davy, who were creating a new scientific revolution. Holmes brings the eye of a literary critic to this discussion. When he writes that Davy's *Consolations in Travel, or The Last Days of a Philosopher* is the "first ever scientific autobiography in English" and classifies it with other romantic memoirs of the time, like Wordsworth's *Prelude* and Coleridge's *Biographia Literaria*, his evaluation is not to be taken lightly. The *Consolations* was written as Davy felt death approaching and is a set of dialogues that summarize his life, a mixture of autobiography, travelogue, geology, imaginary voyages, philosophy, and even an early form of science fiction. One of these dialogues, titled "The Chemical Philosopher" argues that science is a progressive force for good and stated that, "It may be said of modern chemistry, that its beginning is pleasure, its progress knowledge, and its objects truth and utility." It is easy to see why Davy's last work became a guidebook for many in the next generation of scientists.

Holmes suggests that the era of romantic science was rather brief, lasting only a few decades. He argues that unlike the scientific revolution of the late seventeenth century, the most important characteristic of Romantic science may well have been the commitment to communicate with the general public. It was the age of public science, lectures, laboratory demonstrations, and popular textbooks. Davy was certainly successful at attaining this goal; his lectures at the Royal Institute being extremely popular. Perhaps most interesting, he was very successful at attracting young women to his lectures, even though originally the intended audience had been middle-class artisans. (Holmes mentions the large number of Valentine's Day cards that Davy received from his admirers.) In the process a new audience was created for popular science, which prepared the way for authors like Jane Mercet (4), who wrote textbooks for young women.

Over one fourth of the book is devoted to Davy. Even a chapter on Vitalism and the novel *Frankenstein* points out that Mary Shelley's novel was inspired, in part, upon hearing one of Davy's lectures when she was only fourteen years old. Many of the stories Holmes tells may already be familiar, such as Davy's early experiments inhaling various gases, and his work on the chemical effects of electricity, chemical theory, and the safety lamp for miners. Holmes also discusses the personal side of Davy's life, including his puzzling relationship with Michael Faraday, his curious marriage, and his attempts as President of the Royal Society to reconcile the conservatism of that society with the demands of a new generation of young scientists, like John Herschel (William's son) and Charles Babbage. His failure to satisfy these young scientists eventually led to the founding of the British Association for the Advancement of Science in 1831 and a move towards increased professionalization of science. This trend continued into the next generation with Thomas Huxley and the X-men (5).

The general impression that the Romantic poets were anti-scientific seems to have resulted mainly from an 1817 dinner party (Holmes suggests that it was more like an extended drunken luncheon) attended by Wordsworth, Keats, and Charles Lamb among others (p 318). During the rowdy discussion that resulted, both Lamb and Keats mocked the reductive approach of science. These comments were recorded and publicized by the party host, Benjamin Haydon, who was a passionate fundamentalist Christian and was eager to hear any criticism of what he considered to be godless science. Holmes suggests that the absence of both Shelley and Coleridge from this event was especially significant, since if either had been present, the discussion would have likely gone in a much different direction, assumedly more favorable to science.

On the other hand, a later story (p 429) describes how Davy and Coleridge argued about whether science or the arts had the greater effect on humankind. Coleridge said that, "My opinion is this - that deep Thinking is only attainable by a man of deep Feeling, that all truth is a species of Revelation. The more I understand of Newton's work, the more boldly I dare utter to my own mind . . . that I believe the Souls of 500 Sir Isaac Newtons would go to the making up of a Shakespeare or a Milton . . . " In a footnote, Holmes explains that when the quote by Coleridge was repeated at a symposium sponsored by the Royal Society in November, 2000, one of the distinguished scientific participants (whom Holmes does not name) exclaimed, "That is complete and utter *balls* . . . , We don't have to put up with such Rubbish." Apparently, Coleridge may have been less enthusiastic about science than Holmes suggests. It is amusing that even 200 years after his death this dispute between science and the arts could still produce such a strong reaction.

The Age of Wonder is an excellent book, not just because it places science firmly in the context of the

culture of the time but also because it tells great stories. Beyond the many stories about Davy, chemistry teachers will find that the chapter on the early history of ballooning will provide some fascinating anecdotes they can use in their lectures. The book has been widely reviewed and recommended in nonscience publications. *It* won the Royal Society Prize for Science Books in 2009 and was named the number-one nonfiction title for 2009 by *Time* magazine. It seems unusually appropriate for a book that describes the romantic desire to communicate the wonder and meaning of science to the general public to be so widely popular in modern times.

1. T. E. Thorpe, Ed.., *Humphry Davy, Poet and Philosopher*, Nonsuch Publishing, Dublin, 2007.
2. J. Z.Fullmer, *Davy's Biographers: Notes on Scientific Biography. Science,* **1967,** *155*,. 285-291.
3. D. Knight, *Humphry Davy, Science and Power*, Cambridge University Press, Cambridge, 1996.
4. J. Mercet, *Conversations in Chemistry*, Oliver D. Cooke and Co., Hartford, CT, 1826.
5. A. Desmond, *Huxley: From Devil's Disciple to Evoution's High Priest*, Addison-Wesley, Reading, MA, 1994.

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The Alchemy of Glass: Counterfeit, Imitation, and Transmutation in Ancient Glassmaking. Marco Beretta, Science History Publ., Watson Publ., Sagamore Beach, MA, 2009, xv + 198 pp, ISBN 978-0-88135-350-1, $59.95

This short but ambitious treatise summarizes the conclusions of a project that began as an interdisciplinary seminar on glass and its relationship to the development of the chemical sciences from Antiquity to Byzantium and the Early Modern era. The seminar was held at the Department of Cultural Heritage of the University of Bologna in 2002, where the author Marco Beretta teaches history of science in addition to his other appointment, as vice-director of the Institute and Museum of History of Science in Florence. Thinking of alchemy as only a futile and often deceitful attempt at the transmutation of base metals to gold has often distracted scholars from the study of ancient alchemical texts that describe chemical operations and the intellectual efforts of early alchemists to develop a theoretical framework for the interpretation of such transformations. Beretta brings a fresh and innovative approach to the study of these texts. His strategy is to study the evolution of alchemical thought by tracing the history of a specific material, in this instance glass. In the process he offers us inspiring insights into the early debate about the structure and identity of matter.

Four of the five chapters examine the history of glass making from ancient Egypt and Mesopotamia through Greece, Rome, and Byzantium to the early modern era. Chapter Four is reserved for a more in-depth discussion of glass and alchemy. The thorough bibliography of primary and secondary sources alone makes acquiring this book a sound investment. The challenging ideas of the text are further amplified in copious footnotes, which, however, to be appreciated fully require a working knowledge of French, Italian, and Latin.

In Chapter 1, Beretta follows the origins of glass to Ancient Mesopotamia (in ca. 2500 BC) and its migration to Egypt around 1400 BC, correcting along the way the common misconception of glass as a Phoenician discovery. While the Mesopotamian glassmakers were no alchemists, the literary style of Mesopotamian glass recipes and the belief in propitious days for the performance of certain experiments were adopted by alchemy. But already Egyptian glass technology is viewed as giving rise to one of the central questions of alchemical thought, the possibility of artificially producing natural bodies. The question is raised in conjunction with the equivalence of natural and man-made lapis lazuli. Color emerges as a key property and color change as indicative of transmutation.

In Chapter 2, the diverse views on the nature of matter in Greek philosophy are examined, with Greek

speculations about the nature of glass as the backdrop. The classification of glass together with rock crystal and metals as different manifestations of water icosahedra is seen as hinting at the possibility of transmutation. Glassmaking is also thought to have inspired Heraclitus' emphasis on the centrality of fire in the transformations of matter. Chapter 3 is dedicated to an analysis of the rise of glass blowing and its economic impact. This technological revolution transformed the glass industry both qualitatively and quantitatively. The author is even able to connect glass blowing to the development of theories of vision and the descriptive anatomy of the human eye.

For the historian of alchemy and chemistry, Chapter 4 is where the central arguments of the book come together. In the first half of the chapter Beretta revisits the debate about the relationship of the artificial to the natural, which was to become, as mentioned above, a central theme of alchemy. The expansion of the Roman Empire had broadened the gemological experience of its citizenry. With it came the attempt to imitate precious stones with similar objects made of colored glass. Conservative philosophers like Pliny and Seneca derided the attempt to imitate nature, while alchemists like Bolus of Mendes and Pseudo-Democritus viewed such activity as an actual fabrication of the real thing. Here color becomes once again a key property, indicative of the equivalence of real and man-made gemstones just as the ancient Egyptians used color when postulating the equivalence of real and artificial lapis lazuli.

The second part examines the role glassblowing has played in the development of alchemical/chemical laboratory equipment. A thorough survey of Roman and Alexandrian laboratory glassware is given together with the obligatory reference to the inventions of Mary the Jewess as chronicled by Zosimos of Panopolis. While familiar territory for the chemical historian, the section is an excellent source of bibliographical information on the subject.

One of the book's greater contributions is the innovative approach of concentrating on the history of one particular material, glass, to shed light on the evolution of broader issues in the philosophy of matter. It is perhaps interesting to note that an analogous situation arises when we examine the attempts of Islamic and European potters to duplicate Chinese porcelain. They, too, were guided by alchemical reasoning both in developing their ceramic formulations and in deciding on the equivalence of their materials to the "white gold" from China. *Dr. Nicholas Zumbulyadis, Independent Scholar (retired Eastman Kodak Research Laboratories), Rochester, NY 14613.*

Image and Reality: Kekulé, Kopp, and the Scientific Imagination. A. J. Rocke, University of Chicago Press, Chicago, IL, 2010, xxvi + 340 pp, ISBN 978-0-226-72332-7; $45.

There can be little doubt that the development of the structural theory of organic chemistry during approximately the years 1850-1874 marked one of the greatest intellectual achievements of 19th-century science. Regrettably, the teaching of organic chemistry now usually skates lightly over this crucial period. Of course, the argument has been made that the time constraints of standard courses necessitate this omission to permit coverage of material of more immediate relevance to the modern state of the field itself and to cognate disciplines such as cell biology, pharmacology, and medicine. But I believe there is another reason for our reluctance to teach that history: the events and ideas of that time are extraordinarily hard to unravel and set out in some kind of logical development. Modern students would be likely to ask, with some justification, why they have to learn about all those early vague and mostly erroneous formulations, which have no practical application to the present day. Yet modern chemists, after years of research creating and using advanced tools and ideas, surely must look back and reflect on how we got to this point. We have needed a guide to lead us through the thickets of conflicting notional (and notational) schemes of our forbears of that period and to show us how our present ideas emerged. It is hard to think of someone more qualified to do this than the distinguished historian of chemistry, Alan Rocke. Fortunately for us, he has produced the present work which speaks directly to this issue.

The connective thread of Rocke's narrative is the development of the concept of molecular structure. In the first half of the 19th century, key ideas that the modern chemist takes for granted, such as molecules, equivalents,

valences, and bonds, were hazy and imprecise. Even the atomic weights of the atoms were in dispute. It was not obvious that chemists could ever enter what Rocke aptly calls the "microworld" and determine the actual relative dispositions of atoms. How the community of organic chemists surmounted these difficulties is not a straightforward chronicle of events. It required chemists to realize explicitly that each molecule has a specific structure. From the perspective of the 21st century, it is hard to understand how something now so commonplace took so long to become established. Rocke does a masterful job of teasing out the exchanges of ideas and the interactions of diverse personalities that fueled this growth. A special feature of the book is its fascinating exploration, in the final two chapters, of the role of the imagination in scientific discovery. The influence of dreams, the "Eureka moment," and the contributions of modern cognitive science in illuminating the actual mental processes of discovery are examined perceptively.

Chemists will enjoy several prose portraits of some of the pioneers of the structural revolution. Among them was Alexander Williamson, an English chemist of Scottish background. I venture to say that many present-day chemists would be surprised by this assessment, for Williamson is remembered now mostly for his synthesis of unsymmetrical ethers. Rocke, however, convincingly describes his contributions as having much deeper significance in the powerful impetus they gave to the concept of structure, leading the great August Kekulé to call Williamson "that wisest of men and most learned of philosophers." Other fascinating portraits include those of the brilliant but troubled and tragically unstable Archibald Scott Couper, the feisty Alexander Crum Brown, and the delightful polymath Herrmann Kopp. Ever the combative rear-guardsman, Herrmann Kolbe (whose life Rocke has examined in detail in an earlier book), tenaciously contested the full flood of the revolution almost to the bitter end.

Rocke's analysis of Kekulé's leading role in the new thinking is based not only on the published record of scientific papers and books but also on a meticulous and illuminating study of letters, unpublished writings, and other sources. An intriguing insight is the importance of Kekulé's early training as an architect.

Among its other virtues, the present book shows Rocke's singular ability to project his thoughts into the historical situation as the proponents experienced it. This helps us to put aside our own advantage of hindsight and live through the discovery process ourselves. A prime instance of this is his account in Chapter 5 of the debate between Kekulé and Crum Brown on the structure of "pyrotartaric acid," (methylsuccinic acid). As Rocke shows, Crum Brown won the argument at the time. However, what Rocke does not show, but what the alert modern reader will detect, is that although Crum Brown's structure was correct, in the light of what we now know, his reasoning was erroneous. I leave this (as I suspect that Rocke did) for a study problem.

This superb history is one that chemists and general readers, be they students, teachers, practitioners, historians of science, or just persons interested in the growth of ideas, will read with deep interest and pleasure. *Jerome A. Berson, Department of Chemistry, Yale University, New Haven, CT 06520. Mailing address: 200 Leeder Hill Drive, Apt. 205, Hamden, CT 06517,*

Erich Hückel (1896-1980) From Physics to Quantum Chemistry. Andreas Karachalios, translated by Ann M. Hentschel, Boston Studies in the Philosophy of Science, Vol. 283, Springer-Verlag, Dordrecht, Heidelberg, London, New York, 2010, x + 200 pp. ISBN 978-90-481-3559-2; $139.

Erich Hückel and the late American comedian Rodney Dangerfield shared one thing in common. They "got no respect!" Hückel's contributions to molecular orbital theory have been undervalued by the quantum chemistry community for many years. Jerome Berson's 1996 article in the centennial year of Hückel's birth (*Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 2750-2764) played a big part in calling attention to Hückel's contributions, and now we have this fine biography by Andreas Karachalios of the University of Mainz that will allow English-reading scientists to evaluate Hückel's work in detail. Although Hückel wrote an autobiography shortly before his death in 1980 (*Ein Gelehrtenleben Ernst und Satire*, Verlag Chemie, Weinheim, 1975), the lamentable lack of knowledge of German among present day American chemists (your reviewer among them) means that an English language biography is absolutely necessary for US readers to appreciate Hückel's accomplishments.

Karachalios obviously used Hückel's autobiography a great deal in crafting this work, but he also made use of many supporting documents—letters to, from, and about Hückel, minutes from his oral examinations, evaluations in connection with job searches, reports to the Rockefeller Foundation, etc. The result is a thorough description of Hückel's life coupled with a detailed description of his work in quantum chemistry. Over three-fourths of the book touches on events prior to the outbreak of World War II. Sadly, there was not much of significance to report on after the war was over.

The author points out the significance to quantum chemistry of the year 1896, for Robert Mulliken and Friedrich Hund were born in that year along with Hückel. His father Armand was a doctor and an amateur scientist. He encouraged the scientific interests of his three sons, Walter, Erich, and Rudi. Walter, who went on to become an outstanding organic chemist, undoubtedly helped move Erich's research into areas of significance to organic chemistry. Hückel took a doctorate in physics from Peter Debye, worked for David Hilbert and then Max Born, and then took a second degree (the Habilitation) from Debye. His degree was on the theory of strong electrolytes. This resulted in the famous Debye-Hückel theory of electrolytic solutions, probably the introduction for most of us to the name of Hückel. Receiving an international fellowship, Hückel spent time at the Niels Bohr Institute in Copenhagen in 1929, a stay that probably inspired him to apply quantum mechanics to chemistry.

Hückel's first important excursion into quantum chemistry dealt with the nature of the double bond (*Z. Phys.*, **1930,** *60*, 423-456). Scientific thought at that time was of the view that the two bonds were chemically equivalent. Hückel's result was that there were two bonds, bonds that would correspond to what we now say are a π bond and a σ bond. The next year Hückel published his famous paper on aromaticity, a paper much more referenced than read (*Z, Phys.*, **1931**, *70*, 204-286). Like the paper on double bonding, Karachalios goes over this 82-page paper in detail. Hückel actually treated the benzene problem with two methods—one equivalent to the valence bond method and the other with what we now call the Hückel MO theory. His MO results showed that benzene should have special stability but that cyclobutadiene and cyclooctatetraene would not, *i.e.*, results consistent with what later chemists called the 4n + 2 rule. Karachalios devotes about 64 of his 200 pages to these two important papers.

Unfortunately, Hückel's treatment did not carry the day in the 1930s. Pauling and his coworkers pushed their use of resonance theory. Hückel was a weak communicator, while Pauling was superb in that area. In his autobiography Andrew Streitwieser states that Hückel molecular orbital theory did not come into its own until the 1940s (*A Lifetime of Synergy with Theory and Experiment*, ACS, Washington, DC, 1997, p181), and Streitwieser mentions that Hückel himself (p 182) attributed acceptance of HMO theory to Streitwieser's classic book, *Molecular Orbital Theory for Organic Chemists*. Perhaps Streitwieser summed up the situation best with these sentences I quote from p 181 of his autobiography:

> Erich Hückel was a physicist who worked between two worlds. Because he was a physicist, organic chemists paid no attention to him, and because he worked in chemistry, physicists paid him no heed.

Despite Debye's best efforts, he was unable to obtain a permanent position for Hückel. Hückel first wound up at Leipzig with the equivalent of a senior post-doctoral position and then in 1930 went to Stuttgart as a lecturer, where he remained until 1937. All this time he was supported by what we would call in the US "soft money." This probably played a part in his decision in 1934 to join an organization associated with the Nazi party. A position at the University of Marburg became open in 1937. The prime candidates were Hückel, Friedrich

Hund, and Helmut Hönl. The faculty favored Hund, but Hückel's favorable political activity won the day. After the war Hückel suffered various illnesses and fits of depression. He never regained his creativity and drive from the 1920s and 1930s. He retired in 1962 and died on February16, 1980.

I have often wondered why Hückel and for that matter Friedrich Hund never won the Nobel Prize. The optimum year would have been 1966—the year that Robert Mulliken won an unshared Nobel Prize in chemistry for his work on molecular orbital theory. There would have been room for two other people to share this prize. Indeed, in his autobiography (*Robert S. Mulliken: Life of a Scientist*, Bernard J. Ransil, Ed., Springer-Verlag, Berlin, Heidelberg, New York, 1989) Mulliken stated (p 192) that he would have been happy to share the prize with Hund. I imagine in 1966 Hückel would still have been viewed as not at the same level as Mulliken, but surely Hund's stature equaled that of Mulliken. It would be interesting to know whether in the '60s Hund and Hückel had been nominated for the award. Unfortunately, knowledge of Nobel nominations is not available until 50 years have passed after the nomination. So far as name recognition is concerned, present day chemistry students have all heard of Hund (Hund's Rule), those taking organic chemistry know about Hückel molecular orbital (HMO) theory;but very few will ever have heard of Mulliken. Still, I imagine Hückel and Hund would have gladly traded their posthumous fame for a share of the Nobel Prize. One strength of the book is the extensive set of footnotes. Readers should look at them in detail, because often they contain fascinating mini-biographies of significant figures in physics and chemistry. Occasionally the footnotes are used inefficiently. For example, the author uses several footnotes to give biographical details about noted chemists Hermann Mark and Christopher Ingold, when he could simply refer to Mark's autobiography (*From Small Organic Molecules to Large: A Century of Progress*) or to Kenneth Leffek's biography of Ingold (*Sir Christopher Ingold, A Major Prophet of Organic Chemistry*). Also, would it have cost too much to have included just one picture of Hückel? However, these are minor quibbles. This is an important and much needed book. I consider it a must buy for historians of quantum chemistry. Now what we need next is an English translation of Hückel's autobiography. Chemical Heritage Foundation, are you listening? *Dr. E. Thomas Strom, Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019-0065.*

FUTURE ACS MEETINGS

March 27-31, **2011**—Anaheim, CA

August 28-September 1, **2011**—Denver, CO

March 25-29, **2012**—San Diego, CA

August 19-23, **2012**—Philadelphia, PA

April 7-11, **2013**—New Orleans, LA

September 8-12, **2013**—Indianapolis, IN

March 16-20, **2014**—Dallas, TX

September 7-11, **2014**—San Francisco, CA

March 22-26, **2015**—Denver, CO

August 16-10, **2015**—Boston, MA

March 13-17, **2016**—San Diego, CA

August 21-25, **2016**—Philadelphia, PA

April 2-6, **2017**, San Francisco

September 10-14, **2017**, St. Louis

LOST ARTIFACTS?

The Irving Langmuir Film

The May 1931 issue of the *Journal of Chemical Education* contains an unusual article by the famous American surface chemist, Irving Langmuir, entitled "Experiments with Oil and Water" which begins with the following rather curious *Editor's Note* (1):

The following is a stenographic report from an educational talking motion picture in which Dr. Langmuir accompanies his talk with close-up views of his experiments. Necessarily, there are sections of the text which are ambiguous since in the film Dr. Langmuir would point specifically to parts of the demonstrations. Parenthetical insertions have been made occasionally in the text to clarify certain points, and at other places the points have been illustrated with enlargements from the film. The sound track appears to the left of the pictures as a jagged black line. The film, made with RCA-Photophone equipment, was produced by the Motion Picture Department of the General Electric Company. Dr. Langmuir did not talk from a prepared manuscript.

The then editor of *The Journal of Chemical Education*, Neil Gordon, had seen the film when it was shown to the members of the Division of Chemical Education at the Columbus, Ohio, meeting of the American Chemical Society on May 1, 1929 and was apparently so impressed that he decided to print a stenographic version in his journal. As indicated in his introductory editorial comment, the resulting transcript was illustrated by more than 26 enlarged prints taken directly from the film. The fact that Gordon also saw fit to explain to his readers the nature of the jagged sound track, visible to the left of these prints, illustrates just how novel talking movies still were in 1931, the first partial talkie, *The Jazz Singer,* starring Al Jolson, having debuted in October of 1927, only two years before the Langmuir film was shown at the 1929 ACS Meeting.

Both the transcript and the film prints show Langmuir doing a large number of demonstrations illustrating various surface effects using a precursor of the well-known Langmuir-Blodgett trough and spontaneously commenting on them by means of blackboard drawings. In 1932, one year after this article appeared, Langmuir won the Nobel Prize in Chemistry for his work on adsorption and surface phenomena. Quite obviously this film is of great historical significance. A restored DVD version would make a wonderful gift for the historically minded chemist, not to mention for the winners of the prestigious ACS Langmuir Prize. The question is whether this film still exists and, if so, where?

REFERENCES AND NOTES

I. Langmuir, "Experiments with Oil on Water," *J. Chem. Educ.*, **1931**, *8*, 850-866. Reprinted in C. G. Suits, Ed., *The Collected Works of Irving Langmuir*, Vol. 9, Pergamon Press: New York, NY, 1961, pp. 229-246.

Readers having information relating to the above artifacts or questions of their own which they would like to see addressed in future columns, should send their comments and questions to Dr. William B. Jensen, Oesper Collections, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu.

RESPONSE TO THE PREVIOUS COLUMN

No responses were received concerning the previous column dealing with the current whereabouts of the 1869 Anna Lea painting commemorating the discovery of alizarin. This may indicate one of three possibilities: 1) the painting is truly lost; 2) its current owner does not want to disclose its present location; 3) its current owner has not seen the previous column. Though nothing has been uncovered concerning the present location of the missing painting, I have discovered some additional information about the artist. Born Anna Massey Lea in Philadelphia in 1844, she was the daughter of Joseph Lea Jr., a Quaker and influential manufacturer and printer of cotton goods. She studied anatomy at the Women's Medical College in Philadelphia and, after moving with her family to Europe in 1865, studied art under various teachers in Italy, Germany and France. In 1870 the family moved to London, where Lea studied under Henry Merritt, whom she married in 1877. She remained in England after Merritt's death three months later, eventually settling in the village of Hurstbourne Tarrant, where she resided until her death in 1930. Usually described as a Pre-Raphaelite painter, she is best known, under her married name of Anna Lea Merritt, for her Victorian portraits, her allegorical and religious paintings, and her landscapes and floral scenes.

AUTHOR INDEX, *1-35*

Volumes are given in italics (only the first number for double issues, such as 13/14). Unitalicized page numbers follow volume numbers. Biographical sketches of authors are indicated by **boldface**. Translators are designated by a page number followed by T. Authors of book reviews now appear in the author index below (page number followed by R); authors of reviewed books are now included in the subject index.

SUBJECT INDEX, *1-35*

Volume numbers are given in *italics* (only the first number for double issues, such as 13/14). Unitalicized page numbers follow volume numbers. Authors of reviewed books and the main subjects of those books are now included in the subject index.

B

C

D

E

F

G

H

I

J

K

L

M

N

O

P

Q

R

S

T

U

V

W

X

Y

Z

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William B. Jensen, Founding Editor

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