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See Dexter Award Address, p. 1

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"INSTRUCTIONS FOR AUTHORS" see back inside cover

THE 1996 DEXTER AWARD ADDRESS

CONTRASTS IN CHEMICAL STYLE: SIDGWICK AND EYRING

Keith J. Laidler, University of Ottawa

In this address I will say something about two people I came into contact with early in my career, Nevil Vincent Sidgwick and Henry Eyring. They offer a striking contrast in every respect, and the contrast between them illustrates something of which I have become more and more convinced as I have worked on the history of science - that there is really no such thing as a scientific method. There are as many ways of doing good science as there are good scientists. Moreover, one can do little planning ahead in the case of a piece of scientific research; one must constantly make decisions - sometimes daily - as one proceeds with the work.

Let me make a few general comments first, before I come to Sidgwick and Eyring. Nonscientists, and indeed some scientists, often think that scientists are in some way a special breed of people. I have been lucky enough to know personally a considerable number of scientists, many of them extremely good ones, and I have read many biographies of scientists. My conclusion is that scientists are much the same as other competent people and that there are enormous differences between different scientists, even between those working in the same field.

For one thing, many good scientists would have been successful in anything they undertook to do. Quite a number of scientists did not originally intend to be scientists; J. J. Thomson (1856-1940), P. A. M. Dirac (1902-1984), and Henry Eyring, for example, originally wanted to be engineers; it is hard to believe that they would not have been good ones. Joseph Black (1728-1799) took a medical degree and practiced medicine

during the same period that he lectured in chemistry. Thomas Young (1773-1829) and many others, particularly a number of chemists, also began their careers in the practice of medicine. Several scientists, like William Grove (1811-1896) and Joseph Plateau (1801-1883), became lawyers before becoming scientists; Grove, in fact, finally went back into law and became a judge.

Several scientists have won such great renown in fields other than science that they are better known for their other achievements than for their scientific work. An obvious example was the architect Sir Christopher Wren (1632-1723), who was a mathematician and a professor of astronomy at Oxford. There was also the physicist and statesman Benjamin Franklin (1706-1790) and the composer Alexander Borodin (1833-1887), who was a full-time professor of chemistry; for the most part he only composed when he did not feel well enough to do scientific work! Last but not least, there was Chaim Weizmann (1874-1952), who became the first President of the State of Israel, and who would probably not have been chosen for that position if he had not done, in Britain, some very important research in chemistry which contributed to the allied success in World War I.

Scientists, then, seem to be very much like other people who are interested in intellectual pursuits. In their general behaviour also, scientists seem just like other people. Some are generous, and the proportion of generous scientists is not obviously different from the proportion of generous people as a whole. A few scientists have been scoundrels, but again their proportion seems no greater than that in the general population. Religious

belief does not seem to be much affected by whether one is a scientist or not. Michael Faraday (1791-1865) was a Sandemanian, which means that he was a religious fundamentalist; one wonders, incidentally, how he would have taken to the theory of evolution. Henry Eyring was born a Mormon and rose to high office in that church. Some scientists, including Sidgwick, were agnostics; but their proportion seems about the same as that among other intellectuals.

Some scientists are highly gregarious, some are hermits, and most are somewhere in between. Most scientists are enthusiastic about discussing their ideas with others, but some fear that their ideas will be stolen by others and are secretive. Wilhelm Konrad von Röntgen(1845-1923), famous for his discovery of X-rays, is believed never to have discussed his scientific work with anyone. Oliver Heaviside (1850-1925), remembered today for the Heaviside layer in the ionosphere, retired at the age of 24 (perhaps a record for early retirement) and tried to avoid speaking to anyone during the rest of his life.

Now I come to the two men I am going to talk about, Sidgwick and Eyring. First I will say something about the differences in their personalities. Sidgwick was austere in manner and never married, while Eyring was friendly and gregarious, and loved his wife and family. Sidgwick was by no means easy to talk to, while Eyring was just the opposite. Sidgwick was an avowed atheist, while Eyring was a devout Mormon. What they did have in common was a devotion to science and a high regard for the truth. Both had a great effect on the progress of chemistry. Chemists today who may not know much about their work are greatly influenced by what Sidgwick and Eyring did, since it is reflected in the textbooks we use today.

The two men contrasted sharply in their ways of doing science. Sidgwick had little competence in mathematics and made little use of it in his work. All of Eyring's work, on the other hand, was of a mathematical character. Sidgwick was a great scholar of science, by which I mean that he studied the scientific literature with great care, and was thoroughly familiar with the experimental results that had been obtained in all branches of chemistry. Eyring, on the other hand, did not pay too much attention to what had been done before; he preferred to think about science in an intuitive way and seemed to pick up experimental facts (or get his graduate students to pick them up) as he needed them to test his theoretical ideas. Sidgwick based his work on mathematical treatments that had been worked out by others, and he had the knack of understanding their im-

plications without going into all the details; he then collated a huge mass of experimental data on the basis of his interpretation of the theories. Eyring worked the other way round; he arrived at his ideas intuitively, then formulated his theories on the basis of rigorous mathematical treatments, and finally examined the way in which his formulations fitted the experimental results.

Nevil Vincent Sidgwick

Perhaps I may tell a personal story about how I first came in touch with Sidgwick (1, 2; Fig. 1). While at school in England in the early thirties I decided that I wanted to be a chemist; and since the man who taught me chemistry was an Oxford man he thought that Oxford was the best university for me. The system at Ox-

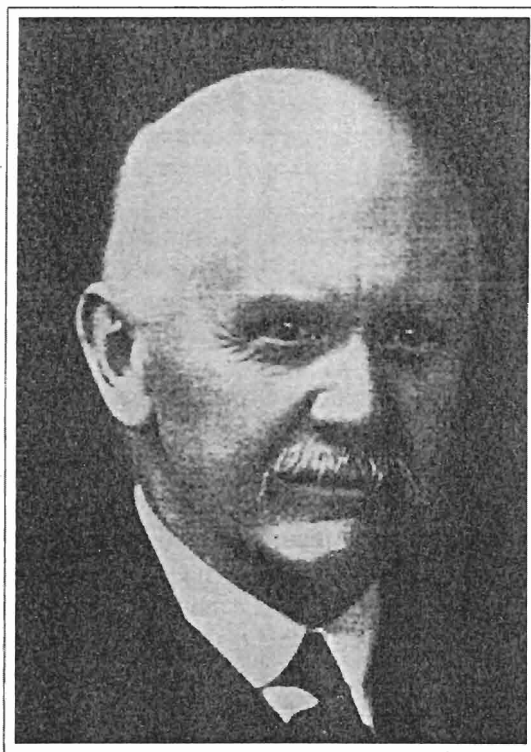


Figure 1. Nevil Vincent Sidgwick (1873-1952), from a photograph given by Sidgwick to the author in the 1940s, perhaps during World War II. He had looked much the same for several decades.

ford is that one must first gain admission to a college, which automatically makes one a member of the University. I again took the advice of my teacher. The outstanding chemist at Oxford, he said, was Sidgwick, who was at Lincoln College; and in fact at school I had already read his famous *Electronic Theory of Valency*

(Clarendon Press, Oxford, 1929). He added that there was also a younger man who was showing great promise - a man called Hinshelwood at Trinity College. I therefore put Lincoln College down as my first choice and Trinity as my second.

In December, 1933 I took the scholarship examination, and I still remember very vividly that when I was doing the experimental part of the examination Hinshelwood came beside me, and in his unforgettable drawl said, "Well, Laidler, how are you getting on?" I made some mumbling reply, now forgotten. A few days later I learned that I had been accepted by Hinshelwood, and as a result I went to Trinity College. There is an amusing sequel to this story, which I learned about only recently. I was in correspondence with Professor Brebis Bleaney, who became professor of experimental philosophy at Oxford in 1956 and has done distinguished work in electron spin resonance spectroscopy. It turned out that he, too, had given Lincoln College as his first choice at exactly the same time. We had both sat the same examination and had therefore been rivals, but he, too, had been turned down by Sidgwick and had been chosen by H. W. Thompson, the spectroscopist, for St. John's College. Thompson, incidentally, had been one of Hinshelwood's students and had perhaps learned from Hinshelwood the art of snatching people away from Sidgwick.

I still clearly remember, although it was over 60 years ago, sitting in front of Sidgwick at his lectures. This was at the time when he was working on his massive two-volume *Chemical Elements and their Compounds* (Clarendon Press, Oxford, 1950). When that book later came out, in 1950, I realized that my lecture notes taken fifteen years before were very much like a precis of the book. The lectures were quite superb; meticulously prepared, they were delivered with great style. At the end of each lecture he picked up his notes and walked out; in those days and in that University there was no opportunity for anyone to ask a lecturer a question. This sounds unsatisfactory, but we had tutors whom we saw for at least an hour once a week. Since my tutor was Hinshelwood, who also was a great chemical scholar as well as a man of great originality, I did not feel deprived as far as getting help was concerned.

Nevil Vincent Sidgwick was born in Oxford in 1873, of a rather remarkable family. His father had been a teacher of classics at Oxford and later a lecturer in politics and political economy. His uncles included Henry Sidgwick, professor of moral philosophy at Cambridge, Edward White Benson, who later became Archbishop of Canterbury, and Sir Benjamin Collins

Brodie, who was Aldrichian professor of chemistry at Oxford from 1855 to 1872. The Archbishop must have been a little discomfited by the fact that Brodie, Henry Sidgwick, N. V. Sidgwick's father, and Sidgwick himself were all fairly militant atheists.

Sidgwick was a student at Christ Church, Oxford, where his tutor was A. G. Vernon Harcourt (1834-1919), one of the early pioneers in chemical kinetics. He gained first-class honors in natural science in 1895 but found that his rather classically minded relatives considered a degree in science to be much inferior to one in classics. Just to impress them he stayed on in Oxford for two more years and then gained first-class honors in Greats, which covers classical literature and philosophy in the original languages, Latin and Greek.

Sidgwick later went to Tübingen University, studying under von Pechmann, and in 1901 was awarded a D. Sc. degree *summa cum laude*, for work in organic chemistry. He was elected to a tutorial fellowship at Lincoln College, Oxford, and from 1901 the College was his home until he died in 1952; he never married. From 1901 to 1916 he carried out research, mainly on the physical properties of organic compounds, but did little work of any distinction until he was in his late forties. This late development in a scientist is unusual but not unique. Sir William Bragg (1862-1942) was also well in his forties before he did anything much in science, and then, with much help from his son Lawrence Bragg (1890-1971), he pioneered X-ray crystallography.

In 1916 Sidgwick moved to the new organic chemistry laboratories, which were directed by Sir William Henry Perkin, Jr. (1860-1929). The two could scarcely tolerate each other. Sidgwick had a deep interest in physical chemistry, which Perkin thought a waste of time; Sidgwick claimed that Perkin on several occasions said to him "Physical chemistry is all very well, but of course it doesn't apply to organic compounds." Since recorded organic compounds constitute over 99 per cent of the total number of chemical compounds, this was hardly an enthusiastic endorsement of physical chemistry.

Sidgwick's later successes followed a suggestion in 1914 from Ernest Rutherford (1871-1937) that he should relate chemical properties to the new electronic and quantum theories, something that had never been done before. Just a year previously Niels Bohr (1885-1962) had published his famous work on which he explained the orbital arrangements of electrons in atoms, work that he had carried out in Rutherford's laboratories in Manchester. At once Sidgwick began to consider how chemical properties could be explained on the basis of

these ideas. In 1916 G. N. Lewis (1875-1946) published his famous paper on his octet theory and in subsequent years developed his ideas in many ways. Irving Langmuir (1881-1957) also made important contributions in this field, and since he was an excellent lecturer he did much to make chemists aware of these important new developments.

In 1919 Sidgwick applied for the Dr. Lee's Professorship at Oxford, but the appointment went instead to Frederick Soddy (1877-1965), who was to receive the 1921 Nobel Prize for Chemistry. The choice, though understandable at the time, turned out to be a poor one, as Sidgwick's teaching and later research would have made him a much better professor than Soddy, who did little research and gave indifferent lectures during his tenure of the chair. In 1922, when Sidgwick was forty-nine, he was elected a Fellow of the Royal Society, and in 1924 he was appointed University Reader in Chemistry. The title of Professor was conferred on him in 1935.

Sidgwick did not do anything highly original, but he followed the work of Lewis and Langmuir; his important contribution was to use it to explain chemical behavior. His detailed knowledge of the facts of chemistry put him into a unique position to apply the electronic theories to a wide range of chemical compounds. His work led to his book *The Electronic Theory of Valency* which appeared in 1927, when he was fifty-four. The book was soon recognized to be a scientific classic. In it Sidgwick skillfully and lucidly gave a fresh unity to the whole of chemistry, which for the most part had been presented as a large collection of isolated facts. This book had a wide influence. At once the textbooks of chemistry, even those used in high schools, began to change; even if they did not mention Sidgwick by name, they were influenced by his ideas.

In 1931 there came a great change in Sidgwick's life and attitude toward others. He was invited by Cornell University to be the George Fisher Baker Lecturer in Chemistry. This was to be his first visit to the United States, and with a prejudice that was rather typical of him he announced that he was 'sure he would not like the place.' Within a week of his arrival, however, he had completely reversed his opinion, afterwards taking every opportunity to return. On his first visit he was fifty-eight, a formidable figure, quite set in his ways. Oxford students had always been in awe of him, but the Cornell students saw him quite differently and were able to penetrate the crusty exterior, finding an amusing and kindly man underneath. They even called him 'Gran'pa,' which delighted him. They paid him the compliment of

inviting him to stay at their fraternity, Telluride House, which he greatly appreciated and enjoyed. From then on he crossed the Atlantic whenever he could, becoming one of the best known British scientists in the United States; in the end he was proud to have visited 46 of the 48 continental states. (I myself, incidentally, have visited all 48 of them; the last one I got to, rather surprisingly, was Maine).

On Sidgwick's return from his first visit to Cornell, in 1932, his energies were mainly devoted to expanding and applying in much greater detail his previous formulation of the electronic theory. He labored for about twenty years on his great book, *The Chemical Elements and their Compounds*; when it appeared in 1950 he was seventy-seven. It consisted of two massive volumes containing a total of about 750,000 words. It was written in a lively style and gave an astonishing and panoramic



Figure 2. A photograph taken in 1910 of Sidgwick in the physical chemistry teaching laboratories at Balliol and Trinity Colleges, Oxford.

view of much of chemistry as it was at the time. This book also quickly became a classic. It is interesting, and rather unusual, that Sidgwick's reputation is based almost entirely on his books, and scarcely on his papers in research journals.

In appearance and personality Sidgwick was unusual. Figure 2 shows him as he was in 1910, and he looks rather elderly. At the time, however, he was only

thirty-seven. When I first saw him twenty-four years later he looked almost exactly the same; only the depth of his collars had decreased. Indeed, forty years after that picture was taken he still looked much the same. He was always conventional in dress and invariably carried an umbrella; even in the hot California sun he would wear a felt hat, a thick English suit, and a raincoat. He cared very little about his surroundings, and his rooms in Lincoln College always looked shabby and untidy.

In his relationships with others he was very prejudiced, either completely approving or completely disapproving; in Leslie Sutton's words(2):

In personal judgments he seemed sometimes to be carried away by the poetic ecstasy of imaginative denigration.

He would aggressively pounce on any loose or inaccurate statement and so made a few enemies; others became immune to being bitten. He made a particular point of being rude to clergymen. He was quite prepared to adjust his prejudices if confronted with adequate evidence as he did after his first visit to the United States.

In 1951, in failing health, he was determined to make what he knew must be his last visit to the United States. After undergoing an operation he returned to Telluride House at Cornell University, where the students helped him to go up and down stairs and took him for trips to see the autumn colors. He had a stroke on the ship returning to England and spent his final months in a nursing home, where he died peacefully on March 15, 1952. Throughout his adult life he insisted that he had no belief in God or in an after life.

Henry Eyring

I mentioned earlier that when I became an undergraduate, my first choice had been to go to Sidgwick's college (Lincoln), but that instead I became Hinshelwood's pupil at Trinity. A similar thing happened when I became a graduate student in 1938. Late in 1937 I applied for a fellowship which would allow me to go to an American university, asking Hinshelwood for advice. Hinshelwood was always in favor of broadening one's experience. Since I was then doing a year's undergraduate research in kinetics with him, his idea was that I should do my graduate work in another branch of chemistry. His advice was that I should give Linus Pauling (1901-1994) as my first choice, and this I did. I also had to give a second choice. My research with Hinshelwood had brought us into contact with what Henry Eyring had been doing at Princeton, particularly his formulation of transition-state theory in 1935. I had in fact myself been

present at a seminar that Eyring had given at Oxford in 1937, a seminar that is still deeply engraved in my mind, because afterwards F. A. Lindemann (later Lord Cherwell), the professor of physics, was publicly extremely rude to Eyring, treating him like a stupid schoolboy who had forgotten his basic physics. I remember that afterwards Hinshelwood was extremely angry at Lindemann's behavior. I also remember that soon after I met Eyring he referred to what Lindemann had said, which he had naturally found very offensive.



Figure 3. Henry Eyring (1901-1981), from a photograph given by Eyring to the author in the 1950s.

Hinshelwood

suggested to me that I should put Eyring down as my second choice. When I was interviewed for the fellowship the chairman of the committee told me that they had decided that I was successful, but mentioned that many Englishmen during the past few years had gone to work at the California Institute of Technology with Pauling; would I mind going instead to Princeton to work with Eyring, my second choice. Would I mind? Of course I was overjoyed. Thus, at a second crucial stage in my life I was given my second choice instead of my first, and I now think that this was fortunate for me. If I had been granted my first choices, Sidgwick and Pauling, my subsequent career would probably have been very different. Instead of working on kinetics, I should perhaps have concentrated on chemical structure, and I have a feeling that I might well have been a complete failure at it.

I mention these two incidents of my being given my second choice to emphasize that sheer luck does play a great role in all our lives. I have often speculated as to what would have happened to Michael Faraday, the son of an impoverished blacksmith living in the slums of London, if he had not got a job with a kindly bookbinder who encouraged him to read the books he bound, or if a

kindly customer had not given him a ticket to go and hear one of Sir Humphry Davy's lectures. Faraday might well have lived in obscurity; at least he might have started his career much later. Similarly, what if Joseph Henry (1797-1878), living near Albany, New York, had not chased his pet rabbit under the village library, from there finding his way into the library, and into the world of books? Would he ever have become a distinguished scientist?

Shakespeare, as always, had something wise and interesting to say about that sort of thing (3):

There is a tide in the affairs of men,
Which, taken at the flood, leads on to fortune;
Omitted, all the voyage of their life
Is bound in shallows and in miseries.

I never made a fortune, but have been fortunate in my career, having been washed along by the tide, avoiding by sheer luck the shallows and miseries that a career sometimes leads to.

I worked with Henry Eyring (4-8; Figure 3) from 1938 to 1940. He was born in 1901 in Colonia Juarez, Mexico, of American parents. After studying mining engineering at the University of Arizona, he went to the University of California at Berkeley, obtaining a Ph. D. degree in physical chemistry under George Gibson in 1927. He taught for a period at the University of Wisconsin (9) and always enjoyed telling that he had been fired from the chemistry department there, as a result of a disagreement with the chairman, J. Howard Mathews (1881-1970). From all accounts Mathews was a difficult man with rigid and old fashioned ideas, and it is easy to see how he and Eyring could never have agreed. Eyring was required to conduct a laboratory course, and Mathews first ordered him to paint the floor, which even in those days was an unusual assignment for a member of the academic staff. Eyring complied, and was not pleased

when Mathews, after inspecting the job, said that it was perhaps good enough for a first coat. Eyring later remarked to a colleague that the department would never amount to anything as long as it was run in the way it was. That remark got back to Mathews, and within an hour Eyring was fired. In those days, of course, one could not grieve – or rather, if one did, one did it alone.

In 1929-30 Eyring spent a year in Berlin collaborating with Michael Polanyi on the construction of the first potential-energy surface for a chemical reaction. In 1931 he was appointed professor of chemistry at Princeton. He had discovered to his surprise that he was officially a Mexican citizen and became a naturalized American citizen in 1935. In 1946 he went to the University of Utah as Dean of Graduate Studies and professor of chemistry, remaining there until the end of his life.

When I arrived at Princeton to work with him in 1938 he had three years earlier made what was perhaps his most important contribution to science, the formulation of transition-state theory. The theory was still highly controversial, and his main interest at the

time was to apply it to problems other than gas reactions. My work with him was first on reactions on surfaces, about which I knew a fair amount because of my work with Hinshelwood. We devised a way of dealing with the partition functions of surfaces and of surface layers and were able to show that the theory is quite satisfactory in interpreting the rates of surface reactions. We also looked at a number of reactions in solution, and they seemed to fit in also. After I had been at Princeton for a year Samuel Glasstone (Fig. 4), then in his early forties, came over from England and joined Eyring's research team. Glasstone was already well known for a number of very lucid books he had written on physical chemistry. (I still refer to them from time to time, as they are excellent on the basic concepts of thermodynamics, statistical mechanics, X-ray scattering, and so forth.) Glasstone also had



Figure 4. Samuel Glasstone (1897-1986), from a photograph given by Glasstone to the author in the 1960s. After a distinguished career in physical chemistry, with several books to his credit, Glasstone became a nuclear engineer, working at the Los Alamos Scientific Laboratory until 1969 and then for the U. S. Atomic Energy Commission at Oak Ridge, Tennessee. He received several awards for his work on nuclear engineering and published books in that field also.

made a name for himself in electrochemistry and had worked on overvoltage. Overvoltage was still something of a mystery, and Eyring, Glasstone, and I worked on the application of transition-state theory to it, with very successful results. At the same time, the three of us decided that the time was ripe for a book on transition state theory. Eyring, never much of a writer, left the actual writing to Glasstone and me; but he contributed enormously to it by his lengthy discussions of the subject matter and his penetrating criticisms of what we had written.

I remember very vividly one of the—always very friendly—arguments we had. Glasstone and I were on one side, Henry Eyring on the other. We broke off for lunch, and Glasstone and I had ours together. As we continued our discussion, we decided that Henry was right after all. When the three of us met again, we admitted to Eyring that *he* was right, but were rather taken aback when he told us that he had decided that *we* were right. The argument then continued, but with the opposing parties reversed, and soon we saw the funny side of it, and could not continue for laughing. Unfortunately, after so long, I cannot remember exactly what sides we were taking at the various times, although I do remember that it was a rather subtle point about the temperature-dependence of an equilibrium constant expressed with respect to concentrations rather than pressures. Needless to say, that problem is now one with which I have no difficulty; having an argument like that, with people like that, does straighten out one's thinking.

Our book, *The Theory of Rate Processes* (McGraw-Hill, New York), came out in 1941. Three of the chapters in it, on electrode processes, reactions on surfaces, and reactions in solution, comprised essentially my Ph. D. dissertation, submitted in the spring of 1940. I remember that after I took my oral examination, the examiners remained closeted together for such a long time that I felt sure that I had failed. When they came out and I was told that I had passed, I asked Henry why there was such a delay. "Oh," he said, "they weren't arguing about you; they were arguing about absolute rate theory" (as transition-state theory was then called.)

Eyring had a friendly disposition and was always happy to discuss his scientific work with anyone who would listen. He was always full of ideas, many of them wrong, but he always welcomed criticism; and his suggestions could always be turned into sound scientific treatments. In a formal sense, Eyring was not a good university lecturer. I have mentioned that Sidgwick was always well organized, but Eyring was just the opposite. He tended to go off on tangents, talking about something

that had perhaps just occurred to him but which did not have much to do with the subject of his lecture. But his graduate classes at Princeton consisted of only a handful of students, and he did not mind at all if we interrupted him with a comment like, "Henry, we've no idea what you are talking about;" he would grin cheerfully and get back to his subject. In the end we all learned a very great deal from him. It had been realized, however, that he would be poor at teaching undergraduates, and I believe he never did so.

Science and its History

In expressing my great appreciation for receiving the Dexter Award, I should emphasize again the enormous role that good luck has played in my career. I got a wonderful start by having C. N. Hinshelwood (10-12; Fig.



Figure 5. Cyril Norman Hinshelwood (1897-1967), from a photograph taken by the author in 1961.

5) as my tutor while I was an undergraduate, and I am sure I derived my interest in the history of science from him. Hinshelwood's work has in some quarters been underrated, and I should like to say a few words about that. In the 1920s and 1930s Hinshelwood did some very original work on explosions in gases and on reactions on surfaces and in solution. This work, in my opinion, was worthy of a Nobel Prize. His Nobel Prize, however,

was not awarded to him until 1956, and by that time his work was of much less originality. Also, he had not kept up well with the latest advances. This was largely because he had many other responsibilities, such as running a large physical chemistry laboratory. When he won the Nobel Prize there was some criticism, because many people were only aware of his later work. I think, however, that if we consider his achievements as a whole and the influence he had on the growth of physical chemistry, the award was fully justified.

Like Sidgwick, Hinshelwood was very much a scholar in the field of chemistry, and he knew the subject through and through. I saw him for an hour or so every week for three years during term time, and we covered every aspect of chemistry. I remember doing with him such specialized topics as the organic chemistry of the anthocyanins. Hinshelwood had a deep knowledge of the history of science, and naturally a lot of that rubbed off on me. I had to write an essay for him every week on some chemical subject, chosen by him, and then read it to him. Today this ancient custom seems old-fashioned and amateurish, but I assure you that it was effective. He listened attentively, and any error of fact, syntax, or grammar was politely but firmly pointed out at the end; naturally one strove to make these criticisms unnecessary by very carefully checking what one had written. I still remember vividly, although it was sixty years ago, reading to him an essay on the decomposition of hydrocarbons and mentioning the work of W. A. Bone, who was then active in the field. I wrote that Bone had obtained certain results, which he had interpreted in terms of a free-radical mechanism. For once Hinshelwood broke his rule of not interrupting, and exclaimed, "What! Old Bone! Old Bone doesn't believe in free radicals." That short statement taught me two important lessons on writing the history of science. First, check your references properly, and second, do not assume that a scientist drew

the conclusion that we today would expect. History must describe what happened, not what we think ought to have happened. I am sure that I derived my initial interest in writing about science and its history from Hinshelwood's influence. I also learned much about scientific writing as a result of my association with Samuel Glasstone in writing *The Theory of Rate Processes*. I feel remarkably fortunate to have been so closely associated with those two remarkable men.

In particular I learned from both Hinshelwood and Glasstone the most important precepts about writing, which were stated by Sir Peter Medawar and which I slightly modify as follows:

Correctness, cogency, and clarity, these three:
But the greatest of these is clarity.

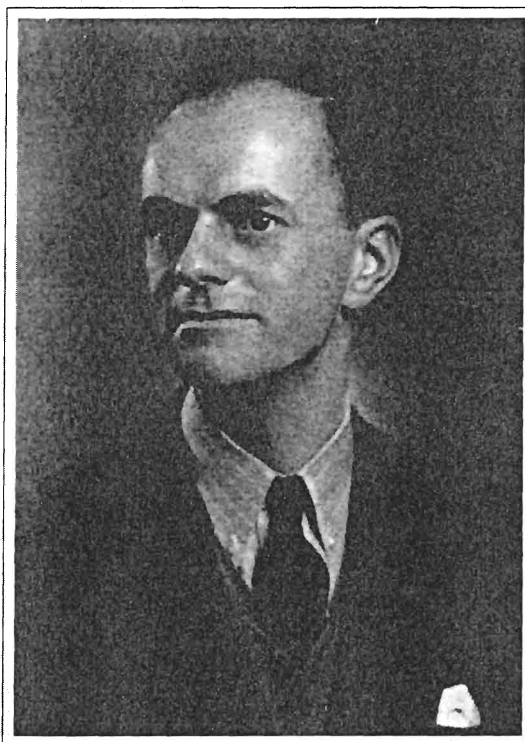


Figure 6. Keith Laidler (b. 1916), from a photograph taken in 1941, the year of publication of *The Theory of Rate Processes*. Photograph by Karsh of Ottawa.

Let me end with a brief comment on these three characteristics. Correctness, of course, speaks for itself; we must get everything right. There is much more to the truth than that, however; we can put forward perfectly correct information but end up with nothing but a big lie. That great historian Lord Macaulay made a very shrewd comment about this. He was concerned with the matter of selecting the appropriate material when one is writing history, and wrote(13):

He who is deficient in the art of selection may, by showing nothing but the truth, produce all the effects of the greatest falsehood.

This is part of what is meant by the word cogency: we must *select* our material in such a way that the reader is left with a correct impression of the truth.

Finally, in writing about science the greatest of the virtues is clarity. It will be obvious that clarity

is important, but we should be aware of some curious problems that may arise. Let me tell a little story, a true one. In my early days of teaching I was once told by a student that the students in my class understood my lectures very well. Then she spoiled everything by adding, "None of us can understand Professor X at all; but then, *he* is very brilliant." For a few seconds I was a

little taken aback. Here was I, working hard to make my lectures clear, only to be regarded by the students as half-witted. I soon recovered and have continued to try to express myself as clearly as possible; but I am puzzled, and also a little concerned, by the fact that quite a few people seem to think that a person who speaks or writes obscurely must be very clever, something I know to be untrue. There are several books about science for the general public which I think are written very obscurely, which have nevertheless sold well. Do some members of the public say to themselves, "I can't understand a word of this book, so it must be a good one, and the author very clever?" The truth is that there is no correlation between obscurity and brilliance.

There is a great need for the public to know more about science, since science and its technical consequences enter so much into our lives. Writing about the history of science is one of the best ways of informing the public, and there is room for much more to be done.

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MORRIS LOEB: OSTWALD'S FIRST AMERICAN STUDENT AND AMERICA'S FIRST PHYSICAL CHEMIST

Martin D. Saltzman, Providence College

In the 1880s, John Servos writes, "...a group of chemists... asserted that their science, through its emphasis on composition and structure, threatened to become narrow and sterile(1)." Chief among these critics was Wilhelm Ostwald (1853-1932), who argued that chemists should have as their major preoccupation the study of chemical affinity. Chemists needed to develop principles which would make it possible to predict the course of chemical reactions and not just the synthesis of an infinite number of organic compounds. Ostwald, an iconoclastic figure, was in many ways a thorn in the side of the chemical establishment of imperial Germany. He, along with his contemporaries the Dutch chemist Jacobus van't Hoff (1852-1911) and the Swedish chemist Svante Arrhenius (1859-1927), can be credited with the founding of the modern discipline of physical chemistry. Ostwald, perhaps more than anyone else, had the most profound effect on the development of American physical chemistry. His many American students who studied with him in Leipzig from 1887 until his early retirement in 1906 spread with great enthusiasm his new *allgemeine Chemie*.

Ostwald's first American student was Morris Loeb (1863-1912), who led an extraordinary life as a chemist, teacher, and philanthropist. Loeb was the first to introduce a physical chemistry course in American education. In his publications he sought to popularize the ionist point of view in America. The attribute of being America's first physical chemist is given in the sense that he introduced the program of Ostwald into American chemistry. It was through Ostwald's influence that physical chemistry became an internationally recognized discipline in its own right. This is not to belittle the con-

tributions made by Josiah Willard Gibbs (1839-1903) in the development of thermodynamics in the 1870s. Gibbs' work, however, was little appreciated because it was presented in the literature in such a way that few if any of his contemporaries could understand what his ideas were. In addition Gibbs, as a physicist and engineer by training, applied his thermodynamics in a purely abstract way to chemical problems. Most importantly he left no school to carry on his work. The American students of Ostwald, such as Arthur A. Noyes and Wilder D. Bancroft among others, were as Servos has written "...critically important teachers and institution builder(1)." These men followed Loeb to Ostwald's laboratory and thus Loeb may be given the appellation of the first American physical chemist.

Morris Loeb was born on May 23, 1863, in Cincinnati, Ohio. His father Solomon (1829-1903) had emigrated from Germany to Cincinnati in 1840 and within a short time became a very prosperous dry-goods merchant. When Morris was two years old the family moved to New York City, where his father had formed a partnership with Abraham Kuhn. The banking house of Kuhn, Loeb & Co. was enormously successful, thus ensuring that Morris would be financially independent. Loeb's primary and secondary education was completed in New York at the Sachs Collegiate Institute, an institution founded by a German immigrant Dr. Julius Sachs. Sachs emphasized classics, language, and Teutonic discipline in his school. Loeb excelled at science but showed no interest in becoming a banker, much to the disappointment of his father., Morris Loeb entered Harvard University in 1879, at the rather young age of sixteen.

Early in his studies at Harvard, Loeb enrolled in the introductory chemistry course taught by Charles Loring Jackson (1847-1935). Morris became fascinated with the science of chemistry as presented by Jackson and decided to major in it along with English. Jackson was a charismatic figure who inspired generations of Harvard chemistry students. He had worked with Robert Bunsen (1811-1899) in Heidelberg for six months in 1873 and August Wilhelm von Hofmann (1812-1892) in Berlin for two and one half years. Jackson returned to Harvard in 1875 and had the distinction of preparing the first new organic compound ever synthesized at Harvard, *p*-bromobenzyl bromide. At Harvard Loeb was also influenced by Henry B. Hill (1849-1903) and Wolcott Gibbs (1822-1908). Hill had also worked in Hofmann's laboratory during 1874 in Berlin and published a large number of research papers in furan chemistry while at Harvard.

Gibbs' major areas of research were inorganic and analytical chemistry. His pioneering work on the preparation and properties of complex inorganic acids, and on those transition metal complexes of cobalt and platinum is noteworthy. When Loeb was at Harvard, Gibbs was teaching in the Physics Department. Here he lectured on thermodynamics and spectroscopy; of Gibbs it has been written, "He inspired his students with a zeal for research...His students had the greatest admiration and affection for him(2)." Loeb carried on research as an undergraduate with Gibbs.

Loeb graduated *magna cum laude* in 1883, being awarded distinctions in chemistry and English. He proceeded to Berlin shortly after graduation to work in the laboratory of the great Hofmann. In 1887 he received his Ph D for his research on phosgene and its reactions with amidines(3). His research in Hofmann's laboratory resulted in his first three scientific papers, published in *Berichte der Deutschen Chemischen Gesellschaft* and *Chemisches Zentralblatt* (4).

Loeb had become disenchanted with organic chemistry by the time he had finished his degree and sought new horizons. This led him to Leipzig and Ostwald after a short detour in Heidelberg. The year 1887 was not only significant for the new Dr. Morris Loeb but also for Ostwald, who had just been called to Leipzig from the Riga (Latvia) Polytechnicum. In that year Ostwald completed his *Lehrbuch der allgemeinen Chemie*, the first textbook of physical chemistry, and founded the



Morris Loeb

Zeitschrift für Physikalische Chemie. A Baltic German, Ostwald was a subject of imperial Russia and thus was always an outsider in terms of the German chemical establishment. Even in Leipzig he was always junior to Johannes Wislicenus (1835-1902), the Professor of Organic Chemistry.

Ostwald's new assistant at Leipzig was Hermann Walther Nernst (1864-1941). Nernst had been introduced to Ostwald by one of Ostwald's former Riga students, Svante Arrhenius (1859-1927). Into this hothouse of intellectual curiosity entered the 24-year-old Morris Loeb. Servos(1) contends that the founders of physical chemistry shared a common background in that they were on the periphery of the German chemical world. Their education was much broader in

terms of scope. Van't Hoff, Arrhenius, and Ostwald had far better training in physics and mathematics than their Germanic counterparts. By the 1870s rigid divisions between the physical sciences existed, and carbon reigned as king as far as chemistry was concerned.

By the time Loeb had arrived in Leipzig, much of the ionic theory of solutions had been worked out by van't Hoff, Arrhenius, and Ostwald. Van't Hoff contributed the proposal that dilute solutions could be treated in a way analogous to gases. Arrhenius solved the anomaly of electrolytic solutions by proposing the concept of dissociation to form ions. Ostwald contributed his dilution law, which allowed for the calculation of the degree of dissociation over a broad range of concentrations. These discoveries of the ionists, as they

became known, were not only of academic interest but were useful in other areas such as the chemical industry, where many processes take place in solution. Applications were also possible in the biological and geological sciences.

Why did Loeb come to Ostwald's laboratory? Charles Baskerville of the City College of New York, in his obituary of Loeb, states, "With the intention of testing the latest views on electrolysis, work which he had begun with Gibbs..., Loeb, with Nernst, carried on a study of the kinetics of substances in solution(5)." It thus appears that Wolcott Gibbs exerted a continued, guiding hand in the career of Loeb. Gibbs, with his interests in physics and chemistry, appreciated the new ideas being introduced by Ostwald and the ionists and may have suggested that Loeb go to Leipzig. In collaboration with Nernst, as well as on his own, Loeb was able to obtain enough results in several months to publish three papers in Ostwald's *Zeitschrift* concerning the kinetics in solution of silver salts and the molecular weight of iodine in solution(6, 7).

With Nernst, Loeb sought to prove the validity of the theory of electrolytic conductivity of Friedrich Kohlrausch (1840-1910). Nernst had worked in the laboratory of Kohlrausch in Würzburg in 1887. Arrhenius had also spent time with Kohlrausch, and the latter's work was crucial in formulating the ionization hypothesis. Among his other accomplishments, Kohlrausch had been the first to measure conductivities of solutions containing electrolytes under various conditions by using alternating current. His work was instrumental in disproving the notion held by many that it was the current that caused ionization. However, Kohlrausch did not believe that ions were present in any significant quantity unless a current was applied. In addition, Kohlrausch developed the concept of molar conductivity and the law of independent migration of ions. He was able to show that the molar conductivity at infinite dilution can be divided into two terms which represent the velocities of the anion and cation, respectively, in the two directions. Interesting relationships were found, in that for pairs of salts with a common ion the velocities were nearly always constant.

Loeb and Nernst calculated the velocity of the silver ion by using Kohlrausch's methods. The study of eight different silver salts resulted in a very narrow range of measured values and thus validated the independent nature of ions in solution. In Leipzig, Loeb had also proved that the molecular weight of iodine varied in solution. Loeb showed this by osmotic pressure measurements. "By the advice of Professor Ostwald, I un-

dertook to attack the problem of molecular weight in its solutions by the vapor-tension method...(7)." Under conditions ranging from extreme dilution to saturation it was possible to determine a constant molecular weight. The molecular weight, which was found to be constant at a particular concentration, always seemed to increase with increasing concentration.

Having now been transformed into a physical chemist by Ostwald and Nernst, Loeb returned to America to spend a year working with Wolcott Gibbs, who had recently retired from Harvard and established a private laboratory near his home in Newport, Rhode Island. The wealth of the Loeb family provided Morris the means to work as a volunteer in Gibbs' laboratory.

Through Gibbs' intervention, Loeb was appointed as a docent in physical chemistry at Clark University in Worcester, Massachusetts in 1889. Clark University had been established in 1887 as a graduate school based upon the Germanic model with programs in chemistry(8), physics, biology, mathematics, and psychology. John Ulrich Nef (1862-1915), an organic chemist who had studied with Baeyer, was the first Professor of Chemistry; Loeb was the only other chemist on the faculty during Nef's brief time at Clark(1889-1891). In 1891, at the age of 28, Morris Loeb was elected Professor of Chemistry at New York University, becoming the first physical chemist to be a full professor in a chemistry department in the United States.

While at Clark, Loeb taught what may have been the first physical chemistry course in the United States in 1889. The introductory lecture to this course found in Loeb's papers was edited by T.W. Richards. This lecture, "The Fundamental Ideas of Physical Chemistry," appears in a memorial volume dedicated to Loeb's scientific work which appeared in 1913, the year after his death(9):

In commencing this course of lectures, whose subject matter and title are avowedly new to the American student, I feel the need of giving some justification, of presenting some reason why I should seek to add one more rung to the ladder of learning already so alarmingly long.

Loeb then lashed out at the tyranny of organic chemistry and the perceived emphasis that chemistry is a practical science and its main role is to make new compounds which may have commercial value(9):

Like to the miners of '49 the specialist in organic chemistry has but one thought. Arrived at his diggings, he delves assiduously, and if favored by fortune and skill is rewarded with many a rich nugget.

But if, resting awhile from his labors he decides to retrace his steps and revisit former scenes, he is astounded to find that lands passed by as cheerless and barren have been occupied by settlers, who with patience and care have cultivated and beautified them, and are now reaping wealth more lasting and productive than his own gold.

Loeb's view just may have been somewhat clouded by his German experience.

Servos has written of the American experience as follows(10):

...American physical chemists confronted both the advantages and disadvantages of their nation's comparative backwardness. Instead of elbowing their way into existing laboratories and institutes, American physical chemists had to build them; instead of asserting themselves against powerful intellectual rivals they had to create traditions of research and scholarship in a country that has long proved resistant to both.

What then is physical chemistry according to Loeb?(11):

Thus our chemical philosophy becomes an attempt to interpret the actions of these imaginary atoms constituting matters under the play of the various forms of energy which pertain to them; and these actions must be supposed to take place in tridimensional space during perceptible time.

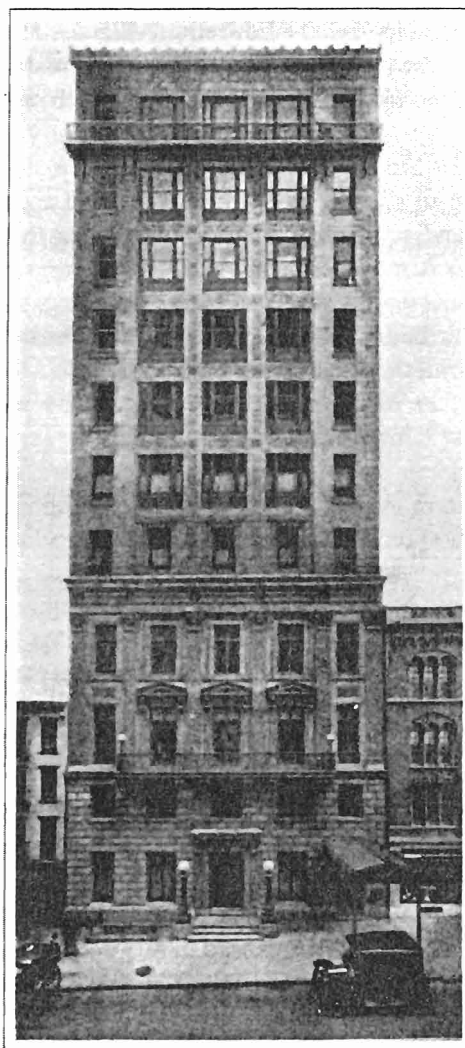
During his brief tenure at Clark University, Loeb made notable contributions on behalf of the cause of physical chemistry. He was one of the 43 chemists who attended the first national meeting of the American Chemical Society held outside of New York, organized by Charles E. Munroe (1849-1938). At this meeting, held in Newport, RI on August 6 and 7, 1890, Loeb presented a paper entitled, "On the Use of the Gooch Crucible as a Silver Voltammeter (12)."

For exact measurements of electric currents, no method is more convenient and more free from objections than the determination of the amount of silver deposited from a neutral solution of a silver salt. The sole source of error, especially where weak currents are concerned, arises from the imperfect adhesion of the silver upon the cathode.

Loeb found that a Gooch crucible with asbestos-covered holes was better suited as a cathode, provided leakage did not occur during electrolysis. Leakage was prevented by replacing the platinum cap with a glass siphon of special form. After the electrolysis has been completed, the siphon action built into the Gooch would drain away the excess silver nitrate solution.

The move to NYU initiated a new chapter in Loeb's life, that of teacher and administrator. His fervor for physical chemistry did not diminish but more and more of his time was being taken up with teaching and other activities of an educational, civic, and charitable nature.

Charles Baskerville writes of Morris Loeb as a teacher, "He was fired with zeal of those captain teachers and his own lighted torch he passed on by students



The Chemists' Building. 52 East Forty-First Street, New York

of his who now reflect in many responsible positions that spirit of the eighties(5)."

The heavy burden of teaching, which Loeb thoroughly enjoyed, had a serious effect on the time available for research. He always tried to keep up with the latest advances in the literature, however. When Solomon Loeb died on December 21, 1903, Morris assumed much of the responsibility previously shouldered by his fa-

ther in the civic, religious, and charitable work associated with the Loeb family. Being one of the most prominent German Jewish families in New York, the Loeb family had their duty to their less fortunate brethren who were arriving from eastern Europe in great numbers at that time.

Morris Loeb served on the boards of the American Jewish Committee, Hebrew Technical School, Jewish Agricultural and Industrial Aid Society, Jewish Theological Seminary, and the Education Alliance. He was a member of the New York School Board and many other organizations too numerous to mention. Loeb was very generous with the family fortune but personally he had, according to Stephen Birmingham "a fetish about money, and a fear of spending it...Morris scrimped and saved pennies and squirreled them away. When the Loeb house was demolished many years later some of Morris' deposits were discovered behind moldings and beneath floor boards; the wallpaper of one room was interlined with thousand dollar bills(13)."

Another recipient of Loeb's generosity was the Chemists' Club of New York, which he served as vice-president and president at various times. During his first term as president in 1909 Loeb proposed that the club should acquire a permanent headquarters "planned to serve under one roof the social, intellectual, and practical needs of the chemical profession not of New York alone, but of our beloved country(14)." A ten-story building was erected on East 41st Street in New York City on a lot donated by Loeb. This building contained social rooms, meeting rooms, a 16,000-volume library, and accommodations for visitors. The top five floors were devoted to laboratories, one of which Loeb used and which was named after him after his death.

The Chemists' Building itself was owned by a stock company, of which Loeb was the chief shareholder, along with other chemists and chemical manufacturers. In his will he left all his shares to the Chemists' Club which made it much easier for the club itself finally to purchase the building. As Loeb remarked upon the opening of the building(15):

The existence of a complete building, devoted solely to the interests of the chemists, will probably be the best demonstration to the American public of the importance which this profession has now assumed from the technical and business point...This building does not owe its erection to some benevolent demigod extending his protecting wing over people unable to care for themselves; it is a building by the chemists, of the chemists, and for the chemists.

Harvard University occupied a very special affection for Loeb and he served on many of its committees, one of which was concerned with laboratory facilities. This committee, on March 27, 1909, recommended that a new laboratory building was needed specifically dedicated to inorganic and physical chemical research(16):

Harvard has always been a leader in university education in this country, and it is still aiming strenuously to maintain that position. Is it not wise, therefore, in planning the education of her students, to give due encouragement to the distinguished staff which is now laboring under exceeding difficulties to maintain a well-earned supremacy in this department?



Wolcott Gibbs Memorial Laboratory, Harvard University

Within a month after this report had been sent to the Board of Overseers, Morris Loeb and his younger brother James donated \$50,000 to the projected \$100,000 cost of the building. At Loeb's suggestion, the building which opened in 1913 was named after his mentor Wolcott Gibbs, who had died in 1908.

In 1891 Loeb was a founding member and first secretary of the New York Section (the second oldest after the Rhode Island section) of the American Chemical Society. One of his major interests was the promotion of international cooperation among chemists and chemical societies. He was one of the organizers of the Eighth International Congress of Applied Chemistry held both in Washington and New York in September, 1912. He also contributed a paper on the speed of reductions of iron (III) by aluminum, manganese, and thorium salts.

As Loeb wrote in an editorial in *Industrial and Engineering Chemistry*(17):

And now we have entered into a new era, practically with the opening of the twentieth century, that of the utter abolition of national boundaries so far as scientific endeavor is concerned. A new chemical discovery in Paris is known in London, New York and Tokyo in far less time than was consumed in the transmission of Priestley's or Cavendish's communications to the Royal Society in London, and the time is rapidly passing when the possession and guarding of a scientific secret could be deemed a national advantage. To meet the leaders of chemical knowledge and of chemical manufacture, from abroad as well as at home, to listen to a free exchange of thought and practical experience, are privileges for which innumerable chemists have traveled to Berlin, London, Paris, Vienna, and Rome. We all now have these chances at home, coupled with opportunity to benefit by free and generous criticism of whatever we may desire to bring to their view.

While in Washington during the Congress, Loeb apparently ate contaminated oysters and contracted typhoid fever, which led to pneumonia. Morris Loeb, America's first physical chemist, died on October 8, 1912, in his forty-ninth year at his estate in Sea Bright, New Jersey. His passing elicited an outpouring of tributes from all those groups he had so generously supported by his hard work and his financial resources and of testimonials to his scientific accomplishments.

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LATENT HEAT AND ELECTRODE POTENTIAL

John T. Stock, University of Connecticut

In 1869, François Marie Raoult (1830-1901) briefly described the influence of temperature and of the state of the metallic electrodes on the electromotive force (emf) of a voltaic cell (1). In the copper-zinc Daniell cell he had found that sheet, electrodeposited, and other types of copper, combined with various types of zinc, produced essentially the same emf. Here the electrodes were solid; Raoult decided to investigate what happens when a metal electrode passes from the solid to the liquid state, or the reverse.

He chose bismuth as an example. The metal, cast in a small crucible and immersed in concentrated H_3PO_4 , was made into a cell with copper in CuSO_4 solution. The two half-cells were electrically joined by an inverted U-tube filled with H_3PO_4 . This liquid was chosen so that the bismuth half-cell could be heated to 300°C . The cell emf fell slowly and the bismuth was attacked, as evidenced by evolution of hydrogen. After several hours, the emf stabilized and was unaffected by stirring the melt with the thermometer. The bismuth half-cell was then allowed to cool and the temperature was observed frequently; the onset of solidification was checked by probing with a fine glass tip. The temperature of the copper half-cell remained unchanged throughout the experiment. Raoult found that, as the bismuth cooled from 280° to 250°C , the emf underwent the slight and irregular change from 23.3 to 23.1 (emf of Daniell cell = 100). He reported a sharp change of liquid bismuth to solid at 264°C . (The mp. of the pure metal is 271.3°C , so possibly supercooling occurred.) He stated that *there is no abrupt change of this force at the moment where the bismuth changes state*. No details were

given of experiments with tin and with lead, but the results were similar.

Raoult pointed out that, if convertible into electricity, the latent heat of fusion of bismuth should produce an emf change of 5.5 (Daniell). This number is 25 times larger than the observed total change, including passage through solidification. Thus the emf of a cell does not depend upon the state of aggregation of the metallic electrodes, but on chemical effects.

In 1875, Emil le Coq de Boisbaudran (1838-1912) discovered gallium, which melts at 29.78°C and can remain supercooled extensively. Jules Antoine Regnaud (1820-1895) used these properties to see whether an electrical response could be obtained, at uniform temperature, from a cell with electrodes of the same metal, but in differing states (2). The 4 mm^2 electrodes, solid and liquid respectively, of the then very rare gallium, were placed on a layer of $\text{Ga}_2(\text{SO}_4)_3$ solution. When connected to a galvanometer, deflections of more than 40° were reported, thus indicating a flow of current and hence

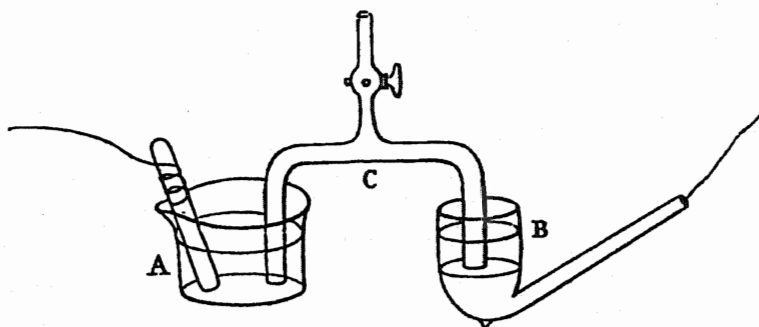


Figure 1. Gore's fusible alloy cell

a difference in the potentials of the electrodes. Regnault noted that the solid electrode was the positive pole, analogous to the copper electrode in a Daniell cell. Raoult's paper was not mentioned; Regnault was probably unaware that his evidence was contrary to Raoult's conclusions.

George Gore (1826-1908), Director of the Institute of Scientific Research in Birmingham, England, knew of Regnault's findings but made no mention of Raoult. Gore continued the liquid-solid studies with alloys of low melting point (3). His apparatus is shown in Fig. 1. The electrode in glass cup A was a bar of the chosen alloy, which was immersed in the electrolyte solution. A portion of this alloy was melted in the bowl of the clay tobacco pipe B and allowed to travel well into the stem. This was to avoid thermoelectric junction effects. After the alloy had solidified and cooled, electrolyte solution was added to B. Some of this solution was drawn up into the siphon tube, thus providing electrical continuity.

Connections to the 100-W galvanometer were made by iron wires. The electrolyte solutions were (a) 1% HCl;

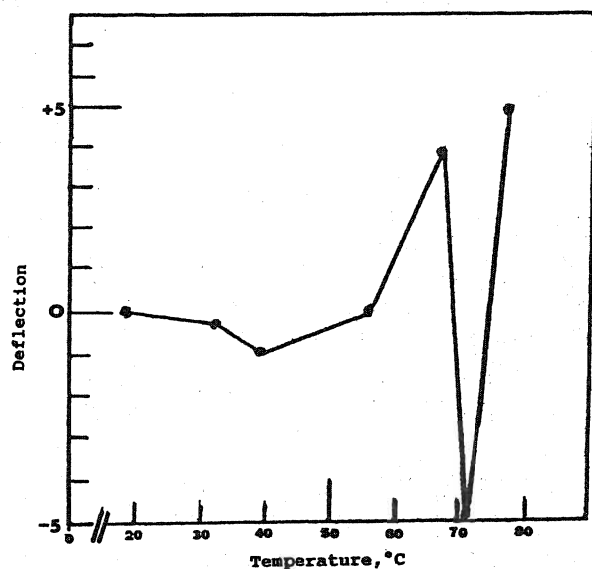


Figure 2. Galvanometer response to the fusion of a cadmium amalgam

(b) 1% NaCl and (c) nearly saturated NaCl solution. Solution (a) at 16° C was used with the alloy: Bi 70 parts, Pb 40, Sn 20, Cd 15; mp @ 66° C. A small flame was applied to bowl B until the alloy melted and the solution above it nearly boiled. Up to the mp the alloy in B gradually became electrically positive to that in A. The galvanometer reading increased suddenly from 20°



Figure 3. William Lash Miller

to 60°, at a point apparently coincident with the melting in B. An experiment with solution (b) gave similar results. The same kind of behavior was shown by an alloy of mp 107° C, used with solution (c).

Subsequent experiments were made with various amalgams. The sudden increase in deflection was small, probably because the amalgam melted gradually. Most successful was the amalgam: Cd 1 part, Hg 4 parts, which was more solid at 16° C than the others. This amalgam was used with solution (b). Fig. 2, sketched from Gore's diagram, shows the galvanometer response as the temperature rose. A deflection maximum just before the complete liquefaction of the amalgam was followed by a sudden depression, with reversal of sign. Then the deflection swung back as shown. Gore attributed the depression to a sudden act of chemical union of the ingredients of the amalgam.

William Lash Miller (Fig. 3) re-examined the problem of emf shift when a metal electrode melts or freezes in Ostwald's laboratory in Leipzig (4). Miller (1866-1940) graduated from the University of Toronto in 1887 and obtained his Ph.D. in organic chemistry from the University of Munich in 1890 but on the basis of research carried out under the direction of A. W. Hofmann. Miller, who moved to Leipzig from Munich, later became one of Canada's greatest chemists.

Miller's cell, shown in Fig. 4, was based on a large test tube. The fusible electrode, which had been melted into the funnel of the J-tube, and the adjacent second

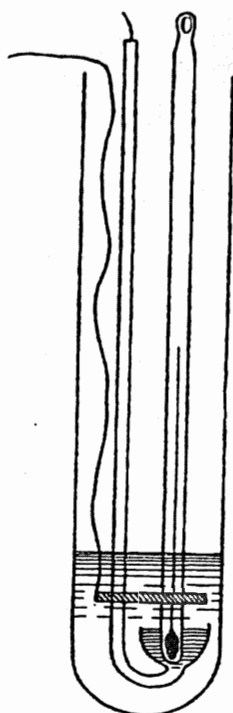


Figure 4. Lash Miller's fusible metal cell

electrode were connected by platinum wires to the potentiometer circuit. Heating or cooling was controlled at approximately $1^\circ\text{C}/\text{min}$. Unless the amount of fusible metal was kept small, the thermometer reading showed an arrest, followed by sudden rise or fall. This caused nonuniformity of temperature within the cell.

Carefully purified lead was used for one electrode; for the other, silver coated with AgCl . A mixture of ZnCl_2 and KCl , which melted at approximately 255°C , was used as a fused-salt electrolyte. Fig. 5, constructed from Lash Miller's data, shows the change, in potentiometer units, as the temperature of the lead decreases.

The total emf change was only 20 mV, with a brief rise of 1-2 mV at the solidification point, 316.5°C as read on the thermometer. With tin as the fusible electrode the electrolyte was an approximately equimolar mixture of KNO_3 , NaNO_3 and $\text{Ca}(\text{NO}_3)_2$, melting at approximately 185°C . In cooling from 268° to 200°C , there was no potentiometric indication of change of state at 225°C , the thermometric solidification point of tin.

Gore (3) had noted that the response at the mp of an amalgam diminished when the amalgam had been remelted several times. From his experiments with these substances, Lash Miller made a similar observation. He concluded that the processes that occur in the melting of amalgams and other alloys were complicated. He finally examined the cell 10% Cd amalgam— Ag/AgCl , 5% NaCl solution, over the temperature range 90° to 45°C . The emf fluctuated irregularly between 650 and 660 mV and underwent no special change at the transition point.

The expectation of a potential difference (pd) at the mp between a solid electrode and its liquid form may have arisen from an extrapolation of a theory proposed by William Thomson (1824-1907), later Lord Kelvin, in 1851 (5). He suggested that the electrical energy ob-

tainable from a cell should be equivalent to the heat of reaction of the chemical processes involved. He found that this was true for the Daniell cell. That Thomson's theory includes all kinds of thermal effects within the cell may have become a common supposition. However, the investigations of Ferdinand Braun (1850-1918) showed that Thomson's theory was valid only when the temperature coefficient, dE/dT , of the emf, E , of the cell was negligible (6). This was the case with the Daniell cell. The theoretical developments by Josiah Willard Gibbs (1839-1903) and Hermann Helmholtz (1821-1894) led to the conclusion that E differed from the value calculated from the chemical heat of the cell reaction by the quantity $T(dE/dT)$, where T is the absolute temperature.

Miller, aware of these developments, also applied a "thought experiment" to the solid-liquid problem. Consider a cell at the melting point X of the electrodes, both of metal M . However, one electrode is liquid, the other, solid. If the cell has an emf, internal electrolysis will occur when the electrodes are connected together. Then, for example, M will dissolve from the liquid electrode and deposition will occur on the solid electrode.

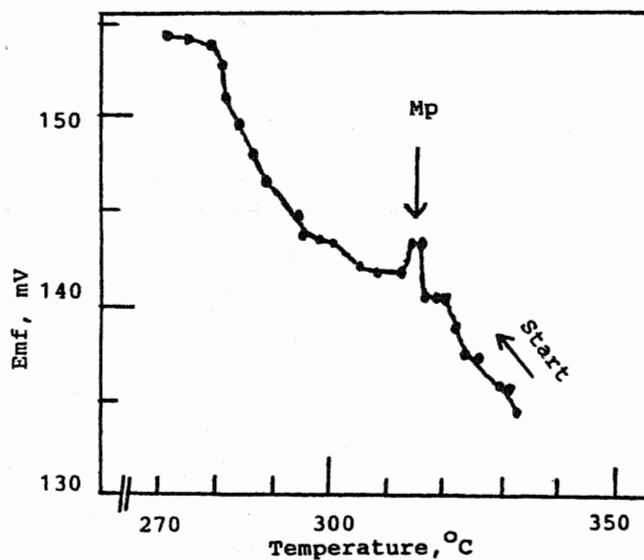


Figure 5. Response of $\text{Pb-Ag}/\text{AgCl}$ cell (from ref. 4)

Now the deposit can be melted without change of temperature and taken back to the liquid electrode, so that electrolysis can continue indefinitely. Further, suppose that the electrodes are connected to a small motor; then we will have perpetual motion. If a short wire resistor replaces the motor, the temperature of the wire will be-

come greater than X. Such results are contrary both to experience and to the principles of thermodynamics.

Theory (7) and experiment indicate that at the mp of M, the liquid and solid forms of M must have the same potential. Although this potential, or the emf, E, of a cell of which M forms one electrode, may change with change of temperature, the E-T curve should be smooth, *i.e.*, should show no irregularity as the temperature rises or falls through the mp of M. However, the small "kink," sometimes observed in the curve, seems to be real. Ostwald suggested that the observed effect is due to a change in the *temperature coefficient*, dE/dT , as change of state occurs (8). This change, F, depends upon the latent heat of fusion L and the absolute temperature, T (9). For lead, $L = 1224/2 \text{ cal eqvt}^{-1}$, or $5121/2 \text{ J eqvt}^{-1}$, and $T = 601^\circ \text{ K}$. Hence $F = (2561 \times 1000) / (96485 \times 601) \approx 4.4 \times 10^{-2} \text{ mV K}^{-1}$. The apparent slope in the 290° to 330° C range in Fig. 5 is approximately 0.25 mV / deg. , so that F is about 18% of this.

Because the change in temperature coefficient is brief when melting or freezing is sharp, the change could be difficult to detect. Raoult and Miller made use of "opposition" or "compensation" potentiometry which, involving instrument adjustment throughout measurements, does not provide continuous indication.

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5. W. Thomson, "On the mechanical theory of electrolytes," *Philos. Mag.*, **1851**, 4, 429-444.
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7. Since liquid and solid are in equilibrium at the melting point, DG, the free energy of fusion per equivalent, and the corresponding potential E must both be zero ($DG = -FE$, where F is the Faraday constant).
8. W. Ostwald, *Chemische Energie*, Engelmann, Leipzig, 2nd ed., 1893, 869.
9. This change, $F = DS/F = L/FT$, where F is the change in dE/dT due to fusion; DS and L are, respectively, the entropy and latent heat of fusion per equivalent.

FOUNDATIONS OF CHEMISTRY

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CALL FOR NOMINATIONS:
DEXTER AWARD
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The Division of the History of Chemistry of the American Chemical Society (ACS) solicits nominations for the 1999 Dexter Award for Outstanding Achievement in the History of Chemistry. The award, which is sponsored by the Dexter Chemical Corporation and administered by the Division of the History of Chemistry, consists of an engraved plaque and a check for \$2000 and is presented annually at the Fall National Meeting of the ACS. The award is international in scope and nominations are welcome from all quarters. Previous winners have included historians and chemists from Canada, Germany, France, Hungary, The Netherlands, and the United Kingdom. Nominations should include a complete curriculum vita for the nominee, consisting of biographical data, educational background, awards, honors, publications, presentations, and other services to the profession; a nominating letter summarizing the nominee's achievements in the field of the history of chemistry and citing unique contributions that merit a major award; and at least two seconding letters. Copies of no more than three publications maybe included, if available. All nominations should be sent in triplicate to Professor Frederic L. Holmes, Chair of the Dexter Award Committee, Section of History of Medicine, Yale University School of Medicine, 333 Cedar Street, New Haven, CT 06520, by January 1, 1998.

THE WISWESSER-LOSCHMIDT CONNECTION *

Alfred Bader, Milwaukee, WI

William Joseph Wiswesser (1914-1989) [Fig. 1] graduated from Lehigh University with a B.S. in chemistry in 1936 and received an honorary D.Sc. from that institution in 1974. He was employed by Hercules, the Trojan Powder Company, the Picatinny Arsenal, the Cooper Union, Willson Products, the U.S. Army at Fort Detrick, and finally by the Agricultural Research Service of the U.S.D.A., Being interested throughout his varied career in simplifying chemical structure descriptions, he developed the Wiswesser Line Notation (WLN), which made possible the single-line depiction of every molecule, no matter how complicated. Research organiza-



Figure 1. William J. Wiswesser

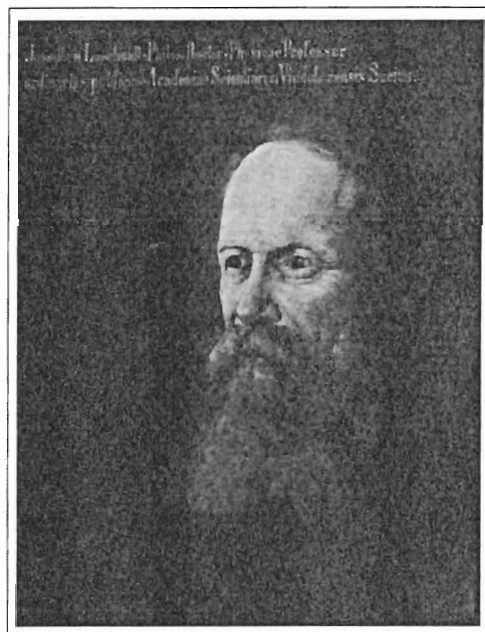


Figure 2. Josef Loschmidt

tions in the 1980's had millions of WLN records in their computers. The Aldrich Chemical Company even offered its catalog in WLN.

Wiswesser learned about the chemical work of Josef Loschmidt (1821-1895) [Fig. 2] from Moritz Kohn's paper in the *Journal of Chemical Education* (1), which is based on Richard Anschütz's paper (2) and reprint (3) of Loschmidt's 1861 volume (4). He felt that he had made a great rediscovery, also believing that this somewhat obscure chemist was the forerunner of the WLN; and he wanted the world to know about it.

He submitted a manuscript to the present author (A.B.) for the *Aldrichimica Acta*, which at the time was being distributed to over 200,000 scientists worldwide. Although the initial response was one of reluctance, I became enthusiastic about the subject after reading Loschmidt's book (3) and some letters, in particular one by Wiswesser to Linus Pauling (see Ref. 16), and collaborated to expand the paper, which appeared in *Aldrichimica Acta* in 1989 (5).

Wiswesser described Loschmidt's chemical firsts:

1. The first correct cyclic structure of benzene and of many aromatic chemicals, 121 in all.
2. The first representation of the allyl moiety.
3. The first representation of the vinyl moiety and of many others.
4. The first representation of cyclopropane, 21 years before it was made by Freund.
5. The first picture book of molecules, containing graphic displays with atomic domains, rather than abstract bond lines.
6. The first double- and triple-bond marks (within the overlaps).
7. The first realistic displays of atomic sizes and bond distances (largest overlap with triple bonds).
8. The first set of diagrams with correct $C = 12$, $N = 14$, $O = 16$ formulas.
9. The first textbook use of atomic-group symbols.
10. The first use of the valence prime marks on these and atomic symbols ("Valenz" was introduced by Wichelhaus in 1868, 7 years later).
11. The first LINE-FORMULA NOTATIONS ("rational formulas").
12. The first revelations of hexavalent and tetravalent sulfur.

The article also outlined Loschmidt's life and work, based largely on the biography Richard Anschütz published with the 1913 reprint. Wiswesser also prepared indices of Loschmidt and Anschütz citations, by author and subject. He translated Loschmidt's chemical names into English and collated structures with page numbers.

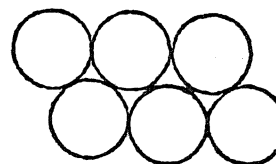
On the occasion of our last meeting in Reading, PA, Wiswesser gave me a great deal of his material on Loschmidt, even copies of the original plates, which he had hand-colored. Expressing concern about his own failing health, he urged me to continue his work on Loschmidt. I remember his pleasure upon receiving the *Acta* containing his article, just a few days before he died.

Since then, I have been trying to continue his work, by giving many lectures, first at the Boston American Chemical Society meeting in April 1990 (6), to which

he had been invited, and then at chemical society meetings and in chemistry departments, and finally by publishing several papers (7). All of these lectures and papers were based on Wiswesser's seminal paper in the *Aldrichimica Acta* (5). I have been greatly helped in these efforts by Professor Christian R. Noe, formerly at Loschmidt's alma mater, the Technical University in Vienna, and now at the J.W. Goethe University in Frankfurt.

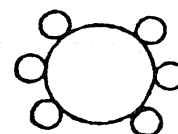
Our papers have been attacked quite sharply by two historians of chemistry, Professors A.J. Roche (8) and G.P. Schiemenz (9). Roche presents three main arguments:

- (1) "Loschmidt clearly believed that the most probable structure for benzene (Schema 182) was a formula constructed from multiple fused cyclopropyl rings, using only single bonds. (8)"



Schema 182

However, all of Loschmidt's more than 100 aromatic compounds are based on Schema 185 as the basic benzene structure.



Schema 185

- (2) "... Kekulé himself did not recognize Loschmidt as a predecessor for the benzene structure because he cited Loschmidt's benzene proposal in his first paper on the subject. If Kekulé had consciously taken the idea for benzene from this obscure source, or regarded the Loschmidt structure as similar to his own, the last thing he would have wanted to do was to draw attention to it. (8)"

Kekulé did not "cite" Loschmidt's proposal. All he said in one footnote in French (10) and one in German (11) was, "I prefer my structure to those of Loschmidt and Crum Brown." Aside from these denigrating footnotes - not citations - and one brief abstract (12), there were *no* references to Loschmidt's book in

the entire 19th century. Rocke points to the *Dictionary of Scientific Biography*, where more space is devoted to Loschmidt than to Kekulé. Loschmidt was indeed well known in the 19th century, but as a physicist, not a chemist. Not until Anschütz's first paper (2) was Loschmidt recognized as a highly competent chemist.

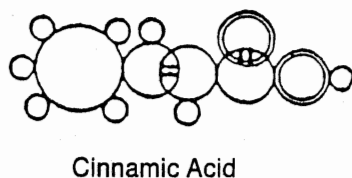
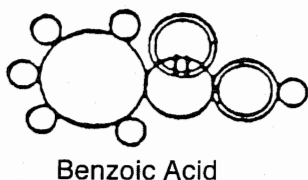
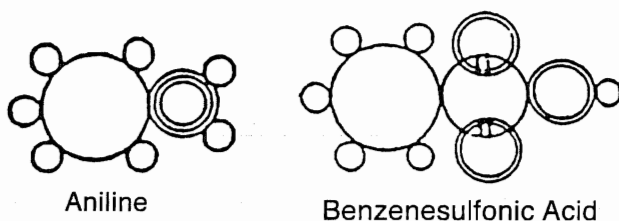
(3) "Even if Loschmidt had suggested a cyclical benzene structure in 1861, I would argue for its insignificance, because no empirical evidence could then be adduced to support the idea. (8)"

This is the kind of argument that can be made against much purely theoretical work.

Schiemenz criticized Wiswesser *inter alia* for claiming that Loschmidt was the first to consider a 6-carbon monocyclic structure for benzene, and also for stating that Loschmidt's book of 1861 was practically unknown and that he was "a shy and self-effacing man."

"Die Idee einer monocyclischen Anordnung der sechs C-Atome des Benzols kommt nach allem bei Loschmidt auch nicht andeutungsweise vor. (9a, 9c)" [*Nowhere is there in Loschmidt's book even the slightest hint of a monocyclic arrangement of the 6 carbon atoms in benzene.*"]

But consider the following structures to represent aromatic compounds aniline, benzenesulfonic acid, benzoic acid, and cinnamic acid.



In a letter to *Chemistry and Industry*, Schiemenz wrote (9b):

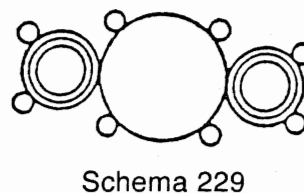
This misunderstanding that Loschmidt's benzene structures might symbolize a monocyclic formula was already discussed by E. Rey in 1965, who aptly commented that one must interpret the circular symbol as what it really means and not as what it could be, and hence not as a circular array of six carbon atoms. The argument also holds true for all of Loschmidt's formulae (by the way, there were not 386!) which may have some superficial resemblance with modern molecular models. To date molecular modeling back to 1861 is just anachronistic.

Schiemenz's English summary of his longest paper states (9c):

In 1989, W. J. Wiswesser claimed that the correct, monocyclic structure of benzene was not conceived in 1865 by A. Kekulé, but already in 1861 by J. Loschmidt. It is shown that this view is neither correct nor new. As a symbol for the benzene nucleus C_6 , Loschmidt used a circle which Wiswesser believed to stand for a cyclic array of the six carbon atoms. In fact, this circle represents, in the two-dimensionality of the printed page, a sphere. Similar, but smaller 'circles' (*i.e.* spheres) represent hydrogen, carbon, nitrogen, oxygen and sulfur atoms. Their sizes are chosen so that the volumes of the corresponding spheres reflect the respective atomic weights (72 for C_6). This meaning soon passed into oblivion. As a consequence, gradually a misinterpretation developed which culminated in Wiswesser's view which recently has been popularized by C.R. Noe and A. Bader.

The most telling indication that Loschmidt thought of a monocyclic structure is in his Schema 229 for *p*-phenylenediamine (13):

Schon der Anblick des Schema zeigt die Möglichkeit von isomeren Modificationen. ["Just looking at Schema 229 shows the possibility of isomeric modifications."]



Schiemenz counters (9d):

Auch eine Anmerkung *Loschmidts* zum 'Semibenzidam' = 'Azophenylamin' (Phenylendiamin), Schema 229, gehört hierher: 'Schon der Anblick des Schema zeigt die Möglichkeit

von isomeren Modificationen' (Loschmidt (1861), 34). Entgegen der Auffassung von Noe and Bader (*Chemistry in Britain* 29 (1993) 402, Corrigendum: S.573; vgl. dies., in Wotiz (1993), 233) einer Interpretation als o-, m-, p- Positionsisomerie noch nicht zugänglich (Anschütz (1913), 132), kann diese Bemerkung nur im Sinne einer Konstitutionsisomerie verstanden werden (vgl. Loschmidt (1861): *Isomerie*, S.8-11). Mithin muß bereits Loschmidt, der anderswo N-N- und auch O-O-Bindungen hat (Schema 176,178), an die Atomverknüpfung des Phenylhydrazins gedacht haben.

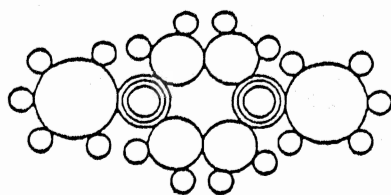
Thus, Schiemenz dismisses this argument by claiming that Loschmidt must have been thinking of an isomer like phenylhydrazine (which had not yet been made). However, in his discussion on isomerism, Loschmidt distinguished between isomers "im engern Sinne," like o-, m-, and p-isomers, and isomers "im weiteren Sinne," like phenylenediamine and phenylhydrazine. The former you can predict just by looking at them, but not the latter (14):

... wir **Isomerie im engern Sinne nennen**. Solche Isomerie findet statt zwischen Milchsäure und Paramilchsäure, zwischen **Alphatoluolsäure und Betatoluolsäure**. Die anderen Arten der **Isomerie im weiteren Sinne sind**: erstens jene Fälle, wo zwei Substanzen denselben Kern und dieselben Aufsatz-Atome haben, wo aber die letzteren zu anderen Aufsatzelementen gruppiert sind. **So haben Nitrotoluol und Benzaminsäure** [i.e., aminobenzoic acid] nicht nur dieselbe Zusammenstellung $C_7NH_7O_2$, sondern auch denselben Kern C_7^{VIII} und dieselben Aufsatzatome NH_7O_2 ." [Emphasis added]

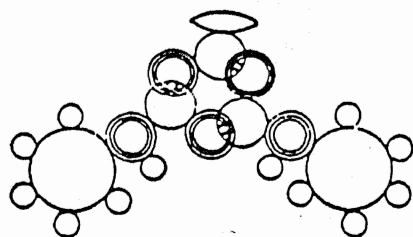
Schiemenz points out that Loschmidt did think of six-atom monocycles such as his Schema 237, 1,4-diphenylpiperazine, and claims that this is "unambiguous proof that he did not think of such an array for [the C_6 nuclei]. (15)" Yet, in fact, Loschmidt came even closer to Kekulé's cyclohexatriene structure in his Schema 239 for the 1,3,5-triazine derived from aniline and 2,4,6-trichloro-1,3,5-triazine.

Nr. 10 Kokele am 27ten März
 Ungarisch 2. 1. 67
 Land 4. Jan 62.
 Lieber Erlenmeyer!
 Ihre gegenwärtig Britisch. des Erd-
 mannschafts Ägyptische Theorie habe ich
 erhalten (- lassen versch.) und habe;
 gänzlich gleichsam als Loschmidt's Confe-
 sions formale. Ich bedauere, daß ich nicht
 zum Britisch des Britisch auffordere;
 ich fühlte natürlich lieber still yaffringan &
 ich glaube sogar ich will wohl Ihre Auffor-
 derung still yaffringan. Ich würde mich nie

Figure 3. Letter from Kekulé to E. Erlenmeyer



Schema 237



Schema 239

Rather than being unambiguous proof that Loschmidt did not think of benzene as a six-carbon monocycle, it suggests that he must have considered such a structure but did not know how to do this without the inclusion of double bonds, hence, his decision to leave that “*in suspenso*. (16)”

Shortly after Loschmidt's book appeared on January 4, 1862, Kekulé wrote a letter to Emil Erlenmeyer [Fig. 3], in which he alluded to “*Loschmidt's Confusions formeln* (sic).” Why would Kekulé have chosen such a description for Loschmidt's structures? Because in 1861, Kekulé stated that you cannot write formulae of constitution, and so considered Loschmidt's structures “*formulae of confusion* (17):

Which of the different rational formulae one wants to use for specific cases is essentially a question of appropriateness. Based on the observations already given, there can be no doubt that one may use different rational formulae for the same substance. At the same time, one must also, of course, keep in mind that the rational formulae are only formulae of reactions (“*Umsetzungsformeln*”) and not formulae of constitution (“*Constitutionsformeln*”), and that they do not in any way describe the constitution, i.e., the position of the atoms in the compounds. This should be clearly stressed, because oddly enough some chemists still believe that by the study of chemical reactions, one can derive with certainty the constitution of compounds, and thus depict the positions of the atoms in the chemical formula. That the latter is not possible warrants no special proof ... Yet a basic task of natural science must of necessity be to discover the constitution of matter or in other words, the position of atoms; this, however, can only be at-

tained by the comparative study of physical properties of the existing compound and certainly not by the study of chemical reactions ... But even when we have succeeded in this, different rational formulae (“*Umsetzungsformeln*”) will still be appropriate. [Emphasis added]

As R.B. Woodward stressed in his 1972 Cope lecture (18):

He [Kekulé] was, in truth, too much under the influence of the theoretical and physical chemists of the time, who were inordinately opposed to the idea of fixed chemical structure—so much so that, until 1886, the infant *Berichte der Deutschen Chemischen Gesellschaft*, born in 1868, would only print structural formulae using dotted-and-dashed lines; the use of solid lines to represent the nearest neighbor relationships would have imputed too much reality to an hypothesis which leading theorists of the day simply would not accept.

Schiemenz (19) has claimed that Loschmidt's 1861 book became well known after its publication. As is clear from Kekulé's letter, he and Erlenmeyer knew of it (20). So did Herman Kopp who reviewed it briefly (12). Before Anschütz's publications of 1912 (2) and 1913 (3), however, there were only three references to it: two brief and disparaging footnotes (10, 11) in Kekulé's papers and Kopp's review (12). If indeed Schiemenz (19) is correct in asserting that Loschmidt's book was widely known, chemists may have ‘borrowed’ from it without bothering to cite it; but that seems unlikely (21).

Schiemenz faults Wiswesser for describing Loschmidt as “a shy and self-effacing man.” How could a man “who was a member of the Imperial Academy of Sciences, founder of the Chemical-Physical Society, institute director and, at one time, dean of the faculty of philosophy of the University of Vienna be ‘a shy and self-effacing man’? (22)” Although this may indeed be difficult to understand, many who knew Loschmidt personally wrote about that very quality. Franz Exner, Loschmidt's successor as professor of physics at the University of Vienna, had known Loschmidt well for many years because Loschmidt had been a student and friend of Exner's father at the University of Prague. At the 100th anniversary of Loschmidt's birth, Exner wrote that Loschmidt had “a rare goodness of heart and modesty; totally without jealousy, he could enjoy the scientific successes of others just as much as his own. (23)” Alexander Bauer, the grandfather of the Nobel laureate Erwin Schrödinger, described his unsuccessful attempts to bring the *Chemische Studien* to the attention of scientists during a trip to England (24):

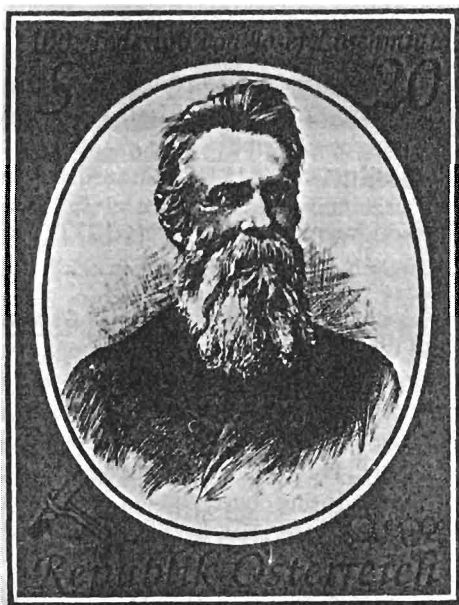


Figure 4. Commemorative Stamp

Only one, the mathematician Liouville (25) in Paris showed great interest and gave it a very favorable review. That publication [*Chemische Studien*] was quickly forgotten. It cannot be denied that its author was much to blame for that, because he later did nothing to draw attention to it, even though he had many opportunities.

Loschmidt's best friend, Ludwig Boltzmann, said, "...everywhere Loschmidt's excessive modesty prevented his being appreciated as much as he could and should have been. (26a)... He just could not stand it, when people talked about him and his merits.(26b)"

Richard Anschütz questioned why Loschmidt did not point to his own work of 1861 at the time of the *Benzolfest* in 1890 which celebrated the 25th anniversary of the correct benzene structure. Anschütz believed that Loschmidt's silence was "...because of the undemanding modesty which was an integral part of his character. The discovery of *Chemische Studien* ... his old, unnoticed and forgotten work, he left to chance (27)"—and, luckily, we must add, to Richard Anschütz and William Wiswesser.

A high point in Loschmidt's recognition as a chemist came at a symposium at the University of Vienna in June, 1995, at which many well known chemists paid tribute to Loschmidt, who had died 100 years earlier in July, 1895. Among the lecturers were Max Perutz, Carl Djerassi, and Sir Herbert Bondi, all originally from Vienna, and Ernest Eliel, Albert Eschenmoser, Christian Noe and Günter Schiemenz. The papers, which dealt

with chemistry and physics, have been published in English by Plenum (28). It was Wiswesser's recognition of Loschmidt's remarkable insights into chemical structure which sparked the renewed interest in and a greater understanding and appreciation of the *Chemische Studien*, culminating in the 1995 Symposium.

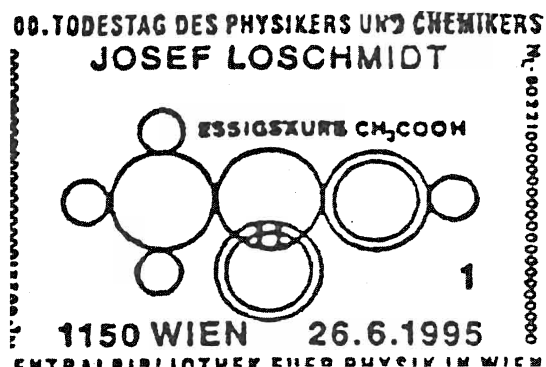


Figure 5. First-day Postmark

The Austrian postal service issued a commemorative stamp [Fig. 4] showing one of Loschmidt's many correct aromatic structures, that of cinnamic acid. The postmark of the first-day cover [Fig. 5] showed the structure of acetic acid, one of Loschmidt's many firsts.

Did Wiswesser make mistakes? Of the twelve "famous firsts," No. 1, "The first correct cyclic structure of benzene and of many aromatic chemicals, 121 in all," is somewhat of an overstatement. Loschmidt was the first to consider a monocyclic six carbon ring, but he did not know what to do with the double bonds. Kekulé's cyclohexatriene of 1865 appeared to be an improvement, but the puzzle about its unsaturation was still to be addressed (29). Wiswesser was correct in describing Loschmidt's other firsts and in ending his paper with, "...that tiny book of 1861 was really the masterpiece of the century in organic chemistry."

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12. Liebig's *Jahresbericht*, **1861**, 1, 335. [See Ref. 3, p. 100.]
13. Ref. 3, p. 68.
14. Ref. 3, p. 15.
15. Ref. 9b; Ref. 9c, p. 47.
16. I want to thank William F. Reynolds for pointing out that Loschmidt was probably reluctant to accept a benzene structure with double bonds, of which he was well aware, since this seemed inconsistent with the known chemistry of benzene. As Wiswesser pointed out in a letter to Linus Pauling (August 2, 1987, copy in author's personal collection), Loschmidt provided "amazingly perceptive graphical visualizations" in 1861 of increasingly tighter, overlapping bonding in ethane (Schema 9), ethylene (Schema 56, 57), and acetylene (Schema 59). Photocopies of this letter are available on request from either the author or the editor of the *Bulletin*.
17. A. Kekulé, *Lehrbuch der organischen Chemie*, F. Enke, Erlangen, 1861, p. 157.
18. R. B. Woodward, unpublished manuscript, courtesy of R. Hoffmann and the Chemical Heritage Foundation.
19. Ref. 9c, pp. 42-43.
20. "Knowing" and "understanding" are not always the same. In the heat of discussion during the Boston American Chemical Society meeting (6), I suggested that Kekulé may have plagiarized Loschmidt. I no longer think so. Kekulé 'knew' Loschmidt's book but did not 'understand' it as Anschütz and Wiswesser did. Loschmidt's Schema 185 for benzene may have led to Kekulé's snake dream, but we can never know for certain whether he even had that dream. The first six-carbon monocyclic benzene structure was Loschmidt's; the first cyclohexatriene Kekulé's. Most recently E. Heilbronner and K. Hafner have reviewed this controversy ("Bemerkungen zu Loschmidts Benzolformel," *Chemie Unserer Zeit*, **1998**, 32, 34). The authors approve particularly of Schiemenz' (Ref. 9c) "ausgezeichneten und akribisch recherchierten Richtigstellung" [Schiemenz' excellent and meticulously researched correction] and of Hafner's "August Kekulé, dem Baumeister der Chemie zum 150 Geburtstag," Justus von Liebig Verlag, Darmstadt, 1980. There (p. 76) Hafner wrote, "...again Kekulé succeeded brilliantly. His irresistible desire for clarity and his unusual power of imagination again helped. Basically the benzene formula is a logical conclusion from structural history. Today it seems obvious, but over a hundred years ago it was an extraordinary mental leap, comparable to the intellectual effort once necessary before man could exchange sled runners for the wheel. *The idea that a hydrocarbon might have a circular structure was totally foreign to chemists of that time. The circle was the symbol for the indivisible, the atom.*" [emphasis added]. But 13 years earlier Ferdinand Kirchoff ("Joseph Loschmidt und die Benzolformel," *Chem. Appar.*, **1967**, 91(2), 48) had written, "*The idea that a compound might have a circular structure was totally foreign to chemists of that time. The circle was the symbol for the indivisible, the atom, and the merit of having depicted the C₆^{vi} nucleus as a circle belongs unquestionably to Loschmidt.*" [emphasis added].
21. Recently, F. W. Lichtenhaler ("Emil Fischer's Proof of the Configuration of Sugars: A Centennial Tribute," *Angew. Chem. Int. Ed. Engl.*, **1992**, 31, 1541) has suggested that Adolf Baeyer, Hugo Schiff, and Rudolph Fittig were the first to depict sugars correctly, around 1870. Anschütz pointed out that Loschmidt was the

- first—nine years earlier—to show the correct structures of mannitol and other sugars (Ref. 3, pp. 119-120, footnotes 63, 66, 69, 70 and 72). But are Baeyer, Schiff, and Fittig likely to have known this?
22. Ref. 9c, p. 57.
 23. F. Exner, "Zur Erinnerung an Josef Loschmidt," *Naturwissenschaften*, **1921**, 9, Heft 11, March 18.
 24. A. Bauer, *Oesterreichische Chemiker-Zeitung*, **1913**, XVI, No. 18, 241, September 15.
 25. Jean Jacques has kindly pointed out that this was Joseph Liouville (1809-1882), but his review of *Chemische Studien* appears not to have been published.
 26. L. Boltzmann, "Zur Erinnerung an Josef Loschmidt," a eulogy presented to the Imperial Academy of Sciences in Vienna on October 29, 1895 and published by the executive committee for the erection of the Loschmidt monument, Vienna 1899; (a) p. 14; (b) p. 16.
 27. Ref. 3, p. 109.
 28. W. Fleischhacker and T. Schönfeld, Ed., *Pioneering Ideas for the Physical and Chemical Sciences*, Plenum Press, New York, 1997; see also Ref. 7g, h, 9e.
 29. For a clear discussion of Kekulé's benzene formulae, see G. P. Schiemenz' "Where did Kekulé Find 'his' Benzene Formula?" Ref. 7b, Ch. 9.

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The German Chemical Society extends an invitation internationally for applications for the Paul Bunge Prize 1999 of the Hans R. Jenemann Foundation. The award consists of DM 10,000, honors outstanding publications in German, English, or French in all fields of the history of scientific instruments. Deadline is September 30, 1998. Information is available at the German Chemical Society, Public Relations Dept., PO Box 900440, D-60444 Frankfurt/Main; FAX 69/7917-322; pr@gdch.de.

CONFERENCE ON HISTORY AND HERITAGE OF SCIENCE INFORMATION SYSTEMS

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WHEN PIPERIDINE WAS A STRUCTURAL PROBLEM

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In 1850-51 August Hofmann in London published his newly developed method for degrading amines, which he was later to call exhaustive methylation, including mention of its potential use on alkaloids (1). Within a year in 1852 Auguste Cahours in Paris announced the isolation of a new liquid base, piperidine, $C_5H_{11}N$, from pepper (2). When organic structural theory was introduced in 1858, the constitution of piperidine became a problem which today seems to have been tailor-made for Hofmann's new procedure. While it now seems hard to believe that such a simple molecule could have offered difficulties, it was not until about 1881 that the structure of piperidine was established. Ironically, although it was Hofmann himself who eventually applied the exhaustive methylation procedure to piperidine, he was unable to interpret correctly the course of the reaction before Albert Ladenburg explained it in 1883. The probable reasons for this lapse as well as other curious aspects of the early chemistry of piperidine emerge from the literature, which is notable for the cautious approach taken to what was considered proof of structure.

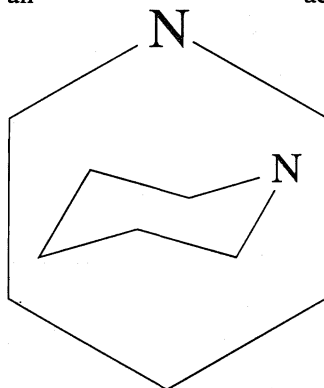
Piperidine became available early in the development of organic chemistry, at a time when few liquid organic bases were known, because it happened to be a component of the crystalline alkaloid piperine, $C_{17}H_{19}NO_3$, which had been isolated as early as 1820-21 from pepper (*Piper nigrum*) by Hans Christian Oersted in Copenhagen (3, 4), who suggested the name, and

by Joseph Pelletier in Paris (5). Since piperine occurs to the extent of 5-10% in peppercorns from various sources (6, 7) and is easily extractable by alcohol, it was readily available to the chemical community across Europe. In fact, piperine became of theoretical interest in connection with early speculations on the nature of plant alkalis: Were they merely associations of ammonia with a carbon compound, or, as Liebig had suggested, did they belong to the class of amides [here meaning any organic radical attached to $-NH_2$] (1a,8)?

In agreement with the latter view, Theodor Wertheim at Vienna in collaboration with Friedrich Rochleder at Lemberg found in 1845 that piperine

was split by aqueous alkali into an acid and a liquid base which they identified as aniline [known since 1826 (9)] solely on the basis of C,H and Pt analyses of the chloroplatinate (10). Later in 1849 Wertheim changed his mind (11) and decided that the liquid base fit better the properties of the isomeric picoline [now known to be α] recently discovered in 1846 (12, 13). Oddly enough, Wertheim made no mention of the boiling point of his base even though the reported atmospheric boiling points for aniline [$182^\circ C$ (14)] and picoline [$133^\circ C$ (12)] differed widely; he apparently had not determined this critical physical property!

It was the putative identification as picoline that led the French chemist Auguste Cahours to repeat Wertheim's isolation. Cahours wished to make a comparison of picoline with aniline, perhaps with the aim of determining the basis for their isomerism. Distilla-





Auguste-Thomas Cahours 1813-1891

tion of a mixture of piperine, water, and potassium/calcium hydroxide, followed by addition of more potassium hydroxide to the distillate, caused the separation of an oily base which Cahours distilled twice to obtain a colorless basic liquid of strong ammoniacal odor and constant boiling point 106°C (15). Although he did not say so, it was presumably this boiling point, much lower than that of either aniline or picoline, which first indicated to Cahours that he actually had a different base; he named the new compound piperidine because of its source (16).

Analysis of the free base and eleven of its crystalline derivatives fixed the formula as $\text{C}_5\text{H}_{11}\text{N}$ [in Cahours' terms $\text{C}^{10}\text{H}^{11}\text{Az}$] which was confirmed by two vapor density determinations, altogether a very thorough piece of work for the time (15). Cahours made no mention of the fact that his analysis of the chloroplatinate of the base from piperine differed appreciably from Wertheim's analysis of [presumably] the same derivative, but he did state that piperidine differs completely in composition and properties from picoline with which Wertheim had confused it (17). It is surprising to the modern reader that no melting points are reported in either Cahours' or Wertheim's papers; melting points had not yet come into general use as criteria of identity or purity (18). Relying on Hofmann's work on amines, Cahours concluded that piperidine was an imide base [= secondary amine] since it formed *mono*-methyl, ethyl, and [iso]amyl de-

rivatives. He further surmised that the two alkyl groups attached to the nitrogen atom might be ethyl and allyl. Beyond this in 1853 there was not much more that could be done in investigating piperidine.

Hofmann at this time was the Professor of Chemistry at the new Royal College of Chemistry in London. Cahours and Hofmann were already known to each other from having corresponded regularly about chemical matters of common interest (19). On a visit to Paris in 1850 Hofmann took the opportunity to become personally acquainted with Cahours (19); the two chemists hit it off well and became good friends. When Cahours visited London for several weeks in 1855 to learn about the state of chemistry there, he stayed with Hofmann, and they began joint investigations which resulted in publications on two topics, neither of which involved nitrogen chemistry (19, 20). They must have discussed piperidine during their time together in London or else in letters, but it was too early for collaboration on a *structure* for this alkaloid fragment. However, after the structural theory of 1858 had been introduced, the question of the structure of the simple piperidine molecule must surely have entered both their minds. Rather puzzlingly, Cahours never published on piperidine again, even though he did work on the structure of nicotine in 1879-83. Nor did Hofmann take up the problem until much later. Cyclic structures were unknown at this time, and perhaps Cahours and Hofmann, considering only acyclic arrangements, regarded the question of which simple alkyl groups were attached to the secondary nitrogen atom as being relatively unimportant.

During the period from 1857 to 1878 several chemists worked on piperine, but they were more interested in the non-basic part from its hydrolytic cleavage (21). Wertheim continued studying piperidine, and in 1863 he investigated the nitrosation reaction and its reversal but got no further before his early death in 1864 (22). In 1871 Karl Kraut in Hannover made several salts from the adduct of piperidine and chloroacetic acid but did not comment on the structure of the base (23). Eventually some evidence of interest on Hofmann's part came from a paper appearing in 1871, the first paper of the twenty one-year old graduate student Julius Brühl, published from Hofmann's Berlin laboratory (24). In it Brühl pointed out that the constitution of piperidine was still not known, and he prepared some salts in the hope of transforming piperidine into a member of a known group of compounds, but without success. By now a cyclic structure was beginning to be considered because Brühl remarked on the likelihood that piperidine was formed from the entry of a bivalent C_5H_{10} group into

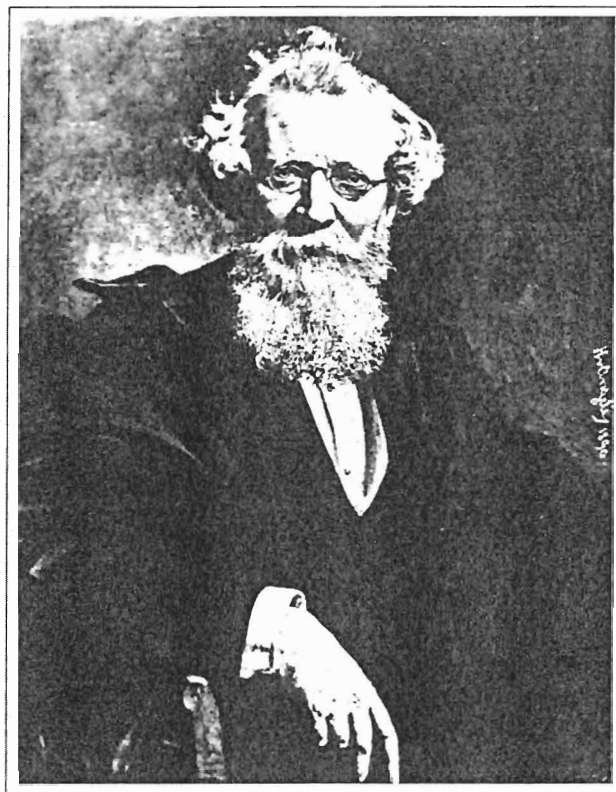
ammonia (25). Finally in 1879, Hofmann published his first work on the structure of piperidine (26).

Although by 1870 five- and six-membered rings were becoming generally accepted [*e.g.* benzene (1865), pyridine (1869-70), pyrrole (1870)], Hofmann pointed out that current chemical thinking still supposed that piperidine $C_5H_{10}NH$ contained two alkyl groups, one being unsaturated, such as ethyl and allyl or methyl and crotonyl, a view unchanged since Cahours' statement in 1853 (15). He did not employ his exhaustive methylation method at first but instead tried to remove one of the [supposed] alkyl groups by the well-known procedure of heating with the strongest hydrochloric acid for days in a sealed tube, even up to $300^\circ C$, but no alkyl halide was split off (26). Nor did dry distillation of the hydrochloride salt give an alkyl halide. Reaction of piperidine with bromine in a sealed tube at $200\text{--}220^\circ C$ afforded a crystalline product of dehydrogenation, $C_5H_3NOBr_2$, soluble in hot hydrochloric acid and in sodium hydroxide solution, which Hofmann was tempted to consider a pyridine derivative. However, because he was unable to obtain the same crystalline product from the reaction of bromine with pyridine [instead a dibromopyridine, m.p. $109\text{--}110^\circ C$, now known to be the 3,5-dibromo-isomer, was isolated], he did not insist on the crystalline product being a pyridine compound (26).

Hofmann was not the only chemist concerned with the structure of piperidine. Fortuitously in the same year, 1879, the young Wilhelm Koenigs at Munich announced in the *Berichte* that he had been able to oxidize piperidine directly to pyridine, albeit in low yield, with concentrated sulfuric acid at *ca.* $300^\circ C$ (27). The pyridine was identified by odor and C,H and Pt analyses of its chloroplatinate salt. He felt confident that the formation of pyridine was structurally meaningful and not an artifact of cyclization, probably because he also found that ethylallylamine gave no trace of pyridine when heated with sulfuric acid (27). Therefore Koenigs proposed the reduced pyridine [*i.e.*, cyclic pentamethylenimine] structure for piperidine.

Almost two years later in 1881 Hofmann finally reported on the application of his exhaustive methylation method to piperidine, first in a preliminary notice (28) followed shortly by the full description (29). While the method had been announced 30 years previously (1), this was the first application to a compound of unknown structure. Hofmann was well aware of Koenigs' oxidation of piperidine to pyridine, but he was skeptical of the significance of the result because of the low yield and brutal conditions; he was still thinking in terms of a dialkylamine and was expecting removal of an alkyl

group when dimethylpiperidinium hydroxide was distilled. When he found by analysis that no alkyl group had been lost, and the product, $C_7H_{15}N$, named dimethylpiperidine by him, formally contained two methyl groups added to piperidine, he was puzzled by this apparent violation of his own rules for decomposition of quaternary ammonium salts: It was not possible to add two methyl groups to the secondary nitrogen atom of piperidine and still have a tertiary amine. As a way out of this quandary, Hofmann was initially inclined to think "dimethylpiperidine" might be a dimethylangelylamine [angelyl = $CH_3\text{--}CH=C(CH_3)\text{--}CH_2\text{--}$]. Although this idea was close to the truth, he rejected it on the basis of the following experiment: When the dry hydrochloride salt of "dimethylpiperidine" was heated, methyl chloride was evolved. The residue from this pyrolysis on treatment with alkali yielded a



August Wilhelm Hofmann 1818–1892

liquid base which he reported to have the same boiling point $107^\circ C$ as the known monomethylpiperidine and to form the same crystalline chloroplatinate derivative as methylpiperidine. Hence, whatever the structure of the C_5 -portion of piperidine might be, Hofmann believed [mistakenly as it turned out] it to be unchanged by the exhaustive methylation to "dimethylpiperidine."

Hofmann's solution to the problem was to suggest that during methylation the second methyl group introduced had become attached to a *carbon* atom of piperidine. In proposing this he was unfortunately misled by his own earlier work in which he and Ernst Mylius had found that trimethylanilinium iodide did undergo thermal change above 220°C to N,N-dimethyltoluidine [ortho from its b.p.], overall a true case of methyl moving from N to C (30).

After another methylation of the "dimethylpiperidine" and distillation of the quaternary hydroxide, Hofmann was again surprised to obtain trimethylamine and a liquid hydrocarbon C₅H₈, but he did not comment on the apparent return of the methyl group from carbon to nitrogen. The liquid hydrocarbon, b.p. 42°C, which he named piperylene, afforded a crystalline tetrabromide, m.p. 114.5°C. He considered several possible structures for piperylene, but a straight chain pentadiene was not one of them. In fairness to Hofmann, the two unexpected results forced him to reconsider what result to expect if piperidine actually did have the cyclic pentamethylenimine structure. He concluded that upon loss of trimethylamine, the carbon chain would reclose to give cyclopentene (31)! He realized that this was obviously not the case because cyclopentene, although not yet known, would give a dibromo derivative. At the end of this publication (29) Hofmann was left without a structure that would explain to his satisfaction all of the experimental results.

Even a year later, after Hofmann's co-worker Carl Schotten exhaustively methylated N-benzylpiperidine and obtained N,N-dimethylbenzylamine plus piperylene, *i.e.* the same outcome as with piperidine itself, the true course of the exhaustive methylation reaction still did not become apparent to them (32). Schotten was also able to convert piperidine directly to dibromopyridine by the action of bromine on dry piperidine hydrochloride at a much lower temperature (180°C) than for Koenigs' sulfuric acid reaction, but he did not comment on any possible significance of this observation for the cyclic structure of piperidine.

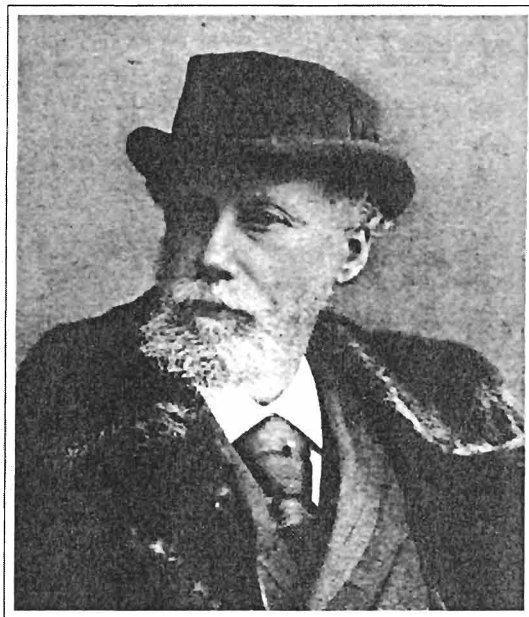
Hofmann continued work on the dehydrogenation and found that N-acetylpiperidine would react exothermically at room temperature with two molecular equivalents of bromine to form dibromopyridine [3,5-isomer], monobromopyridine [presumably the 3-isomer], and pyridine (33). Hofmann now accepted the cyclic six-ring structure for piperidine, but he still did not understand the exhaustive methylation results.

Finally in 1883 Albert Ladenburg, who had been working on the reaction of piperidine hydrochloride with methanol, had the insight to see clearly what had happened when dimethylpiperidinium hydroxide was heated: one of the ring bonds to nitrogen had been broken, and "dimethylpiperidine" was really CH₂=CH-CH₂-CH₂-CH₂-N(CH₃)₂. Further methylation and decomposition produced trimethylamine and piperylene which Ladenburg formulated as CH₂=CH-CH₂-CH=CH₂ (34). Much later it was found that piperylene was really the conjugated pentadiene CH₂=CH-CH=CH-CH₃ (35), but Ladenburg had no reason to suspect this.

In the subsequent two years 1883-85 Ladenburg made further discoveries that removed any lingering doubts about the structure of piperidine. First he managed to isolate small amounts of piperidine from the sodium/ethanol reduction of pyridine (36) and later improved the procedure to give almost complete reduction of pyridine and better yields of piperidine (37). Finally, dry distillation of 1,5-pentamethylenediamine

dihydrochloride provided a direct synthesis of piperidine from a noncyclic precursor (38).

As noted earlier, Hofmann's major stumbling block to understanding the true course of the degradation of the quaternary hydroxide of piperidine was his conviction that the piperidine structure had survived this reaction unchanged. While he had considered the possibility that a cyclic piperidine might have been opened on heating the quaternary ammonium hydroxide, it did not occur to him that a ring might have been reclosed during the preparation and pyrolysis of the hydrochloride salt of "dimethylpiperidine" (29); Ladenburg did real-



Albert Ladenburg 1842-1911

ize this possibility. Only later in 1891 did Georg Merling carefully demonstrate that "dimethylpiperidine" did cyclize on treatment with hydrogen chloride, not to N-methylpiperidine, but to the isomeric N, α -dimethylpyrrolidine, b.p. 96–97°C (39). The two compounds can be distinguished by boiling point (10° difference) and by melting points of derivatives to which Hofmann's laboratory had evidently devoted insufficient care.

The problems in Hofmann's laboratory over the struggle to visualize the changes occurring during the stepwise exhaustive methylation of piperidine and the two-year lag before the correct explanation was forthcoming from another laboratory reveal in a striking manner the difficulty chemists had in adjusting their thinking to include the consequences of cyclic structures. A similar and even more difficult situation would be experienced somewhat later when *three*-dimensional cyclic structures were encountered in terpene and alkaloid investigations.

ACKNOWLEDGMENT

The author would like to thank Professor Alan Rocke for commenting on a preliminary draft of this manuscript.

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ABOUT THE AUTHOR

Edgar Warnhoff (Ph. D., Wisconsin, with W. S. Johnson, postdoctoral work with D.H.R. Barton and G.H. Büchi), Professor Emeritus of Chemistry at the University of Western Ontario, London, Ontario, Canada, N6A 5B7, has been professing and practicing organic chemistry in the U.S. and Canada for almost fifty years. He now researches the roots of organic chemistry in the literature of the nineteenth century.

BOOK REVIEWS

Traces of the Past: Unraveling the Secrets of Archaeology through Chemistry. J. B. Lambert, Addison-Wesley, Reading, MA, 1997, xiii + 319 pp. Cloth, \$30.

Chemistry enjoys a uniquely utilitarian tradition among the scientific disciplines; long before the emergence of the modern atomistic paradigm and associated principles that established this new science during the nineteenth century, artisans had developed a wealth of empirical methods for the molecular transformation of natural materials into metals, glass, and ceramics. In *Traces of the Past: Unraveling the Secrets of Archaeology through Chemistry*, Joseph B. Lambert tells the engaging story of how chemical analysis of such artifacts provides insights into the cultures that created objects of practicality and beauty.

Traces of the Past assumes no technical knowledge on the part of its readers, and essential chemical concepts (from isotopes to infrared spectroscopy) are briefly described in the text. An extensive glossary of specialized terms makes it a useful reference for the novice, but Lambert does not shrink from the inclusion of representative data, in the form of tables and graphs reproduced from the primary literature. While the author offers succinct explanations, an individual who has never seen a ternary composition plot, for example, may have difficulty learning its interpretation here (p. 84). Each figure contains appropriate references, and over 18 pages of suggested "Further Reading" propel the student into the monographs and research articles of archaeological chemistry.

The eight chapters and epilogue are organized into a hierarchy of increasingly complex manipulation, from stone carving to the dyeing of cloth, to the production of "foods" such as chocolate and beer. A final chapter chronicles the history of early humans, including diet

and lead poisoning, as revealed in relic stools and bones. A common theme is the interdisciplinary nature of archaeological research, and Lambert devotes as much space to anthropology as to chemistry.

The author, who holds the Clare Hamilton Hall Chair in Chemistry at Northwestern University, is well qualified for his task. He has carried out extensive research in collaboration with archaeologists for three decades; he received the Society for American Archaeology's Fryxell Award in Scientific Archaeology for 1989. He is also highly regarded as a teacher and has served as Director of Northwestern's Integrated Science Program. Lambert is an individual with wide-ranging interests, who in addition has made fundamental contributions to the study of structure and bonding in organosilicon chemistry, being recently recognized by the Kipping Award of the American Chemical Society (1998).

Traces of the Past relates intriguing instances of how chemists have uncovered apparent forgeries, as in the 1936 discovery of a brass plate bearing an arcane inscription with a date of 1579 and the name of navigator Francis Drake. Controversy ensued because the artifact was found in northern California, a site not known to have been visited by Sir Francis; elemental analysis confirmed that the alloy contained too much zinc (35%) and was suspiciously homogeneous to have been smelted before the nineteenth century.

Chemical analysis often supplies critical evidence to identify the provenance, or origin, of a particular artifact. Archaeological excavations in Mexico have yielded many examples of majolica, a lead-glazed pottery, originally brought by Spanish explorers and traders at the outset of the sixteenth century. However, levels of trace elements (cerium lanthanum, and thorium)

as well as isotopic ratios for lead have definitely shown that such technology was indigenous to Mexico about 1550.

In conclusion, this book constitutes a valuable resource for a course in archaeological chemistry (as a textbook), and it may also provide the analytical chemistry teacher with novel applications to enliven the class-

room. More generally, *Traces of the Past* is a well written introduction that will be enjoyed both by nonscientists and professional chemists with an interest in the deep past. *William J. Hagan, Jr., School of Mathematics and Sciences, College of St. Rose, Albany, NY 12203-1490.*

Justus von Liebig: The Chemical Gatekeeper. William H. Brock, Cambridge University Press, Cambridge, 1997.

It is remarkable that Justus von Liebig, a central figure in the development of nineteenth-century chemistry, has escaped a full biographical treatment since Jakob Volhard's two volume biography published in 1909. Brock's biography is the first to appear in 25 years, the first English language biography in almost 100 years, and the first ever full biography by a professional historian of science. Historians of chemistry have long had to rely on Volhard's *Justus von Liebig* (Leipzig, 1909) and the fragmentary pictures of Liebig's career provided by Frederic Holmes' introductory essay to the facsimile edition of Liebig's *Animal Chemistry* (1964) and his biography in the *Dictionary of Scientific Biography* (1973), Margaret Rossiter's *The Emergence of Agricultural Science: Justus Liebig and the Americans, 1840-1880*, and Morell's seminal 1972 *Ambix* article on Liebig and Thomas Thomson as "The Chemist Breeders." Brock's biography is therefore a very welcome contribution to the literature on nineteenth-century chemistry and complements the recent full biographies of Edward Frankland, Hermann Kolbe, and Eilhard Mitscherlich.

Fortunately for his biographers, Liebig left an enormous literary trail consisting of letters, books, and articles. Much of his correspondence has been published and many unpublished letters remain in his *Nachlaß* at the Bayerische Staatsbibliothek. Despite these rich sources, however, Liebig's life has remained practically unexamined relative to other nineteenth century figures of his stature, and Brock is one of the first schol-

ars to make extensive use of these and other archival sources. He also incorporates much of the existing secondary literature on Liebig, including two insightful, but previously unpublished dissertations on Liebig by Bernard Gustin (*The Emergence of the German Chemical Profession*, 1975) and Pat Munday (*Sturm und DUNG: Justus von Liebig and the Chemistry of Agriculture*, 1990). The book contains a comprehensive index and two appendices. The former includes a translation of an 1840 report by Carl Wilhelm Bergemann to the Prussian minister on Liebig's laboratory in Giessen, complete with a floor plan of the laboratory. The second appendix contains a list of Liebig's British and American students.

In the first three chapters, Brock details Liebig's educational development from his childhood in Darmstadt to the 1830s, when his laboratory in Giessen was reaching its peak of activity. Much of the success in Liebig's early life can be attributed to the guidance of his first teacher at Bonn and Erlangen, Karl W. G. Kastner. Kastner appears to have engineered Liebig's matriculation (and arranged a small stipend) into the University of Bonn, for Liebig did not have the *Abitur* necessary for admittance. He also personally appealed to the Grand Duke of Darmstadt to support financially Liebig's crucial period of study in Paris with Guy-Lussac. When Liebig wished to be appointed to the University at Giessen, Kastner also arranged the awarding of an essentially honorary (without a dissertation) doctoral degree from the University of Erlangen. The most fascinating portion of Liebig's student years is his little known homosexual affair with a poet of aristocratic background, August Graf von Platen (1796-1835). Using extracts from Platen's diaries and the correspondence

between Platen and Liebig (from a 1990 biography of Platen), Brock recounts the passionate, but short-lived affair between the two men.

Of course, Liebig's most famous contribution to chemistry was the creation of the instructional laboratory at Giessen. If Kastner had proved essential in guiding Liebig's education and appointment, Liebig's success at Giessen was due to his own intelligence, hard work and his political savvy with the university. Brock raises a few interesting suggestions about the formation and administration of the laboratory. He argues that it was the emerging friendship with Friedrich Wöhler, combined with his duty to train pharmacists for the state, that ultimately caused Liebig to focus his efforts on organic chemistry during the late 1820s. In 1825 Liebig became the *Ordinarius* of chemistry at Giessen, and his primary duty was to teach chemistry to matriculated students in the medicine and philosophy faculties. His laboratory, however, began as a private institute, unaffiliated with the university because the philosophical faculty did not wish to train "apothecaries, soap-makers, beer-brewers, dyers, and vinegar-distillers" at a university dedicated to producing civil servants. Liebig's success at Giessen can be attributed to a number of factors: the ability to attract nonmatriculated students (and their fees) to increase his class size, the modest support from the state, a focused research program determining the composition of organic compounds, and a new efficient piece of apparatus (the *Kaliapparat*) to determine that composition. Liebig's appointment as editor of the *Annalen für Chemie und Pharmacie* in 1836 also created the vehicle with which he could and did express his views to the international chemical community.

Brock treats Liebig's life after 1840 thematically rather than in a strict chronological narrative. There are chapters devoted to Liebig's ties to Britain, commerce, agriculture, physiology, food, and sewage. Immediately striking in these chapters is the number of Liebig's attempted commercial ventures, driven equally by his love for chemistry and the search for additional income (perhaps to compensate for his own modest background). Some projects, such as his formation of a meat extract company, today a portion of the multinational Unilever company, were successful ventures. Others, such as bread made from baking powder and coffee extract, were not at all successful. What tied all the ventures together

was Liebig's consistent belief, derived from his mentor Kastner, that knowledge of chemistry could improve the commercial prospects for all of these seemingly unrelated areas. All could become "scientific" with the proper application of chemical principles. Even if many of his attempts to transform the ancillary disciplines of medicine, agriculture, and pharmacy were not entirely successful, many of his ideas concerning the recycling of sewage and replenishment of the soil have a distinctly modern sound to them, and the fact that these disciplines today have a large chemical component to them is due to Liebig. He also effected a profound change on how chemists viewed their own profession, transforming it from a pure science concerning the composition of materials to the "central science" that could be applied to many diverse areas.

Brock is at his best describing Liebig's life before 1840. Although he provides an excellent overview of Liebig's enormously varied interests, the thematic approach does tend to weaken the overall picture of Liebig's life. Because Brock abandons a strict chronological narrative (he mentions Liebig's appointment to Munich many times before he gets to the specifics), it is difficult to see how Liebig's various interests might have interacted with each other aside from the central importance of chemistry. Brock also includes little about Liebig's family life until the last chapter. Finally, there are a few claims that are not followed up completely. For example, Brock makes the intriguing remark that "it has been plausibly suggested that the vehemence of Liebig's attack on *Naturphilosophie* in 1840 may have been a mask for his feelings of repugnance for homosexuality after his marriage (page 26)." I awaited eagerly, but in vain, for him to draw out the possible connection between homosexuality and *Naturphilosophie*, or give a reference to the plausible suggestion.

These are, however, minor problems with Brock's account. Constructing a full biography of a scientist has long presented problems for historians in how to meld the science with the life without ignoring one at the expense of the other, or without making an artificial division between them. Brock has balanced these needs well, creating a picture of Liebig and his influence that can be enthusiastically recommended to chemists and historians alike. *Peter J. Ramberg, Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218.*

A History of Metallurgy. Fathi Habashi, Métallurgie Extractive Québec, Sainte Foy, Québec, 1994, 307 pp, 123 illustrations. Distributed by Librairie des Presses de l'Université Laval, Cité Universitaire, Sainte Foy, Québec, Canada, G1K 7P4.

Dr. Habashi has undertaken the ambitious project of preparing a comprehensive review of metallurgy from 5000 BC to the early 1900's. By compiling and editing previously published articles, he has produced a valuable undergraduate textbook that will also be a useful reference for practicing metallurgists, physical scientists, engineers, and historians of science. Archaeologists, conservators, and curators will also find this a valuable reference work. Unfortunately, many readers outside of this book's target audience, undergraduate metallurgists, may find the book somewhat disappointing.

The author has selected the nine most pertinent articles from the multi-volume *History of Technology* series, which was published by Oxford University between 1954 and 1958. His approach allows excellent coverage of a 7,000-year time span. The book begins with the earliest extraction and processing of gold, silver, lead, copper, antimony, tin, and bronze in central Asia and closes with the electrolytic refining and powder metallurgy of the late 1800's to early 1900's. The main advantage of this approach is that it allows a balanced coverage. No section of the book is skewed towards a single

author's area of expertise or academic prejudices. This reviewer was particularly impressed by the inclusion of many non-ferrous and non-precious metals. There were also excellent sections dealing with such ancillary technologies as assaying, coal mining, and coke production. The disadvantage of Habashi's approach is that some of the articles seem very dated and should at least have been annotated to incorporate more of the current research in the field. The absence of experimental re-creations of historic processes and of recent archaeological research is particularly noticeable.

Before using the *History of Metallurgy* as a college textbook, the instructor will have to consider carefully the academic majors of the students. Chemists, engineers, and metallurgists will have little difficulty. Nonscience majors attracted to such a course to help fill a science requirement may need assistance with the terminology and some of the chemical concepts. This should not discourage anyone from adopting the book, however. Students planning careers in archaeology, history, conservation, or museum studies will find the book an excellent reference and will use it for years to come.

This work features a number of excellent, high-quality illustrations, which are well chosen to convey concepts discussed in the text. Despite its limitations, the *History of Metallurgy* is an impressive contribution to the historiography of science. *Kevin K. Olsen, Wyeth-Ayerst, Pearl River, NY 10965.*

Instruments of Science: An Historical Encyclopedia. R. Bud, D. J. Warner, and S. Johnston, Ed., The Science Museum, London, and National Museum of American History, Smithsonian Institution, Washington, in association with Garland Publishers, Inc., New York, 1998. xxv + 709 pp.

Over 230 contributors world wide have participated in providing information on hundreds of instruments. Included are fairly simple to highly complex and ancient to modern examples. Some examples: abacus, chromatograph, compass, cosmic ray detector, eudiometer, melting point apparatus, planimeter, protein sequencer, seismograph, slide rule, string galvanometer, thermopile, Wheatstone bridge, and X-ray apparatus. The narrative portion includes information about dis-

covery, function, development, and uses of each item. Most are depicted by photographs, which have been provided by individuals, academic institutions, archives, industries, learned and professional societies, and museums, and all of which are acknowledged. The somewhat oversized book is sturdily bound for continual use; it will surely serve as an invaluable reference source for scientists and nonscientists. An extensive index of 36 pages greatly enhances its utility. The editors of this impressive tome have been recognized by the awarding of the 1998 Paul Bunge Prize for an outstanding publication in the field of history of scientific instruments. This award of the Hans R. Jenemann Foundation is administered by the Gesellschaft Deutscher Chemiker and the Deutsche Bunsen-Gesellschaft für Physikalische Chemie. *Paul R. Jones, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.*

Chemistry and the Chemical Industry in the 19th Century: The Henrys of Manchester and other Studies. Wilfred Vernon Farrar. Richard L. Hills and W. H. Brock, Ed., Variorum, Aldershot, Hampshire, Great Britain, 1997. xii +334 pp. Cloth (Typeset), \$94.95.

The lives and works of ordinary and not so ordinary British chemists whose contributions are long forgotten, and sometimes led to nowhere in particular, might seem unworthy of extensive study, let alone of a full length monograph. But every rule has its exceptions, as the late W.V. Farrar (1920-1977), research chemist turned historian of chemistry, found through diligent and painstaking research undertaken around three decades ago. Now we have the opportunity to rediscover the fruits of his work most conveniently bound between two covers. It is abundantly clear that the stories of Farrar's heroes sometimes tell us as much about the development of chemical sciences as do many accounts of more famous personalities.

Farrar spent most of his adult years in Manchester, once the center of British applied chemistry, so it is entirely appropriate that his principal focus was on Mancunian life, particularly during the vibrant period 1760-1860 that encompassed the heyday of the Manchester Literary and Philosophical Society, the spread of Unitarianism, and the rise of the chemical-based textile industry and gas lighting. Manchester and surroundings also witnessed the ascent from quite inauspicious backgrounds of men such as John Dalton and the emergence of severe environmental problems.

Farrar, jointly with his wife Kathleen and Leonard Scott, made a special study of the Henry family and its interaction with science, education, medicine, and industry. This resulted in a series of outstanding papers published in *Ambix*. Here, for the first time, they appear together, as the authors originally intended, comprising the first part of *Chemistry and Chemical Industry in the Nineteenth Century*. The Henry family fortune derived from a milk of magnesia factory that actually survived until the end of the 1920s. The family activities led, through the Lunar Society, to contacts with the Watts, and, through geographical closeness, to a connection with John Dalton and theories of the existence of atoms. Indeed, William Henry's law of partial pressures contributed towards atomic theory.

The second part of the book covers an equally fascinating range of activities, not all directly related to greater Manchester. From the hallowed towers of 1860s Oxford, Sir Benjamin Collins Brodie applied the work of the mathematical logician George Boole to theories

of fundamental chemistry that, although they ran counter to received opinion, do reveal much about how consensus was reached over novel concepts. By contrast, the much traveled Richard Laming, at one time partner in an east London gas works, suggested the existence of sub-atomic electrical particles in the 1840s, long before others predicted and then provided evidence for the electron. At a more practical level, Lewis Thompson's early work on the capture of atmospheric nitrogen led to the discovery of cyanides as byproducts of iron smelting in blast furnaces. Laming and Thompson, incidentally, worked together in Paris during the 1840s. In Scotland, the roguish Andrew Ure contributed to the development of gas lighting, lobbied successfully for his own promotion as head of an observatory near Glasgow (although he was not the best candidate), and is best known to historians of chemistry for his highly useful, but not always reliable, *Dictionary of Arts, Mines, and Manufactures* (1839). As an interlude, we have Farrar successfully tackling science and the German university system during 1790-1850, using the example of Liebig's laboratory to mirror the changes taking place during the later years.

Of Robert Angus Smith, expatriate Scotsman in Manchester, Farrar concludes that he "was not a great scientist...he was a half-trained amateur...His theories were often wrong and his quantitative results unreliable...It is for his example rather than his results that he is remembered." (Chapter XII, pp. 255-257). Smith brought credit to his profession for his work as the first Alkali Inspector (1863); by demonstrating great diplomacy in his dealings with polluting manufacturers, he showed them how to profit from the conversion of harmful waste into useful products. That was far from an ordinary achievement.

Farrar's expertise as an organic chemist was put to excellent use in his survey of the manufacture of artificial dyes (including guano-derived murexide and picric acid, both made in Manchester) before William Henry Perkin (in London) discovered mauve in 1856, and in his account of the life of (Henry) Edward Schunck, of Manchester. Schunck earned a doctorate at Giessen under Liebig in 1841, and, benefiting from the availability of products used in the family textile printing business, subsequently embarked on a life of private study into natural dyes. This came in useful when he was asked to analyze samples of byproducts from the synthetic alizarin process worked out by Perkin. Schunck's research into anthraquinone derivatives and related products was of the highest order, as chemical investigation of his surviving samples by Farrar dem-

onstrated, although he suffered from a lack of input by younger colleagues.

This book is a welcome addition to the Variorum Collected Studies Series and serves as a timely reminder of the great debt that we owe to a historian of chemistry

who pioneered the study of regional themes and lesser events and individuals. *Anthony S. Travis, Sidney M. Edelstein Center for the History and Philosophy of Science, Technology and Medicine, The Hebrew University, Givat Ram Campus, Jerusalem 91904, ISRAEL.*

A NEW BIBLIOGRAPHY OF GERMAN DISSERTATIONS IN CHEMISTRY

Dr. Günther Beer, Museum der Chemie, Göttingen, has just completed the compilation of a bibliography of chemistry dissertations from Universität Göttingen, 1734-1900. The 216-page book, *Die chemischen Dissertationen der Universität Göttingen*, Verlag Museum der Chemie, Göttingen, (ISBN 3-932427-00-9), can be purchased at a cost of DM 34. Send orders to:

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