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The Cover... Sidney Edelstein's Book Plate, courtesy, Edelstein Center.

FIFTY YEARS OF THE DEXTER AND EDELSTEIN AWARDS

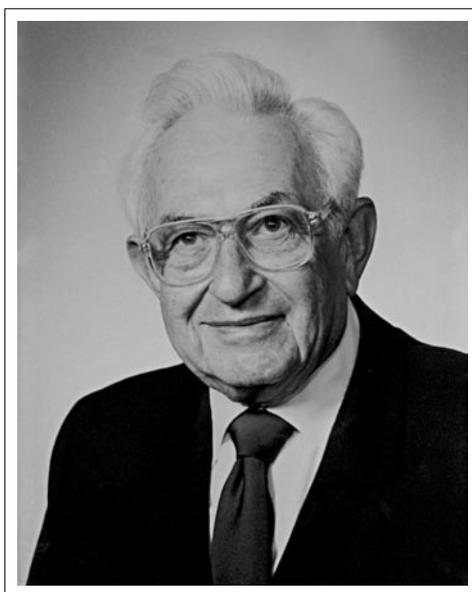


Photo courtesy Edelstein Center

At the 232nd national meeting of the American Chemical Society in San Francisco in September, 2006, the History of Chemistry Division (HIST) sponsored a symposium to celebrate fifty years of an award established by Sidney Edelstein in 1955 to recognize outstanding contributions to the history of chemistry. Originally called the Dexter Award, after the Dexter Chemical Company which Edelstein also founded, the award was renamed the Edelstein Award in 2002 after his death. Sidney Edelstein served faithfully as secretary-treasurer of HIST from 1948-1965. His legacy of support lives on in this HIST award, the

Sidney Edelstein Center at Hebrew University, Edelstein fellowships administered through the Chemical Heritage Foundation, and the SHOT Edelstein Prize, funded by Ruth Barish. This issue of the Bulletin contains a paper based upon the symposium address by the 2006 Edelstein Award recipient, Dr. Peter J. T. Morris, along with several other papers presented at the symposium. We anticipate additional papers from the symposium will appear in future issues.

The Editor

WRITING THE HISTORY OF MODERN CHEMISTRY*

Peter J. T. Morris, Science Museum, London

Significance of Twentieth Century Chemistry

Before discussing the history of “modern chemistry,” we need to define what modern chemistry is. After all, as late as 1954, Arthur J. Berry wrote a book entitled *From Classical to Modern Chemistry* which stopped in the early twentieth century (1). By modern chemistry I mean chemistry in the twentieth century (the same definition as the Commission for the History of Modern Chemistry of the International Union of History and Philosophy of Science). One could argue that it should be chemistry after 1945 but this would narrow the field too much, although it is remarkable that we can still describe chemistry a century ago as “modern.” The twentieth century was a period of immense growth in chemistry, however we measure it. Using that incomparable source of statistical information, *Chemistry In America*, we find that the number of chemists in the USA rose twelvefold from 9,000 in 1900 to 110,000 in 1970, the number of papers published rose from 3,940 in 1913 to 106,552 in 1980 and the doctorates conferred in the USA rose from only 69 in 1900 to a peak of 2,224 in 1970 (2). Turning to the chemical industry, we find that the number of chemists employed in industrial research laboratories in the USA rose elevenfold from 3,830 in 1921 to 42,800 in 1960 (3). These chemists were very productive: 52,411 US chemical patents were taken out in 1961-5, against 4,001 in 1896-1900 and the output of “chemicals and allied products” in the USA grew 33-fold between 1899 and 1957 (compared with 10-fold for total manufacturing) (4).

Relative Insignificance of the History of Modern Chemistry

Yet when we turn from chemistry to the history of chemistry, we find a different picture. Even the last three decades of the twentieth century, the history of modern chemistry has been overshadowed by three periods which have been more popular with historians of chemistry: alchemy and chymistry, the Chemical Revolution and the nineteenth century. Indeed it could be argued that the last two or three decades of the nineteenth century have been neglected compared with the earlier part of that century. Taking the nineteenth century as our benchmark, for simplicity, and examining the number of papers in the leading journal *Annals of Science* between 1970 and 1986, there were only 2 for the twentieth century, compared with 16 for the nineteenth century. If we look at the number of papers in *Ambix* between 1986 and 2000, there were 24 for the twentieth century against 58 for the nineteenth century, a ratio of 41:100. We might have expected the situation to be better in the case of biographies, as the remembrance of more recent chemists would be fresher in the collective memory. The situation is better but not by much. Of the biographies reviewed in *Ambix* between 1970 and 2003, 12 were about chemists mostly active in the twentieth century against 21 for their nineteenth century counterparts. And this bias is reflected in general histories of chemistry. It is difficult to make accurate estimates as it is not easy to allocate individual pages to one century or the other, but if we look at three recent examples by William Brock, Bernadette Bensaude-Vincent and Isabelle Stengers, and Trevor

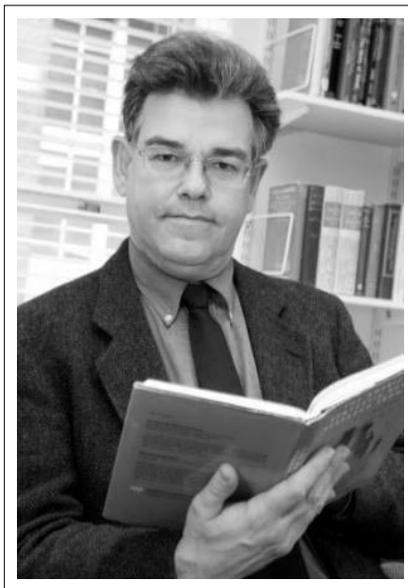
Leveré, we find that the percentage ranges from about 15 to 30%, with Brock making a particular effort to cover the twentieth century (despite being the former director of a Victorian studies center) (5). The situation regarding books is much the same for the history of industrial chemistry although as a genre one might have expected a bias toward more recent histories. Of the 66 books about the chemical industry recorded in the British Library OPAC as published between 1970 and 2003, 22 (33%) were recorded as being twentieth century. Of the 52 books on "industrial chemistry" reviewed in Ambix up to 2003, 36 (69%) had significant content about the twentieth century. This higher figure is partly a result of the "long" nineteenth century, as several of the books went up to 1914.

Problems of Writing the History of Modern Chemistry

Even if we assume historians of chemistry have a personal bias in favor of the chemistry of earlier periods, the relative lack of material about modern chemistry suggests that there must be something problematic about writing its history. My personal experience has confirmed that this is the case. Although the chemistry of earlier centuries has its own difficulties, it is universally recognized that twentieth century chemistry is, technically speaking, very advanced, requiring a chemical training of some kind. This problem is compounded by the ever-increasing use of jargon and highly stylized writing in chemical publications. This trend is strikingly demonstrated by *Accounts of Chemical Research*. When I first read it in the mid-1970s, some chemical knowledge was required but it could be easily read by a nonspecialist. When I subscribed to it briefly two decades later, I found it completely unreadable. There is a vast amount of written material, especially in archives of the chemical industry, but there is a lack of personal correspondence and other personal material compared with the nineteenth and early twentieth centuries, and there is an increasing lack of paper material thanks to telephone and emails. There is also the issue of the destruction of material shredded by archives trying to keep their holdings within bounds, put into the trash when factories are closed or thrown away by their families (6). This demonstrates the importance

of preserving our chemical heritage and finding archives for this important material.

Key Features of Writing the History of Modern Chemistry



Dr. Peter J. T. Morris,
photo by Jennie Hills

What are the main features of writing the history of modern chemistry? Based on my own experience, I would stress the importance of interviews and oral history. This is not only a matter of finding out the details of what happened, by whom and when. Indeed interviews of elderly chemists are often an imperfect way of doing this, although they may also be our only source of information. Their main value lies in giving us the broad picture on one hand and the subtle relationships and interconnections so rarely captured by physical documentation on the other. A person's personality often provides the key for understanding why something happened and not something else and this is best provided by oral history as this often provides an assessment of their

character by those who worked with them. At the same time the historian has to be acutely aware of the pitfalls of oral history. Not only are elderly chemists attempting to recall, usually without documentary assistance, what happened fifty or more years ago, but they are open to all the partiality and personal bias of any form of autobiography. Self-justification and self-glorification can never be completely absent, but I have usually found my interviewees to be as objective about their past experiences as one can ever hope to be in these circumstances.

If it is not possible to interview participants, correspondence offers an alternative, and in writing letters my correspondents often thought more carefully about what they were saying than they might have done in an interview and used physical documentation while they were writing the letter (and sometimes enclosed a copy of this documentation with the letter). The advantage of the interview is that you can ask the questions more directly and follow up with supplementary questions which is difficult to do in correspondence.

Once the basic research and writing have been done, it is crucial in my experience to have this work reviewed

by the chemists involved or who were at least familiar with the developments being studied. This review can show up all kinds of confusions and misunderstandings and is extremely valuable in improving our understanding of the history of chemistry. The dual importance of interviewing and review by the chemists involved means that the historical research should be done while the leading actors are still alive if this is possible. Once these chemists have passed on, it becomes much more difficult to reconstruct what actually happened, as I know well to my cost.

Any historian of modern chemistry—and especially the historian of the chemical industry—has to be able to scan huge quantities of written material, seeking out the truly informative documents and at the same time be able to tease useful information out of historically uninteresting documents (formal minutes, laboratory reports etc).

Having established these basic points, I will now illustrate them by a number of case studies of research I have carried out over the last three decades. They range from the history of industrial chemistry to biography, from the USA to Germany, and from organic synthesis to chromatography. If they do not form a completely representative sample of the history of modern chemistry, they are at least a varied one.

History of Synthetic Rubber in IG Farben

When I came to this topic in the late 1970s, there were a few histories already available, but they were very diverse and often turned out to be wrong, the major exception being the booklets produced by BASF's archives and which I was fortunately able to obtain while I was working in a nursing home in Ludwigshafen in the summer of 1977. The key archives were evident from the outset, namely the Bayerarchiv in Leverkusen, the IG Zentralarchiv at Hoechst near Frankfurt, and the British Intelligence Objectives Subcommittee collection which was then at BL Boston Spa (now stored at the Imperial War Museum at Duxford). The papers of the war crimes trial, US vs IG Farben, were crucial and were fortunately available—at a price—on microfilm. I also found useful material at Chemische Werke Hüls in the Ruhr and at the Imperial War Museum (the Speer archives).

The Bayerarchiv kindly put me in touch with several useful interviewees, notably Heino Logemann, Curt Duisberg, and Claus Heuck. I did not feel able to travel to a remote part of the Alps in winter to interview Albert

Speer, although he was very insistent, and unfortunately he died before we were able to meet. To my disappointment, the key actor Otto Ambros refused to meet me although the Bayerarchiv tried to persuade him. However Speer and Ambros corresponded with me and also Franz Broich—formerly at Schkopau and Hüls—who was particularly informative about the manufacture of butadiene from monovinyl acetylene, a process which hardly appears in the physical documentation at all.

As I gathered information from the trial records and the various archives, I created a “card” index (actu-

ally A5 slips of paper) which collated documents from different sources by date. In this way I was able to reconstruct runs of correspondence and link letters to meetings, and meetings to subsequent events. Eventually I successfully reconstructed the history of synthetic rubber in Germany



Buna exhibit at the Four-Year Plan Exhibition in Berlin, 1937, courtesy of the author

and developed a strong argument about the relationship between IG Farben and the Nazi regime, but I would like to have done more on the scientific aspects of its development, for example, the development of redox polymerization. The feedback about my thesis—which was completed in 1982—was generally positive from both participants (including Otto Ambros) and historians (such as Peter Hayes) (7).

Synthetic Rubber in America

By contrast with the IG case, there was already a strong historical literature when I began my work on the synthetic rubber research program in America, and Herbert and Bisio's book was published just after I started in 1985 (8). Once again, the major archives were soon clear, namely the US National Archives, the University of Akron archives, and the AT&T archives. I also used the

archives of the University of Illinois and Goodrich, but not Firestone or Goodyear. I interviewed some participants, including an oral history of Paul Greer, a program administrator who died recently at the age of 101, but this was not a major aspect of my research; but my interviews did confirm that I was on the right track.

The main source of information for my book was the technical literature. The card index—and it was a card index this time round—in this project tracked the literature rather than letters and minutes. My major difficulty was constructing a strong argument. Because of a lack of information and a certain reticence on the part of some participants, the personal aspects of the rubber program were lacking to some extent. I feel I produced a successful reconstruction of the history of the research program, even if it was perhaps rather brief, but I have had very little feedback (9). A group of rubber industry retirees said that they had read my book during a reunion dinner and they were going to send me their comments, but they never did.



Courtesy U.S. National Archives

R. B. Woodward and Organic Synthesis

During my Edelstein fellowship in 1991 I was invited by Arnold Thackray to work with Otto Theodor (Ted) Benfey on a book about Robert Burns Woodward (10). This arose out of an exhibition about Woodward (with an accompanying booklet) put together by Ted and Mary Ellen Bowden (11). Ted edited the Cope lecture and I wrote the introductions to Woodward's most important publications. In order to do this, I interviewed and cor-

responded with colleagues of Woodward (Gilbert Stork, David Ollis, Claude Wintner, Ray Bonnet), but it was mainly the result of library research. Fortunately the Science Museum Library is particularly strong on twentieth century books and journals up to about 1970. Not being near Harvard, and not having the funds to travel there, I made no use of archives at all. *Chemical Reviews* and *The Alkaloids* series published by Academic Press were particularly useful.

In this case, I would particularly emphasize the importance of the feedback on my work by experienced chemists, including Gilbert Stork, David Ollis, and Stephen Mason. It also illustrated the value of having a major science library close at hand. I am glad to say that our book was well received with no criticism of my introductions to Woodward's papers, but the format is inevitably limited as a historiographical technique. It was however a fairly rare example of a historical book that appealed to active chemists. I once met a young chemist who had become a venture capitalist at a dinner in Cambridge who had enjoyed reading it very much.

My Research on Walter Reppe

This is a good example of a less successful project. It was planned as a continuation and expansion of my earlier work on synthetic rubber, but the existing historiography was very limited. To my disappointment, I found that the archives were also of limited value; I used the archives at BASF and the Deutsches Museum. Hence, this project rapidly became very dependent on a few key books and documents, never a good idea. Furthermore, I only carried out a couple of interviews, and neither of those was particularly useful, partly because of language difficulties. This was an interesting topic because of the light it shed on the development of the organic chemical industry, but Reppe himself was not an interesting person. To make matters worse, personal information about Reppe was very limited and I did not try to contact his family. It is very doubtful if the final product could have been constructed as a biography and would have really only worked as a history of industrial research with Reppe as the central (but rather shadowy) character. In the end, this project was abandoned because of changing priorities at the Science Museum, and I published what I had gathered as a paper in *Determinants* and as an entry in the *New Dictionary of Scientific Biography* (12). While it has not been completely wasted, this case study does show the difficulties facing the historian of modern industrial chemistry if the main actor is no longer alive.

The ECD and the History of DDT Analysis

This project in the late 1990s stemmed from a need to show the importance of the electron capture detector (ECD) to justify putting it on display in the Making of the Modern World Gallery at the Science Museum and from a desire on my part to explore the contribution of chemists to the development of environmental protection. I was struck by James Lovelock's claim in various publications, most recently in *Homage to Gaia*, that his development of the ECD helped Rachel Carson to write her famous book *Silent Spring* (13). Given the timing I found this claim very surprising, and I soon showed that this was not in fact the case (14). It had the effect, however, of making me focus on the use of the ECD to detect pesticides rather than its later and more celebrated use to detect CFCs in the South Atlantic. The gap between the events and the information gathering had been about 40 years in the case of synthetic rubber and it was about the same here, but to my surprise hardly any participants had survived or were available for interview except Lovelock himself, who has been very helpful, I am glad to say. There was also a problem of distance; I had no funds to visit California and in any event there were no obvious archives, which is not to say there are none at all. I did not try to use the Shell archives and there was no material at National Institute for Medical Research at Mill Hill in north London, where Lovelock worked in the 1950s.

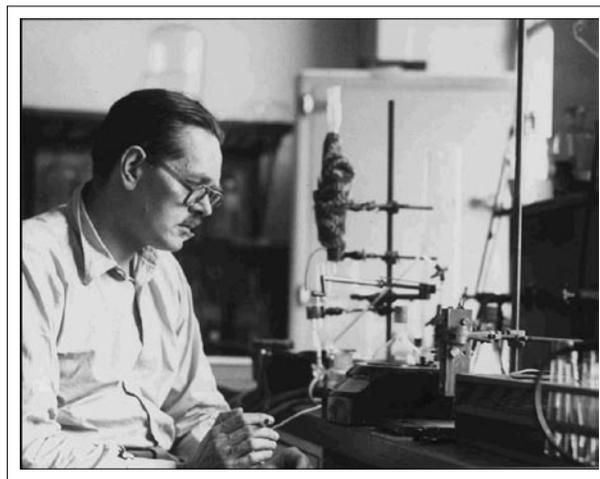
The historiography of pesticides and pesticide analysis is still developing, for example Edmund Russell's book *War and Nature*, and while this was of some use, I was largely dependent on technical literature and Lovelock's autobiographical writings (he very kindly lent me a manuscript version of *Homage to Gaia* before it was published) (15). An obscure book by a journalist Rita Beatty, *The DDT Myth*, was very useful in setting the scene for me (16). This once again shows the importance of having access to a first-rate library. A copy of the *Pesticide Manual* I had bought by chance in a charity shop was also very helpful (17). Fortunately the internet was now available as a major source of information.

Another major problem was the lack of suitable chemists to review my findings, which shows the need to develop links with the relevant expert community. The outcome was successful but perhaps lacks depth, and there is no doubt that it would have benefited from archival research (18). There was also a marked lack of feedback afterwards, which reflected the lack of survi-

vors in this field and repeated my experience with the American synthetic rubber research.

Writing the Biography of Archer Martin

Fortunately my research on early chromatography in the Lovelock project paid dividends when I received an unexpected commission from the *Oxford Dictionary of National Biography* to write the entry on the Nobel Laureate Archer J. P. Martin. I was able to draw on three important contacts I had obtained through my research on DDT analysis: Leslie Ettore, James Lovelock, and Edward (Ted) Adlard. Through Adlard I made contact with Martin's family, which was crucial for the project's success. There were no archives, but once again I made extensive use of the internet, for example, genealogical indices. I also carried out a "meta-analysis" of the multiple obituaries and biographies of Martin that were available. The final product was greatly improved by an exhaustive revising process, whereby successive drafts were critiqued by Leslie Ettore, who also contributed many recollections of working with Martin. In the event, the final entry was very successful. It immediately became the biography of the month when it was published online in January 2006, and led to a commission to write the entry on Archer Martin for the *New Dictionary of Scientific Biography*.



Archer J. P. Martin in his laboratory at Mill Hill, early 1950s, courtesy of the National Institute for Medical Research

The Life of Derek Barton

I was also invited to write the entry on Sir Derek Barton. My interest in Barton arose from a more general interest in the history of organic synthesis and from the

proximity of his beloved Imperial College to the Science Museum. Our paths could have easily crossed at some point but—for better or worse—I never met the great man (nor did I ever meet Reppe or Martin). In contrast to Martin, there were a number of books available, Barton's autobiography *Gap Jumping*, the very useful *Bartonian Legacy* edited by Ian Scott and Pierre Potier, an entry in the *Oxford Dictionary of National Biography* by Noel Coley, and the obituary in the *Biographical Memoirs of the Royal Society* by Steven Ley and Rebecca Myers (19). In the circumstances, as time was short, archival research was not really necessary; and I made less use of the internet than in the case of Martin, except to track down his son whom I decided not to contact anyway.

Writing the actual entry was more a matter of developing a fresh approach to Barton's life and career than trying to find new material. In the time available, I was not able to get behind the façade of Barton's autobiography and to discover what really drove Barton to become a great chemist. Various drafts were read by his former co-workers and students, David Widdowson, William Motherwell, and Anthony Barrett, and I found to my cost that Barton's circle was fiercely protective of his reputation. Nevertheless, I believe that my final version was a balanced account of his life, without saying anything much that was really new.

What Lessons Can We Draw?

What are the conclusions I would draw from my own experience of writing the history of modern chemistry? I have found that it is possible to write the history of modern chemistry, but I have also discovered that it is necessary to write about it in a way that is accessible to a broad audience: chemists, historians, journalists, and the educated public. The audience for this subject is already tiny; any failure of communication—for instance by using jargon or a lot of chemical terms—reduces it to zero. It is therefore necessary to employ a certain rhetoric to capture the reader's attention. When I switched from the history of industrial chemistry to the history of chemical instrumentation, it took me several years to develop a new rhetorical style. One of the biggest problems for me has been the lack of feedback, especially my work on American chemistry for some reason.

I sense that my work has been reasonably successful with historians of chemistry as demonstrated by the 2006 Edelstein Award, but I feel my publications have had little impact outside our community. This is a problem for all of us. How much of our work is read by mainstream

historians, chemists, or journalists? In my experience, with the marked exception of the American Chemical Society and its publications, journalists and publishers assume only scientists can write the history of (modern) science. I often wonder if they know we exist. I suspect they are aware (dimly) of our existence, but they worry about irritating scientists whom they perceive—probably correctly—as their main audience as historians of science are seen as somehow being “anti-science” as a result of the so-called “Science Wars” (20).

Future of the History of Modern Chemistry

Ignoring the fact that our “modern chemistry” will soon become “old chemistry,” what is the future for the history of modern chemistry? At the beginning of this paper, I pointed out the importance of chemistry and the chemical industry in the twentieth century. Despite recent improvements, the historiography of the period does not reflect its significance. I am concerned that the backlog is mounting while the number of historians working in this field is decreasing, particularly outside the USA. I am also worried that the raw material for this research, the documentation and the oral histories, are not being kept, while libraries and archives are actually being broken up or at least pruned. For without this material how can we ever write the history of modern chemistry?

However, there are some signs that the situation may be slowly improving if we compare the present day with two decades ago. Between 1981 and 1985, there was 1 paper in *Ambix* about twentieth century chemistry compared with 18 for the nineteenth century, a ratio of 6:100 (cf. 41:100 for the period 1986-2000). Between 2001 and 2005, there were 16 papers in *Ambix* about twentieth century chemistry compared with 13 for the nineteenth century, a ratio of 123:100. Twenty-six percent of the history of chemistry entries in the British Library OPAC were twentieth century in the period 2000-2004, compared with 4% in 1980-1984 (in fact just one book: A. S. Travis, *The High Pressure Chemists*) (21).

So how do we make the situation even better? My own work shows that it is possible to write the history of modern chemistry to a high professional standard. Given the advanced knowledge of chemistry required for writing the history of this period, we need to attract more chemists into this field. They can be either retired chemists or young chemists who have decided to pursue a career as a historian or curator, but this will be a difficult task given the low status of history in today's chemical community. We need to develop ways of attracting chem-

ists into the history of modern chemistry (which may appeal to them more than the history of earlier periods of chemistry) and find ways of training them which are effective, quick and at the same time, appealing.

If the supply side gives me concern, so does the demand side, Sadly, college libraries are sharply reducing orders for books in order to pay subscriptions for online journals. There is little evidence that individuals buy many (or any) books on the history of chemistry, and the price is often prohibitive. Is it worth writing the history of modern chemistry if no one is reading it? This is a very good question and needs to be taken seriously.

Nevertheless, I do believe there is a future for the history of modern chemistry. Many chemists are enthusiastic when they encounter it, not least because it addresses the question raised by any community or profession of "how did we get here?" to a much greater extent than, say, the history of nineteenth century chemistry (not that I have anything against the history of nineteenth century chemistry, I hasten to add). The web offers a way of introducing the history of chemistry to audiences that have hitherto not been aware of our work. Ever-increasing digitization of journals and books has greatly increased our access to printed material. I only wish science journals before a certain date were open-access in the same way that medical journals have recently been made available. Amazon sells books that would not be available in any "real" bookshop, often at a discount. All this must be good for minority subjects such as our own.

I would like to conclude this paper by saluting the sterling work done by many people in this area, especially Arnold Thackray for making the history and preservation of the heritage of modern chemistry the main focus of the Chemical Heritage Foundation; Jeffrey Seeman for his seminal series of autobiographies by leading organic chemists which have underpinned much of my recent work; and Christoph Meinel for setting up the Commission for the History of Modern Chemistry, which has promoted the field by holding regular conferences.

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formal publication, but an unpublished resource created by a schoolteacher (as he then was) for a local educational project. This search of the British Library OPAC somehow failed to pick up the companion volume, *The Colour Chemists* (1983) which eventually became A. T. Travis, *The Rainbow Makers: The Origins of the Synthetic Dyestuffs Industry in Western Europe*, Lehigh University Press, Bethlehem, PA, 1993.

ABOUT THE AUTHOR

Dr Peter J. T. Morris, Manager of Research and Residencies at the Science Museum, London, SW7 2DD, England, has published on many aspects of modern chemistry. Before joining the Science Museum in 1991, he worked at the Open University and the Center for the History of Chemistry (which has become the Chemical Heritage Foundation). Dr Morris is the editor of *Ambix* and served for ten years on the ACS National Historic Chemical Landmarks Advisory Committee.



Division of the History of Chemistry of the American Chemical Society

Citation for Chemical Breakthroughs



Call for Nominations

The Division of History of Chemistry (HIST) of the American Chemical Society solicits nominations for one of its award programs, Citation for Chemical Breakthroughs. This award recognizes breakthrough publications, books and patents worldwide in the field of chemistry that have been revolutionary in concept, broad in scope, and long-term in impact. The award consists of a plaque that will be placed near the office or laboratory where the breakthrough was achieved. Up to 10 awards will be presented for 2007. Nominations consist of a full literature citation and a short (200 word maximum) supporting statement. All nominations must be received by April 1, 2007. Selections will be determined by a panel of distinguished chemical historians and scientists. Further information can be found on the HIST website under the heading "Divisional Awards": <http://www.scs.uiuc.edu/~mainzv/HIST/> Submit nominations or questions to: hist_ccb@yahoo.com.

A PERSONAL HISTORIOGRAPHY OF THE CHEMICAL INDUSTRY SINCE 1956*

Peter J. T. Morris, Science Museum, London

Introduction

In this paper and its associated bibliography, I will examine what I consider to be key books in the last fifty years (and more) in the historiography of the chemical industry. I am not saying these are the only good books published in this period, as it is impossible to cover every book, but each of these books did make a notable contribution to the historiography of the chemical industry. The last fifty years have not seen a steady and uniform production of books about the development of the chemical industry. There have been bouts of activity, with quiet spells in between, and most of these spurts of publications have been characterized by a certain type of historiographical approach. For each period, I will discuss a book which exemplified and even to some degree shaped the contemporary historiography and several other key books in less detail. It is curious that many of the historiographical "fashions" in the last fifty years had a forerunner which appeared about a decade earlier.

It is important at the outset to make clear the basis of my selection. I have only chosen books in the English language; no papers or foreign language books. To keep this survey within bounds, I have defined the chemical industry narrowly, and I have therefore not covered the soap industry or the production of metals or pharmaceuticals. In general, I have also chosen not to cover plastics manufacture or petroleum refining, but I have been inconsistent here and have included two books I consider to be pioneers in their field. By the same token, I have not tried to survey the growing literature in the history

of chemical engineering, which has been, so far, a very different field. In order to concentrate on what is really worthwhile in this field, I have only considered scholarly works, except for the very earliest period, when the academic study of the history of the chemical industry hardly existed. A personal bias in a process like this is inevitable, and I duly confess to a predilection for the history of the British chemical industry, synthetic dyes, and research and development. As this paper was originally produced for a symposium to mark the fiftieth anniversary of the Dexter/Edelstein Award, I have included all Dexter Award winners in this field. The historiography of the chemical industry is extremely diverse, so much so that one might wonder whether any sustained analysis of it would be possible. There are many possible approaches to the subject, ranging from a straightforward treatment of process development, biography, business history, the broader remit of economic history, and the study of research and development in the industry to the rather different approaches used by geographers, industrial archaeologists, and economists. And the chemical industry can be studied at many different levels, starting at the plant level, and working up via the factory and firm to the level of a region or a nation-state before reaching the final stage of the continent or even taking the relatively rare step of looking at the industry on a worldwide basis. That an analysis of the historiography is feasible in practice is largely a result of a concentration on a limited palette of approaches in any given period.

The Situation in the Mid-1950s

A number of books on the history of chemical industry were already available to the serious inquirer in the mid-1950s. The British industry was seen as the forerunner and exemplar of the modern industry, beginning with sulfuric acid and the Leblanc soda process, followed by the Solvay process, dyes (where Britain had lost its early lead to Germany), and explosives. The main emphasis was on the creators of this industry, the development of processes, and the evolution of the firms which made up the then-modern industry. Even in the early 1950s, certain issues had come to the fore including the loss of the dye industry to Germany and the relationship between pure chemistry and the chemical industry.

The Forerunner

Although it had been published in 1931, Stephen Miall's *History of the British Chemical Industry* was ahead of its time and was still influential in the 1950s. It established a schema for the history of the industry which was organized by industrial sectors rather than chronology, which was imitated as recently as 2000. This way of dividing up the historical account was of course made possible by the fact that certain sectors (acids, soda, dyes, and explosives) were important in different periods, but also led to the neglect of other parts of the chemical industry which did not fit into this sequence, for instance wood distillation and solvents. Miall's work concentrated on people and firms, providing very useful "family trees" of firms and several timelines of developments. In many respects, it represents a good family history of an industry which was then only a few generations old (for instance Sir Charles Tennant, the grandson of Charles Tennant, the founder of St Rollox, had died as recently as 1906).

The Key Work

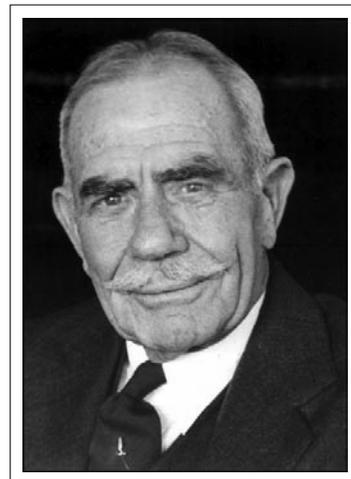
William Haynes's massive six-volume history of the American chemical industry was head and shoulders above any other history of the chemical industry in this period. A project of this size needed sponsorship (even in the 1930s) and was made possible by Haynes's close relationship with the two major boosters of the chemical industry. Francis Garvan of the Chemical Foundation commissioned Charles Herty to write the history in 1934, and when Herty died in 1938, Haynes took over. However, the appeal for funds led by the chemurgist William J. Hale of Dow Chemicals was initially unsuccessful and the project was close to being abandoned when Dow, at

Hale's behest, stepped in and provided enough money to keep it going. Monsanto then agreed to share the financial burden, and Haynes began work on his history in 1940. The first volume dealt with the period up to 1911, the next four volumes with the 1910s to 1930s, and the sixth volume was a compilation of over 200 company histories supplied by the firms and edited by Haynes.

As a journalist, Haynes (Dexter Award, 1957) was of course a superb writer, and the amount of information he assembled was astonishing. His compilation of tariff duties and imports in the 19th century is particularly noteworthy. Above all he was able to keep the technology, economic aspects, and corporate history in a fine balance. Even half a century later, his *American Chemical Industry* withstands comparison with anything published today. It is perhaps not surprising that no one has ever undertaken a similar history of the US industry. His compilation of company histories was later imitated by D. W. F. Hardie and J. Davidson Pratt in their *History of the Modern Chemical Industry*, a rather standard account of the British industry published in 1966.

Other Important Works

Walter Gardner's *The British Coal-tar Industry* brought together reprints of many papers about the British dye industry, mostly polemical in nature but with some historical value, and thus it was the forerunner of the long-running debate about the British and German dye industries and the "British decline."



William Haynes, courtesy HIST

Gilbert Morgan and David Pratt's *The British Chemical Industry* provided considerable detail about many existing processes and specific technical developments—for example coke production or superphosphate manufacture—but the broader history of the industry is lacking. The most innovative history in this period was the Clows' *Chemical Revolution*. They broke new ground in placing the chemical industry in the context of the Industrial Revolution and the Chemical Revolution. However, the Clows attached too much importance to the

Scottish industry, and it is unfortunate that they adopted Lewis Mumford's classification of technological development which may have appeared relevant at the time but does not add anything to their analysis and only makes their work appear dated to the modern reader.

The Chemical Industry: Past and Present by Trevor Williams (Dexter Award, 1976) provided a highly readable history of the industry, which placed its development in the context of the economic boom it was then enjoying. Williams shared Miall's emphasis on alkalis, sulfuric acid, dyes, and explosives, thus taking a retrospective view of the industry from the industrial organization of the 1950s. By contrast, Frank Sherwood Taylor's posthumous *History of Industrial Chemistry* was a curious book that contains a considerable amount of pure chemistry and which hardly ever mentions the name of a chemical company (with the exception of BASF). However, as a historian of alchemy, Taylor did cover a longer period than any other historian of the industry.

One of the few histories of R&D in the industry in the mid-1950s was Frank Miles's *History of Research in the Nobel Division of ICI*, published by ICI. This is a very clear history of Nobel's research since Alfred Nobel's early experiments on nitroglycerin in the 1860s; but, typically for this period, Miles failed to address the corporate or commercial background of the developments he presented. It is instructive to compare his description of the development of Ardil protein fiber with David Hounshell and John K. Smith Jr's account of the development of nylon three decades later (see below).

On the biographical side, there was J. Fenwick Allen's *Some Founders of the Chemical Industry*, which gave sketches of pioneers such as James Muspratt, Peter Spence, and Walter Weldon. J. M. Cohen, *The Life of Ludwig Mond* was one of the few full-length biographies of an industrial chemist in this period. It covered the development of Mond's factories fairly well, especially the early Winnington years, with appendices on Mond's processes. But Mond is not an easy person to uncover; and, as the author admitted to me in a 1989 letter, Cohen's "ignorance of scientific technology was .. total."

Germany and Economics: 1958-1971

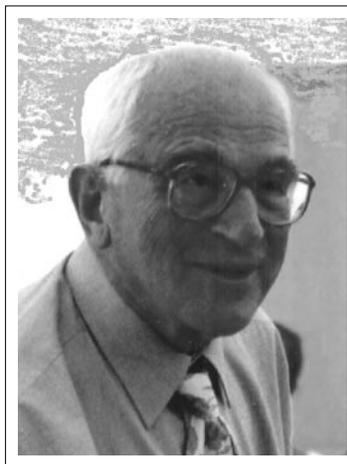
The late 1950s and the 1960s saw a complete shift of emphasis from Britain (and America) to Germany and Europe as a whole, and from technical and corporate developments to the study of the economic evolution of the chemical industry and its growing importance to

the nation-state, above all the new nation of Germany in the late nineteenth century. This shift essentially set the terms for any subsequent history of the industry up to the present. We might emphasise different factors in the industry's development or point out that the impact of the industry on the environment has been overlooked, but the framework in which we make these observations was established by L. F. (Lutz) Haber (Dexter Award, 1988) in 1958.

The Forerunner

The crucial aspect of Haber's work is that he had no forerunner. He had Williams Haynes's history as a general model, but there was nothing comparable to Haynes for the European chemical industry. Nearly all British volumes on the chemical industry up to that time focussed on Britain. Sherwood Taylor's book, published only a year before Haber's *Chemical Industry during the Nineteenth Century*, covered the worldwide industry but it pales into insignificance alongside Haber's volume.

The Key Works



L. F. Haber, courtesy HIST

This period opens and ends with a pioneering book by Haber. His *Chemical Industry during the Nineteenth Century* introduced a new kind of historiography with a greater emphasis on economic history. This approach had been pioneered by Haynes, but had not been hitherto applied to the more important case of Europe nor had it been used by a

trained economist. With his German background (he was the son of Fritz Haber), Lutz Haber also wrote about Germany and France and not just Britain and used a much wider range of sources than his predecessors. Given the revolutionary nature of his book, Haber began rather cautiously. He was clearly uncomfortable at this stage dealing with the history of the chemical industry as this was then very much the province of "boosters," among whom we have to include Haynes and Morgan, and in Germany, even Nazi propagandists such as Walter Greiling and Claus Ungewitter, who was in some respects

Haber's closest predecessor as a historian of the German chemical industry. Like Sherwood Taylor and John Beer (see below), Haber thus approached the subject in terms of applied chemistry. Indeed this is very much a history of applied chemistry, for the chemical industry is presented in terms of the economic development of specific regions and the technological development of processes rather than the corporate history of firms (although this volume is an excellent source for the history of small companies). What is revolutionary, however, is the other half of Haber's subtitle: *A Study of the Economic Aspects of Applied Chemistry*. For the first time, the evolution of industrial chemistry was subjected to the scrutiny of a trained economist. But Haber's genius was to use his training as an economist to write a general history of the chemical industry, which was accessible to historians of chemistry, rather than a dense econometric analysis of the kind that was later developed by John Enos, Paul Hohenberg, and Peter Murmann.

Haber's *Chemical Industry, 1900-1930* shares with his earlier volume its coverage of European developments and a focus on economic history. Yet it is a very different book, with emphasis on the large corporations and technical change rather than applied chemistry. This style reflects the difference between the 19th and early 20th century—the latter period was dominated by the formation of IG Farben in 1925—but Haber was also influenced by Bill Reader's history of ICI; he read the typescript of the first volume before it was published in 1970. Haber knew much more than he ever published, and it is frustrating that he never covered the period after 1930 or wrote much about technical developments. His reluctance to cover the late 1930s and 1940s was clearly connected to his own family's fate in this period; and as an economist (and as the son of a famous chemist), he may have been unwilling to risk his reputation by writing about the chemical side of the industry. From personal experience, I know he was very anxious about making mistakes and took every effort to correct them. This perfectionism may have inhibited Haber from writing any further volumes. It is also unfortunate that he did not train any successors while he was at the University of Surrey; as far as I am aware, I was the only young historian who benefited from his advice.

Other Important Works

Haber's focus on the German industry was shared by another German émigré, John Joseph Beer in his *Emergence of the German Dye Industry*. Beer was always

surprised by the success of his book and told me that he was simply repeating what had been well known in his native Germany. He concluded that the development of dyes had been driven by fashion, and the German industry was successful because of its influence on university education and the patent law system, the same conclusions reached in 2003 by Peter Murmann, who used a much more elaborate method (see below).

In 1962 there appeared a very unusual book, which aimed to analyze development of processes (specifically in petroleum refining) in terms of their technical and economic performance. Most unusually, John Enos's *Petroleum, Progress and Profits* is also an excellent history of an important period in petroleum refining and deserves to be better known. His analysis is both accurate and thought provoking. It is a great pity that it has never been emulated to any extent, and that Enos himself left the field for many years, until he published a sequel, *Technical Progress and Profits*, in 2002. In a conversation in 1981, he appeared to consider writing the history of the chemical industry to be a waste of time, assuring me that (pure) economics was the only proper way to study technical innovation.

Beer's book is easy to read, which, sadly, was not the case with Paul Hohenberg's *Chemicals in Western Europe, 1850-1914*. This was, however, the first book to try to explain the growth of the soda and dye industries in the 19th century using a higher level of economic analysis than Haber's approach. Like most economists (but unlike Enos or Haber), Hohenberg had little to say about the technical developments themselves. Described by its author as an "interpretive essay," *Chemicals in Western Europe* was a strange combination of snippets of information and economic theorizing. Hohenberg reached the rather unsurprising and fairly vague conclusion that economic growth depended on "sustained technical effort."

Petroleum, Progress and Profits raised the possibility of studying the development of one chemical (or plastic) in depth in order to shed light on industrial development. Morris Kaufman's *History of Polyvinyl Chloride* was an unique case study of a single plastic. He looked at the individual stages of PVC manufacture, showing how they evolved to create a cheap stable material, drawing on patent literature and postwar intelligence reports. Kaufman did not cover the economics of PVC production. He was good, however, at comparing the relative progress of the German and American industries and showed that the Americans often did better than their German counterparts.

History of Localities: 1971-1980

Although Haynes and Haber had been very much aware of the regional nature of the chemical industry, their analysis had been on the national and continental level. As the result of the development of regional geography—in particular the study of why certain industries were located in specific regions—in universities and perhaps also a growing popular interest in local history, the 1970s saw a new emphasis on localities in the history of the chemical industry.

The Forerunner

D. W. F. Hardie essentially established this approach in his *History of the Chemical Industry in Widnes* back in 1950; but, stemming from a career in industry rather than academia, his work was not emulated for many years. In a highly readable presentation, he demonstrated a real feel for the interaction between the geography of a region, the local entrepreneurs, and developments in the chemical industry. The appendices are particularly interesting for the historian of the industry.

The Key Work

By 1980 several authors (including Reader) had covered the development of the soda industry in Britain, but a real sense of how the industry evolved in economic and geographical terms was lacking. As a geographer, Kenneth Warren was able to bring a new perspective to the subject and did so brilliantly in his *Chemical Foundations* (1980), which examined the industry region by region (and with maps). Just as earlier historians had benefited from the coincidence that each sector of the chemical industry appeared in a historical sequence, Warren was able to capitalize on the shift of the British alkali industry from Glasgow to Newcastle, then to Widnes, and finally Winnington. Taking each area in turn, he was able to show that the location of the industry there was not a historical accident but the result of specific geographical and economic factors, especially the availability of raw materials (as the raw materials for the soda industry are heavy) and transport links. Warren had not realized the general significance of his work for the history of the chemical industry (as opposed to locational geography) until I met him in 1981, and sadly—like Hardie before him—his approach has not been used by other historians to any extent.

Other Important Works

Alec Campbell's *Chemical Industry* may have notionally been a book about industrial archeology, but it was the result of his work on the industry on Tyneside. His book is remarkable for the clarity of the description of how the processes that underpin the chemical industry were developed and the locales in which these developments occurred.

John Graham Smith's *Heavy Chemical Industry in France* was similar to Campbell's work in many ways, although it was more detailed and scholarly. Despite the "national" title, it was very much about regions; and it is a pity there were no maps. Nonetheless, Smith shows how a new industry grew up during the revolutionary and Napoleonic periods in certain regions of France, the role played by chemists and governments, and the impact of the industry on the region. As the technology was new and the times were unsettled, the industry was only transient in some regions and longer lasting in others.

Robert Multhauf's *Neptune's Gift* (1978) illustrates the problem of trying to cover several different aspects of the chemical industry in the same volume. Multhauf (Dexter Award, 1985) used his wide knowledge of the history of the industry to produce a very technical account—which thus lacks the popular appeal or breadth of Mark Kurlansky's later work, *Salt: A World History*—but which almost paradoxically does not have much to say about the role of salt in the chemical industry. *Neptune's Gift* is very much a book of its time in paying considerable attention to localities and geography.

Large-scale History: 1987-1990

In a remarkably short period in the late 1980s, there was an explosion of books about the chemical industry, which shared an interest with large corporations or projects. This was partly a result of scholarly and political interest in the effectiveness of large-scale government programs and large firms, but it also stemmed from the series of corporate histories in the 1960s and early 1970s, which celebrated the centenaries of the major German chemical firms followed by Reader's history of ICI and Joseph Borkin's contentious history of IG Farben.

The Forerunner

The forerunner of these studies was W. J. Reader's official history of Imperial Chemical Industries, the first volume of which dealt with the forerunners to ICI, published in

1970. The second volume, which covered the first twenty-five years of the British firm, followed in 1975. Reader's volumes owed much to Haynes and Haber, but in essence formed a sequel to Sir Charles Wilson's magisterial history of Unilever, which appeared in 1954. Reader had been a student of Wilson at Cambridge and had worked as a research assistant on the Unilever history. Reader emulated Wilson in his concern for the broad sweep of corporate history, which essentially treated business history as an offshoot of diplomatic history. He differed from his teacher, however, in a liking for human drama; and in the second volume, he brought out "the interplay between men and events" in the development of ICI. I remember Reader giving a paper on the tragic fall and suicide of Roscoe Brunner in 1981 (he intended to write a novel based on these events), and it was clear he relished the dramatic and human elements of this prelude to the creation of ICI. In his history of ICI, Reader covered the technical side adequately, but without the same brio. Nonetheless, it was the first serious scholarly history of a major chemical company.

The Key Work

The publication of *Science and Corporate Strategy* in 1988 was a major milestone. Written by David Hounshell and John K. Smith, it was the first major study of R&D in a chemical firm that drew on the scholarly literature about R&D and corporate development, especially the work of Alfred D. Chandler. They showed how R&D moved in the period between the wars from being simply important to completely crucial to the firm's future. Unlike Reader, Hounshell and Smith were able to take the story almost up to the present. After World War II, DuPont searched for another nylon with limited success. In the inevitable retrenchment, the basic research that had produced nylon lost out to clearly defined, directed research. While drawing lessons about the role of R&D in the modern chemical firm, Hounshell and Smith were also able to describe the important technological developments—neoprene, nylon, and Mylar among others—in considerable detail.

Other Important Works

Peter Hayes's *Industry and Ideology: IG Farben in the Nazi Period* shared Reader's concern with politics, but was shaped by the debate about the role played by German firms just before and during the Third Reich. Hayes covered technical developments well—in fact better than Reader—but they were clearly not his main concern.

Ray Stokes's *Divide and Prosper* (1988) analyzed the breakup of IG Farben in depth and showed how it was largely a matter of international and German politics. Hayes and Stokes thus introduced a new kind of history of the chemical industry, which showed how it was shaped by politics.

Peter Spitz's *Petrochemicals* (1988) opens in Germany in 1945, like *Divide and Prosper*, but that is where the similarity ends. There is hardly any technology in *Divide and Prosper*, but *Petrochemicals* gives an insider's view of technology development while retaining the broader picture, a rare achievement. The interplay between economics, engineering, and chemistry is described clearly; and Spitz's choice of case studies was excellent. Above all, Spitz recognized that the history of the organic chemical industry is essentially shaped by its feedstocks, an insight he had gained from Carl Heinrich Krauch of Hüls.

Alfred Chandler's *Scale and Scope* (1990) was a comparison of managerial capitalism in the USA, UK, and Germany. IG Farben, ICI, and DuPont were crucial to this comparison. But it was not a history of the chemical industry, nor did it add much to that history. However, it did perform the valuable service of putting the major firms into their economic context (e.g. the importance of wood distiller HIAG compared with the other chemical firms before its *raison d'être* was destroyed by the Pier synthetic methanol process).

Peter Morris's *American Synthetic Rubber Research Program* (1989) was different from the other volumes mentioned here. Concerned with a project involving many firms—rather than internal R&D—and its impact on the development of polymer science in the USA, Morris (Edelstein Award, 2006) sought to draw lessons about cooperative research programs. Influenced by the "evolutionary economics" of Richard Nelson and Sidney Winter, the author argued that radical innovation was best promoted by free competition and that cooperative programs only generate incremental improvements (which can be important nonetheless).

The "Konferenzzeit": 1991-2000

After this flurry of activity, the 1990s was characterized by a series of conferences that were subsequently published—hence the German title of *Konferenzzeit* ("conference period") on the basis of such periods as the *Gründerzeit*. As conference proceedings, the quality of these books was inevitably uneven, but they contained

important material and were generally of a higher standard than earlier books in this genre. The 1990s also saw the publications of books that were to some extent a revisiting of earlier publications. Anthony Travis revised Beer's classic, and Stokes questioned the standard historiography of the postwar period presented by Spitz.

The Forerunners

The Brent Schools and Industry Project in northwest London strove in the period 1980-1985 to interest school pupils in the industrial history of their local area. As Perkin's dyestuffs factory at Greenford Green was within the London Borough of Brent, the dye industry was an obvious topic for this project. One of the chemistry teachers involved with the project, Anthony Travis, developed the topic into a series of three educational books, which appeared between 1983 and 1984 but were never formally published. The first, *The Colour Chemists*, dealt with Perkin and the rise of the synthetic dye industry. Its sequel, *The High Pressure Chemists*, covered the development of the Haber-Bosch and Bergius processes in Germany. The final volume, *Farbenindustrie*, described the IG Farben. These books were written without any knowledge of the contemporary academic work being done in these fields by Peter Hayes, Peter Morris, Willem Hornix, and Ernst Homburg; but they were pioneering in their use of the history of the chemical industry for educational purposes. This approach, taken up by the Salters' Chemistry Course developed at the University of York, is integral to the 21st Century Science curriculum which has just been introduced in England. It also was the starting point for Travis's later work on the history of the dye industry and the Haber-Bosch process.

The Key Work

Travis's *Rainbow Makers* replaced all earlier histories of the 19th century dye industry. He wove the science, technology, legal issues, and corporate developments into a finely written and accurate narrative, which placed Perkin's discovery and later work into its scientific, economic, and social context. Above all, he showed that alizarin, rather than mauve or fuchsine, was the crucial synthetic dye in the development of the industry. But Travis did not stop there: in a series of first-rate papers he fleshed out the account given in the *Rainbow Makers* in several directions, including the development of aniline black, dyes in postage stamps, and (with Peter Morris) a broader history of the synthetic dye industry which took it up to the late twentieth century.

Other Important Works

The first of the conference volumes—published in 1992—was a special issue of the *British Journal for the History of Science* covering the history of the dye industry. It contained Ernst Homburg's seminal paper on research laboratories. This was supplemented by Carsten Reinhardt's paper on the BASF research laboratory in *Chemical Industry in Europe, 1850-1914*. This conference volume was noteworthy for its papers on the chemical industry and pollution and Travis and Schröter's paper on different approaches by Britain and Germany in this period. The concentration of these two volumes on the synthetic dye industry was counterbalanced by *Natural Dyestuffs and Industrial Culture in Europe, 1750-1880* (1999), which covered the scientific and geographical aspects of natural dyes, the role of the factory in the natural dyestuffs industry, and the shift from natural dyes to synthetic dyestuffs.

Determinants in the Evolution of the European Chemical Industry, 1900-1939 (1998) suffered from a polarization between the IG Farben scholars and those studying the chemical industry on the European periphery. Travis published an acclaimed paper on the Haber-Bosch process, and Morris presented his work on synthetic rubber in IG Farben. The latter was also the focus of the final conference volume, *German Chemical Industry in the Twentieth Century* (2000). This was the summing up by some of the key players in the field of two decades of research on the German chemical industry.

In *Opting for Oil* (1994), Stokes wrote the history of the postwar West German chemical industry from the political perspective of *Divide and Prosper*. As a result, he reached the controversial conclusion that the replacement of coal by oil in the West German chemical industry was not inevitable. This went against the viewpoint of all previous historians: that cheap oil had driven the development of the postwar chemical industry. Recently, however, his analysis has received sympathetic attention from academics working on the development of sustainable manufacture of chemicals.

New Waves: 1998-2006

After another (relative) lull, the period after 1998 saw a huge explosion of books about the history of the chemical industry. This time, however, they fell into several distinct categories and thus there is no single key work. One group of books shared Paul Hohenberg's interest in the relationship between economic growth and industrial

chemicals. Another group was concerned with developing an environmental history of the chemical industry. There were also—perhaps coincidentally—several books about the history of German companies, and finally there was a revival in the writing of biographies.

Economics

This revived interest in the economics of the chemical industry largely stemmed from Ralph Landau's entry into this field in the mid-1990s and his concern about America's leadership of the chemical industry with its implications for US economic growth. He drew on the work of historian Nathan Rosenberg, economist Richard Nelson, and, of course, the work of Alfred Chandler. The first product of this new wave was *Chemicals and Long-term Economic Growth* (1998) by Ashish Arora, Ralph Landau, and Nathan Rosenberg. The most useful chapters for historians of the chemical industry were Landau's study—as a former practitioner—of innovation in the industry, which complements Spitz's work, and Murrman and Landau's comparative study of the German and British industries, a preoccupation that goes back as far as Gardner and even earlier.

Peter Murmann published *Knowledge and Competitive Advantage* in 2003, which largely repeated the exercise carried out by Hohenberg but using Nelson and Winter's evolutionary economics. Murmann concluded that a complex interplay between firms, technology, and national institutions gave German firms dominance of the industry because of Germany's patent laws, educational system, and a strong alliance between the industry and academic centers of excellence in organic chemistry. This conclusion is not surprising—it was foreshadowed by Beer in 1959—but the detailed argument was difficult for noneconomists to follow (in keeping with Murmann's other predecessor, Hohenberg).

Following on from his study of electronics—and energized by his interaction with Ralph Landau—Alfred Chandler finally published a history of the chemical and pharmaceutical industry, *Shaping the Industrial Century*, in 2005. In a mainly narrative history, Chandler argued that chemicals had run out of steam in the 1970s, were supplanted by pharmaceuticals and now were being displaced in turn by biotechnology.

Environmental History

The other group of historians could hardly be different. With no social connections between them and largely

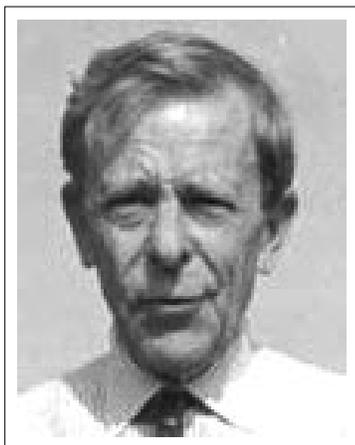
uninterested in economics, they sought to bring environmental issues into the field. It is remarkable how histories of industrial chemistry have largely ignored the environment completely until recently. Of course, this did not apply to the effects of the Leblanc soda industry in the 19th century, but more recent environmental effects were only notable by their absence.

A team of historians led by Colin Russell (Dexter Award, 1990) at the Open University made the first conscious attempt to write a history of the chemical industry that covered the environment. *Chemistry, Society and Environment* (2000) was a successor in other respects to D. W. F. Hardie and J. Davidson Pratt's *History of the Modern Chemical Industry*, a standard history published in 1966 (noteworthy mainly for its potted company histories along the lines of Haynes's final volume). Russell and his coauthors were determined that the environment should be at the heart of their narrative. Based on a well tried structure of industrial sectors combined with periods, the book is a clear history of the British industry very much along the lines of Campbell's earlier book and an Open University course unit on the chemical industry. As the authors intended, the environment does appear in the book, but the reader gets the feeling that it has been tacked on rather than underpinning the whole narrative. The idea was commendably bold, but the resulting execution of it was disappointing.

Travis was more successful with his history of the Calco works in New Jersey, *Dyes Made in America, 1815-1980*. He set out to show why the factory was initially successful but eventually closed. He demonstrated the importance of environmental factors and pointed out the irony that the environmental problems were finally solved just before the factory was shut down. It is, however, a pity that the long environmental section is separate from the operational history of the factory.

Just as Warren brought a new perspective to the history of localities, his fellow geographer Vaclav Smil's *Enriching the Earth* has recently brought a new approach to the history of high-pressure chemistry and the environmental history of food production and the chemical industry. In admirably clear and forthright prose, Smil presents an excellent argument for the importance of the Haber-Bosch process, but the result is strangely un-historical, except for his excellent account of the actual development of the process at BASF.

Despite all these efforts, we still lack a history of the industry that completely integrates the environmental factors into the main narrative. In some cases, the



C. A. Russell, by his permission.

divergence from the standard model will be small as the environmental aspects were minor. In other cases, however—perhaps even the majority—taking into account the environmental aspects in describing the introduction of a new process or the financial history of a chemical firm will make a striking difference in the way

we understand the history of the industry's development. This is the same way that the consideration of the role of R&D has transformed our view of the chemical industry since the 1950s.

History of German Companies

It is striking how many books about the German chemical industry have been published in the last three years. There have been three major waves of German corporate histories if one includes those written in German. The first was in the 1960s, to mark the centenary of the major firms. On the whole these were not scholarly works. The second wave was in the late 1980s and early 1990s. This third wave perhaps reflects a willingness on the part of German chemical firms to confront their history, as the Third Reich recedes into history and anyone associated with that period even in a junior role has now retired. The history of BASF was the most ambitious but suffered from having several authors with different styles. Peter Hayes's history of Degussa is magisterial and Hans-Liudger Dienel's history of Linde may be the best of the group.

Biography

Twenty-five years ago, biographies were considered to be old-fashioned, and there were never many of chemical industrialists (at least in English in contrast to German). But biographies have now returned to the history of science. Reinhardt and Travis's *Heinrich Caro and the Creation of the Modern Chemical Industry* illustrates how a good biography can show the connections and movements of people and ideas, which are impossible

to convey in a history of the chemical industry or even a firm. We now need biographies of the key figures who mediated between academia and industry.

Now for Something Completely Different

In the course of writing the original version of this paper for a conference presentation in September 2006, I found a completely new kind of history of the chemical industry on the new books shelf in the Science Museum Library. Esther Leslie, *Synthetic Worlds* is very different from anything else covered here. It opens with a quotation from *Gravity's Rainbow* and is closer in approach to Pynchon than Haber, Travis, or even Hayes. Written by the Reader of Political Aesthetics at Birkbeck University of London, it is a complex wide-ranging book which links the development of synthetic dyes (and Ferdinand Runge) to changes in aesthetics and also the rise of the Nazis: "the poetics of carbon," as she puts it. Leslie's analysis is avowedly Marxist and when she presents the history of the chemical industry—surprisingly infrequently—her style is similar to that of the histories of IG Farben produced in the former GDR or by Joseph Borkin. One might have hoped she would have woven the literature I have covered into a wholly new tapestry. Strikingly, however, her "select [but long] bibliography" does not list any of these books, which illustrates the pressing need for historians of industrial chemistry to engage with scholars outside that field.

Conclusions

Writing the history of industrial chemistry is clearly a complex operation involving a number of different approaches and different levels of analysis. Several parts of the industry have failed to interest historians for one reason or another, or have died out, such as wood distillation. Similarly the historiography of the industry has been dominated by large firms and the forerunners of companies which still exist, what one might call the "history of the survivors." There are histories of May & Bayer, but not of Thomas Tyrer's chemical works. As historians, we are still struggling to incorporate several features of this history, in particular the environmental and social factors. Is there a way of bringing the technology and the corporate aspects into harmony? Can we engage fruitfully with scholars in other fields who have a very different approach to the history of the chemical industry? We have clearly failed in the case of *Synthetic Worlds*, but at the same time, I am currently collaborating with a chemist working on the issue of new sustainable feedstocks for

the chemical industry, who is familiar with much of the literature presented here. I would argue that the ideal history of the chemical industry (of any period) has still to be written. For a variety of reasons, perhaps it cannot be written; indeed, given the lack of success of *Neptune's Gift*, is there any point in producing a comprehensive account? Rather, we should perhaps aim to integrate the history of the industry into broader perspectives. It is after all one industry among many and with links to other industries, rather than an unique phenomenon to be studied on its own, which has been the standpoint of many historians in the period reviewed here.

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SCIENTIFIC BIOGRAPHY IN THE HISTORY OF CHEMISTRY: THE ROLE OF DEXTER AND EDELSTEIN AWARD WINNERS IN THE LAST FIFTY YEARS*

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The genre of biography maintains a great appeal among general readers as well as among scholars of the academic community. A 1994 poll on reading habits in Great Britain revealed biography to be the most popular category of non-fiction book and a genre considerably ahead of contemporary fiction (19% to 14% of readers) (1). Within the history of science profession, the June 2006 issue of *Isis* included a special section on scientific biography, with essays by Joan Richards, Mary Terrall, Theodore Porter, and this author (2). In my essay in this volume, I examined different genres of scientific biography: the inevitable process by which biography brings together the lives of the biographical subject, the author, and the reader; and the diversity of audiences for which biographies may aim. Peter Dizikes examines some of these same issues in his essay "Twilight of the Idols" in the November 5, 2006 issue of *The New York Times Book Review* (3).

By way of marking the fiftieth anniversary of the Dexter and Edelstein Awards for Outstanding Achievement in the History of Chemistry, it is instructive to emphasize the role that biography has played in the history of chemistry, especially as practiced by the chemists and historians who have received the Dexter and Edelstein prizes. These prizes extend from the first Dexter award to Ralph E. Oesper in 1956 until this year's Edelstein award to Peter J. T. Morris. A review of the names of past awardees shows that at least twenty of them have tackled the art of biography, including James R. Partington, whose four-volume *History of Chemistry* draws part

of its strength from its original and detailed biographical sketches, as does Aaron J. Ihde's *Development of Modern Chemistry* (4).

Partington's approach of short biographies was adopted by several Dexter award winners who crafted or edited volumes that tell the history of chemistry through sketches of the lives and works of important figures in the history of chemistry. Bernard Jaffe's *Crucibles: The Story of the Great Chemists* is exemplary of the genre. It was first published in 1930 and received the \$7,500 Francis Bacon Award sponsored by Forum Magazine and the Simon and Schuster publishing house. Jaffe's much beloved book went through numerous editions, the most recent of which is still available as a Dover paperback, first published in 1976 with the subtitle *The Story of Chemistry from Ancient Alchemy to Nuclear Fission*. Jaffe, who was born in 1896 and died in 1986, chaired the physical science department at James Madison High School in Brooklyn for many years and received the Dexter Award in 1973 (5).

Eduard Farber, Dexter winner in 1964, edited the biographical compendium *Great Chemists*, published in 1961, as well as a smaller volume on *Nobel Prize Winners in Chemistry, 1901-1950* (1953), which he updated a decade later in 1961. Farber, like Jaffe, was a man of the nineteenth century, born in 1892, and Farber found his way into the history of chemistry while reading Ernst Meyer's *Geschichte der Chemie* as a student in Leipzig. Farber later studied and wrote history of chemistry while

working in the chemical industry in Germany and the United States (6). The 1976 Dexter winner Trevor I. Williams edited an important biographical dictionary as the *Collins Biographical Dictionary of Scientists*. It went through four editions from 1969 to 1994.

On a grander scale than Farber or Williams's dictionaries, historians of chemistry, like other historians of science, embraced biography and entered its practice on an ambitious scale in the 1960s with the huge editorial project of the *Dictionary of Scientific Biography (DSB)*, now underway in its third phase in a *New DSB*, edited by Noretta Koertge. The first of the eighteen volumes of the *DSB* appeared in 1970 under the editorship of Charles Gillispie, followed by supplementary volumes edited by 1994 Dexter Award recipient Frederic L. Holmes (7).

From the beginning of the *DSB* project in the 1960s, some scholars expressed objections to perpetuating the writing of the history of science as the biographies of great men and great ideas. Feminist scholars pointed to the absence of women scientists in older big-history narratives and called attention to historical prejudices that excluded women from the company of male heroes, with the notable exception of the glorious but tragic story of Marie Curie (8). Social historians and sociologists challenged historians to write about ordinary scientists as well as heroic figures and to study the technicians and instrument makers who do most of the work of science. A leader among these social historians has been 1983 Dexter awardee Arnold Thackray. One of his early books, *John Dalton: Critical Assessments of His Life and Science* (1972), focused on the traditional figure of Dalton, but other work has described chemical inventors and entrepreneurs, most recently in Thackray's volume (2000) co-authored with Minor Meyers, Jr. on twentieth-century chemical instrument-maker, manufacturer, and philanthropist Arnold Beckman. Thackray notably joined with Lewis Pyenson, Steven Shapin, and others in the 1970s who argued for the importance of prosopography, or group and institutional biographies in the history of science, as in Thackray's 1981 book with Jack Morrell on *Gentlemen of Science: Early Years of the British Association for the Advancement of Science* (9).

Some scientists, like historians, counseled a different approach to the history of science than the heroic genre. Among these was the physical chemist Michael Polanyi, who turned from doing chemical research to writing about the nature of science. In 1962, he advised historians to pay attention to ordinary workers in the scientific community, modestly saying that, while (10):

The example of great scientists [like Einstein] is the light which guides all workers in science, . . . we must guard against being blinded by it. There has been too much talk about the flash of discovery and this has tended to obscure the fact that discoveries, however great, can only give effect to some intrinsic potentiality of the intellectual situation in which scientists find themselves. It is easier to see this for the kind of work that I have done than it is for major discoveries.

Scientific biographies of the last few decades show the influence of discussions provoked by the *DSB* project and by points of view like Polanyi's. Of course, biographies of superhero celebrities continued to appear. Galileo, Newton, Darwin, and Einstein fall into this category, as does Marie Curie. Among chemists, in addition to Curie, Lavoisier has been the most popular subject of biography. Six Dexter scholars have written one or more books about Lavoisier. Douglas McKie was one of these biographers. Born in 1896, McKie completed his Ph.D. in chemistry in 1927 under F. G. Donnan at University College London. McKie resigned an appointment in the UCL chemistry department in 1934 in order to join a unit that became the Department of History and Philosophy of Science (11). His first biography *Antoine Lavoisier: The Father of Modern Chemistry*, which appeared in 1936, has a title that carried into the twentieth century the nineteenth-century feud about the origins of modern chemistry as a "French science." McKie's 1952 biography *Antoine Lavoisier: Scientist, Economist, Social Reformer* goes on to portray the complexity of Lavoisier's life and activities in Enlightenment and revolutionary France.

The 1980 Dexter winner Maurice Daumas was an expert on scientific instruments, and he emphasized the innovation and superior quality of Lavoisier's laboratory equipment in the book *Lavoisier, théoricien et expérimentateur* in 1955. The 1972 Dexter Award winner Henry Guerlac examined the continuities or roots of Lavoisier's so-called chemical revolution in the continental mineralogical and pharmacy tradition, on the one hand, and in British pneumatic chemistry, on the other hand. Guerlac did this in *Lavoisier—The Crucial Year* (1961) and in *Antoine-Laurent Lavoisier: Chemist and Revolutionary* (1975). The latter was written specifically for the *DSB* project. Ferenc Szabadvary, who received the Dexter Award in 1970, wrote a biography of Lavoisier for a German-language readership in 1987.

Taking a different tack, 1997 Dexter Award winner Bernadette Bensaude-Vincent, in her biography *Lavoisier: Mémoires d'une révolution* (1993), critically examines earlier interpretations of the role of Lavoisier

in chemistry. She treats Lavoisier as the last great figure of an eighteenth-century chemical tradition and a consummate insider in the scientific elite, rather than as a maverick breaking with his peers.

Biographies of Lavoisier highlight a perennial problem facing the scientific biographer. As I noted in *Isis*, we may very well wonder whether the best scientific biographies, as a rule, are books about the scientist or books about the science (12). For instance, consider the recent biographical interest in the chemist Fritz Haber. An article in the *New York Times* in late 2005 notes the debut of Daniel Charles's biography *Master Mind: The Rise and Fall of Fritz Haber, the Nobel Laureate Who Launched the Age of Chemical Warfare* (13). There is the play "Einstein's Gift," written by Vern Thiessen, about Haber and Einstein; the short German film "Haber" by Daniel Ragussis; and the opera "Zyklon" by jazz musician Peter King. "I learned nothing about science [while] working on the project," remarked Thiessen, "but I learned a tremendous amount about *scientists*." His aim, Thiessen added, was to enable the audience to "understand the passion behind the work (14)." Thiessen's comment might have pleased Polanyi, who argued in essays and in his book *Personal Knowledge* that historians should not only portray the reason and logic of a scientist's work, but the passion that undergirds scientists' commitment and quest for scientific knowledge (15).

In this vein, some biographies are framed as a *Bildungsroman*, or a narrative of self-development in which the biographer and the reader are obliged to seek the coherent self within the diverse themes of the subject's life. In reflecting on the writing of biography in general and in his own book on the immunologist Niels Jerne, Thomas Söderqvist writes that an aim of biography is a study of life as an achievement or a deed, of how one lives and crafts a life (16). In my biography of Patrick Blackett, I found myself asking how this gifted experimental physicist came to make choices of how he would live his life: what scientific problems he would study, how he would organize his laboratory, what administrative responsibilities he would take on, what political issues he would address publicly, how he would serve his country during the Second World War, and how much open controversy he was willing to endure in science and in politics. The biography came to be one that asked questions about the nature of leadership in a scientific community and the moral courage of a scientific life, as well as about Blackett's scientific experiments and theories. Ethical questions are at the core of Vern Thiessen's play and of Daniel Charles's book about Haber: the story they tell,

says Thiessen, is one of a man "who wants to do good and fails miserably (17)."

The technical science that is the daily pastime of a large part of the scientist's life and passion has to play a large role in scientific biography, as in 1978 Dexter awardee George Kauffman's biography *Alfred Werner, Founder of Coordination Chemistry* (1966) and Trevor William's *Robert Robinson: Chemist Extraordinary* (1990) (18). No historian studied more carefully than did Frederic L. Holmes, the Dexter winner for 1994, the detailed technical work of scientists. Holmes's dense narratives of scientists' laboratory work and their investigative pathways appealed mainly to a narrow audience, however, rather than to a broader public or college readership—unlike, say, Bernard Jaffe's *Crucibles*.

In fact, Holmes's study of Lavoisier, *Lavoisier and the Chemistry of Life: An Exploration of Scientific Creativity* (1985), had a very different goal from that of an inspirational biography of a great chemist or a chapter in the history of chemistry or the probing study of individual development typical of a *Bildungsroman*. As in his two-volume study of Hans Krebs (1991, 1993) and in his very first book, *Claude Bernard and Animal Chemistry: The Emergence of a Scientist* (1974), Holmes aimed to use Lavoisier's work to explore the nature of scientific creativity in general, as well as the tortuous, interwoven, and unpredictable pathways by which scientific experimentation and reasoning really work. Laboratory notebooks were the essence of Holmes's story, not the political, administrative, philosophical, or psychological hours of Lavoisier's life.

The biographical focus can also be an effective means for exploring and analyzing the politics of scientific practice and the cultural formation of natural knowledge. The tried-and-true "Life and Times" approach often has had this goal, as do newer approaches in history and sociology of science that emphasize the social construction of scientific knowledge. Among biographies written by Dexter Award winners, a good number achieve these ends, while also explaining the details of the technical scientific work that was the passion of the biographical subject. These biographies include [2003] David M. Knight's *Humphry Davy: Science and Power* (1992), [1995] William Brock's *Justus von Liebig: the Chemical Gatekeeper* (1997), [1990] Colin Russell's *Edward Frankland: Chemistry, Controversy and Conspiracy in Victorian England* (1996), [1984] Maurice Crosland's *Gay-Lussac: Scientist and Bourgeois* (1978, 2002), and [2001] William Smeaton's 1962 *Fourcroy: Chemist and Revolutionary* (1962).

Alan Rocke's biographies of Kolbe and Wurtz are among the exemplars of the kind of biography that was demanded by skeptics of the *DSB* in the 1960s who objected to the *DSB* project as a perpetuation of great-man history. The biographical subject is the subtitle, rather than the main title, of Rocke's book *The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry* (1993). The main title, like the biographical study as a whole, interrogates the traditional trope of schismatic revolution and introduces the idea of a "quiet revolution" that took place in organic chemistry in the 19th century, with a focus on the organization and conduct of the German scientific community and on the meaning and role of research schools and traditions. Rocke's 2001 book *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry* extends this approach to chemistry in France, in an examination of the general question of how scientific change comes about and what roles are played in scientific development by failed revolutions, as well as by successful ones.

More typically, the 1969 Dexter Award winner Walter Pagel highlighted the biographical subject *first* in his titles for books on *Paracelsus: An Introduction to Philosophical Medicine in the Era of the Renaissance* (1958, 1982) and *Joan Baptista van Helmont: Reform of Science and Medicine* (1982). Pagel's books were novel and important at the time in Pagel's general interpretations of the relationship between Renaissance medicine and chemistry and in his argument for the importance of religion and magic in early science.

Michael Polanyi wanted portrayals of scientists and of their science that were painful, as well as pretty. He thought that the most penetrating and moving representations of the "young scientist's struggles" come from novelists, such as Sinclair Lewis, C. P. Snow, and Neville Shute. Polanyi wanted accounts from historians, philosophers, and scientists that would render the scientist's life, including the darkest moments, with feeling and imagination (19):

We want to know . . . about the kind of research team which 'is a death-trap for young scientist[s] and a slough of despond for the older ones.'

Polanyi's own biographers William T. Scott and Martin X. Moleski have written precisely this kind of biography in *Michael Polanyi: Scientist and Philosopher* (2006), self-consciously following Polanyi's triumphs and anguishes as he moved, day after day, from his laboratory to meetings with colleagues and friends, and to evenings at home with his family where, as his biographers describe,

Polanyi turned his thoughts to poetry, art, literature, philosophy, politics, or prayer.

The biographer's choice of the means for effecting a biographical interpretation reflects the author's own beliefs not only about the nature of scientific work, but about chance, fate, character, or cunning in the lives we all live. Richard S. Westfall arrived at the insight that the Puritan ethic that informed his own life furnished the set of categories that he used to construct his picture of Isaac Newton, even while Westfall began increasingly to feel that the real Newton was eluding him (20). Thomas Hager, who spent much time with Linus Pauling before Pauling's death in 1994, and who published his biography in 1995, wrote that he began the project as a Pauling enthusiast and remains one, but came to realize that "below the surface charm. . . was a fiercely competitive and emotionally constricted man (21)."

Chemists themselves have written some of the most lively and informative accounts of themselves and their work in autobiographies. Exemplary in this genre are the twenty autobiographies published since 1990 in Jeffrey Seeman's series "Profiles, Pathways, and Dreams," which documents the development of modern organic chemistry. Some chemists have written both autobiography and fictionalized biography, as in Carl Djerassi's *The Pill, Pygmy Chimps, and Degas' Horse: The Autobiography of Carl Djerassi* and *Cantor's Dilemma: A Novel* (22).

In coming to a conclusion, it is striking that many of the historians of chemistry who have been recognized with the Dexter and Edelstein Awards have used biography as a means of writing the history of chemistry and in working out new methodological approaches that have been social or prosopographical or psychological or entrepreneurial or intellectual in character, rather than heroic or hagiographical. As a genre of historical writing and analysis, scientific biography is an effective means for engaging readers in the struggles, successes, and failures of scientists crafting their own lives as they explore and construct knowledge of the natural world. Scientific biographies that are rich in science and that are engaging as lives can have great appeal to audiences that are literate and even illiterate in the sciences. For historians of chemistry, the writing of such biographies has illuminated the changing character of chemical practices and chemical theories, as well as explored the lives and character of individual chemists of the first and all ranks.

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UNINTENDED TECHNOLOGY TRANSFER: ACETYLENE CHEMISTRY IN THE UNITED STATES*

Anthony S. Travis, Edelstein Center, Hebrew University

Introduction

Peter Morris, recipient of the 2006 Edelstein Award, through several splendid essays focusing on science and industry in Germany and the United States, has shown that it was less preconceived policies that transformed chemical industry during the 1930s and early 1940s than the expediencies of war economies, in other words, political and strategic priorities (1). This is clearly exemplified by the rise of high-pressure acetylene chemistry, as originally described by Morris in his 1982 doctoral thesis (2). Though acetylene chemistry rapidly declined from the 1960s, apart from the production of 1,4-butyne-3-diol, it did have some considerable and long-lasting impact in the United States at the General Aniline & Film Corporation, particularly at its Linden, New Jersey, facility. Until 1942, this corporation, originally a leading producer of indanthrene vat dyes and azo dyes, was under the ownership of I. G. Farben (3).

The corporate behemoth I. G. Farben was the outcome of the 1925 merger of the main German dye-manufacturing firms, BASF, Bayer, and Hoechst, founded in the 1860s. Until 1914, they had dominated the manufacture and supply of coal tar dyestuffs. However, following the outbreak of war in Europe, and in direct response to shortages of the essential chemicals previously available from Germany, the modern US chemical industry emerged. Meantime the German dye firms had begun to diversify, which included work in high-pres-

sure chemistry, particularly the Haber-Bosch ammonia synthesis (4).

In the United States the wartime situation stimulated the rapid development of technologies based on complex aromatic chemistry (5). This led to an advanced science-based industry that during the 1920s also embarked on diversification. However, even then, access to German innovations was still needed, including the new high-pressure Bergius coal-to-oil process. Such was the perceived importance of I. G. Farben's processes that in Germany the corporation was plagued with industrial espionage, and it was not unknown for I. G. Farben's intelligence department to break up spy rings acting for French and American interests.

At the same time, the Germans wished to regain dye markets lost during the war. This led to a singularly important merging of American and German interests, the General Dyestuff Corporation, in 1925. This was predecessor to the General Aniline Works, established by I. G. Farben in 1929, which was renamed General Aniline & Film in 1939. The main manufacturing sites were at Linden, on the Arthur Kill, opposite Staten Island, and the former Bayer works at Rensselaer, New York, on the Hudson River. There was also the AGFA-Ansco facility at Binghamton, New York. The latter was responsible for the word Film in the name. A unique strategy for control of production of dyes, intermediates, photographic products, and detergents was implemented at the German

controlled General Aniline & Film (hereafter GAF), and affiliates.

Reppe Chemistry

During the 1930s, I. G. Farben embarked on a completely novel area of diversification based on high-pressure acetylene chemistry. This had previously been considered far too dangerous since acetylene under pressure is inherently unstable and explodes with extreme violence. This reflects its great reactivity that derives from the triple-bond between the two carbon atoms. As a result of the I. G. Farben investigations, the development of acetylene-derived chemicals in Germany represented a major technology breakthrough and became an outstanding commercial success. The basic research for safely reacting the highly flammable gas with other chemicals under high pressures was done by J. Walter Reppe (1892-1969) at the Ludwigshafen laboratories of I. G. Farben from the late 1920s.

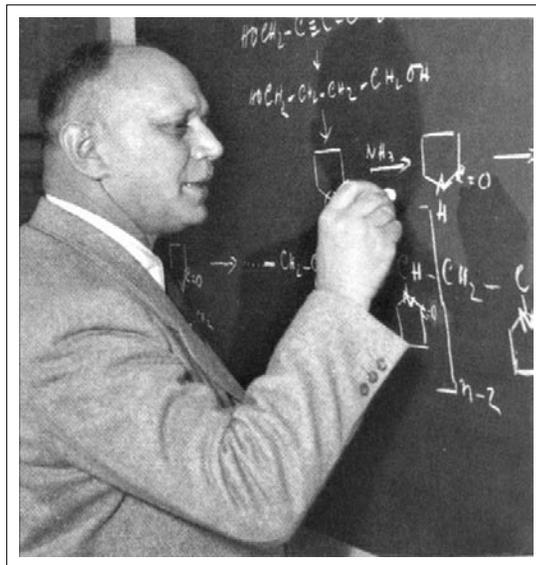
As Morris has pointed out, Reppe "bravely pioneered dangerous research on the reactions of acetylene under pressure, and thereby opened up entirely new fields of industrial organic chemistry (6)." In 1934 Reppe was appointed head of the new Ludwigshafen Intermediates and Plastics Laboratory, and in 1938 of the main Central Research Laboratory. With acetylene, there were certainly daunting technical hurdles to overcome. Engineers and chemists fixed the problems in much the same way that they had overcome difficulties with ammonia reactors two decades earlier. In England, Imperial Chemical Industries (ICI) had undertaken similar studies in the 1930s, but, because of the enormous danger, worked on a very small scale.

Reppe's team, meantime, developed large-scale robust and reliable manufacturing equipment, as well as designs for suitable buildings that were capable of withstanding explosions.

The acetylene research had a tremendous impact on the development of several processes, including the production of synthetic rubber, which became strategi-

cally important once the second Nazi Four Year Plan was inaugurated in September, 1936. The technical potential of acetylene chemistry had been realized following Reppe's 1927 conversion of acetylene into butadiene. This and the directives of the plan stimulated further studies, including reactions in which the triple bond was retained. This was successfully achieved by Reppe in 1937 when he treated acetylene with two molecules of formaldehyde to afford 1,4-butynediol. The reaction provided a new route to butadiene, the building block for Buna synthetic rubber. As a result of this and other developments, as Morris has pointed out (7):

At I. G. Farben (in contrast to American companies), a central role was played by acetylene. By the late 1930s, acetylene underpinned most of I.G.'s heavy organics (with the exception of methanol), most notably the copolymer synthetic rubbers.



Walter Reppe at the blackboard preparing a diagram of the vinyl pyrrolidone process. BASF Archives.

Such was Reppe's fame that in 1945 the American Chemical Society nominated him a major target for the Allied investigators that were hunting down leaders in German science and technology. Four years later the Department of Commerce published its eagerly awaited Reppe Report. Industrial acetylene chemistry based on Reppe processes thrived for a time in Germany and, as summarized here, at GAF in the United States. How this came about requires some nonchemical explanation.

Patent Transfer and US Government Ownership

During the late 1930s, concerns over possible Nazi influences on American industry led investigators at the Securities and Exchange Commission to investigate the ownership of GAF. The situation was confused by the existence of dummy companies set up by I. G. Farben in Holland and Switzerland that claimed ownership of GAF and other facilities outside of Germany. The investigations were intensified after war broke out in Europe during 1939. Fearful of loss of important assets in the

largest chemical-consuming market on earth, the patent committee of I. G. Farben on April 30, 1940 convened to discuss assignment to GAF and U.S. affiliates of certain of 2,208 out of 5,500 American patents and applications. According to the minutes of the meeting, August von Knieriem, chairman of the board of directors, supported the measure (8):

[I]n considering the transfer, it should not be asked whether the transfer is a profitable business venture, but the transfer should be regarded above all as a protective measure taken for the safe-guarding of the I.G. patents. These patents will be in the possession of a friendly business enterprise.

New York based Walther H. Duisberg, son of Bayer's Carl Duisberg, "a patent attorney and consulting chemist," would be the intermediary in the transaction. Duisberg also supported transfer, since Americans would be expected to honor the arrangement and were unlikely to sequester patents belonging to a foreign corporation whose ultimate ownership, unlike Bayer during World War I, was uncertain: "American opinion takes a much more legalistic view of such assignments as we believed hitherto." Moreover, the chairman explained, "German public opinion has changed and does no longer, as was the case at the beginning of the war, regard any such safe-guarding as defeatism. The Reichs Minister of Economics urges again and again that I.G. should follow the example of other German business enterprises and should assign its patents to American business enterprises. It is the task of the Patent Committee to fix the specific terms under which such a transfer may appropriately be made." Mr. Redies of the Lower Rhine factory group, however, was against transfer of the patent rights, in part because he doubted that the United States would enter the conflict:

There are two possibilities; either we make a genuine sale of the I.G. patent rights or we refrain from doing so and bear the risk inherent in such action. If the patent rights are not sold, disadvantages to I.G. will arise only if the United States enters the war and if later on German patents will be seized as was done in the First World War I doubt very much whether this possibility will materialize and therefore the risk existing at present is a very doubtful.

The transfer, however, was considered the safest strategy, since, as von Knieriem emphasized (8):

the Reichs Ministry of Economics expects that the transfer of our most important patents and patent applications will be made...Furthermore, many American inventions are protected by German patents. The United States owns valuable patents in Germany. In the event of war, these patents will be subject to seizure

by the German Government and for this reason the American Government will be compelled to exercise considerable restraint.

The transfer of patents, including the acetylene-based processes, was made a few days later, on May 4 (9).

However, this did not turn out to be in the best interests of I. G. Farben, whose influence in the United States came to an abrupt end following American entry into World War II in December, 1941. GAF was now a corporation belonging, even if in a convoluted way, to an enemy country. The US Treasury Department, unable to sequester the corporation immediately because of the uncertainties concerning ownership, installed seventeen secret service agents in the main offices and plants of the corporation to ensure American control of all activities, and to prevent disclosure of sensitive information to Germany. Then in January, 1942, the Department ousted five German-born executives, all naturalized American citizens, for personifying the Nazi domination of the company. Treasury Department agents closely monitored the activities and communications of all research staff. FBI agents conducted extensive interviews with all employees (10). Former GAF chemist Barry Bochner, for example, remembers that at Linden quite a few were "Ready to die for Hitler," and were removed by the FBI.

Fifty executives and key workers, regarded as un-dependable, or as security risks, were fired or taken into custody. On February 16, 1942 the Secretary of Treasury issued an order for transfer of stock to the government, that is, formal seizure of the assets of GAF as enemy property. Four American businessmen were put in charge as appointees of the Treasury and began redirecting activities to the war effort.

The only former German chemists allowed to remain at GAF manufacturing sites were the few who were Jewish, were married to Jewish women (which was the reason that Dr. Paul Nowialski was sent by I. G. Farben to America, as was probably also the case for Dr. Werner Freudenberg; both worked at Linden), or who had expressed strong anti-Nazi sentiments. They included Dr. Wilhelm Von Glahn, director of process research at Rensselaer, who "had a very thick German-Jewish accent" and bore the ultimate Prussian mark of honor, "terrible looking dueling scars all over his face (11)." Several I. G. Farben chemists of Jewish origins had already been assigned to posts outside of Germany, including at AGFA-Ansco, by sympathetic managers at certain divisions (12). As a result, the ethnic composition at former I. G. Farben-owned factories in America would

henceforth be quite unlike that found at other American chemical factories. This was perhaps ironic, since US chemical firms tended not to hire Jewish chemists until after 1945.

Patents for America

As a result of the 1940 transfer of patents to GAF, an important strategic and military asset came into the hands of the Americans. Under US government ownership, GAF engaged in diversification based on prewar German innovations, particularly in the new Reppe acetylene-based processes.

A principal contributor was Hans Beller (1901-1984), one of the German chemists assigned to a GAF manufacturing site. Beller was born in Munich, where in 1924 he received a doctorate in chemical engineering from the institute of technology. He then joined BASF at Ludwigshafen as chemical engineer, and then he was transferred to GAF. He was highly vocal in his opposition to the Nazis, and for this reason was assigned to Linden. There his first challenge, in 1942, was development of carbonyl iron, also based on patents and know-how previously acquired from I. G. Farben. His endeavors enabled the Linden plant to produce carbonyl iron powder suited to the manufacture of radio frequency electrical cores needed by the military (13).

Prior to 1942, GAF had depended on I. G. Farben for research to support all of its business areas. Though GAF had not duplicated I. G. Farben research in the United States, details of a few innovations made at Linden were sent to Germany. These related mainly to dye-stuffs. A small amount of research was carried on in the photographic film plants for the AGFA-Ansco division. Certainly, no fundamental research or expansion into new fields was done. In 1945, it was reported that (14):

the result of this policy was the complete subservience of [GAF] to [I. G. Farben], for the results of the German research were never disclosed to [GAF].... in many cases important material was only communicated verbally to the most trusted employees of [GAF] on the occasion of their visits to Germany.... The information thus obtained was not disclosed to other employees of [GAF in the US]. Thus on several occasions when the man in possession of information died [GAF] was obliged to send another employee to Germany for instruction in the particular process.

In other words key processes carried out in the United States were carefully controlled from Germany.

The GAF and the I. G. Farben Central Research Laboratories

The outcome was that after the government takeover in 1942, GAF was in possession of almost 4,000 I.G. Farben patents but lacked the technical staff to commercialize the inventions. The American management team then committed \$10 million to create a first-class research organization, known as the Central Research Laboratory, established at Easton, situated in Pennsylvania's Lehigh Valley, in the summer of 1942. By the autumn, some fifty chemists, engineers, physicists, and technicians had been brought together both from within the corporation and from leading scientific institutions. The laboratory was among the largest industrial research centers in the United States. Several German chemists at GAF manufacturing sites, including certain senior managers believed to have close ties with their homeland but not considered to be high security risks, were reassigned to the Easton laboratory.

The early effort at Easton was focused on dye chemistry but was soon extended into broader fields, including research into photographic materials. The constitutions of the important AGFA color formers, rivaled only by those of Kodak, and previously kept secret, were quickly worked out and their production was commenced in 1942. The hot topic was high-pressure acetylene chemistry. The Easton laboratory developed thirty acetylene-derived products that showed potential commercial applications.

Progress was also made in Germany. At the end of the 1930s, Reppe's chemists at the Ludwigshafen Central Research Laboratory had developed an acetylene-based process that afforded vinyl pyrrolidone in five steps. This was then converted into its polymer polyvinylpyrrolidone (PVP), in the presence of catalysts, according to the first patents filed during 1938 and 1939 (15). Suggested uses included as textile assistants and thickening and sticking agents (16). However, PVP was transformed into a blood plasma substitute, called Kollidon by Helmut Weese and Gerhard Hecht of the Elberfeld (Bayer) pharmacological laboratories (17). It was chosen after Weese had tested colloidal substances received from all divisions of I. G. Farben in response to the needs of the Wehrmacht. For intravenous use Kollidon was dissolved in water containing inorganic salts and named Periston. Trials were carried out by H. Bennhold at the University of Tübingen. Introduced probably at the end of 1940, Periston was considered highly important by the German military. The product was improved by increasing the

PVP content, leading to greater efficacy in maintaining blood pressure. During 1943 a similar product, Subtosan, was introduced in France by Rhône-Poulenc.

After the war it was reported that Periston (18):

is said to have saved the lives of tens of thousands of German soldiers. In addition, because of the difficulty of obtaining plasma in wartime Germany, it was used extensively and successfully in civilian hospitals in shock and similar conditions.

One of the chemists engaged in this work was Curt Schuster, who from 1939 had participated in studies on the reactions between acetylene and carbon monoxide that afforded acrylic esters. In May, 1943 he was arrested by the Gestapo; he had probably been under suspicion for some time, as a member of a group helping Jews and opposed to the Nazi regime. On February 15, 1944, Schuster was sentenced to three years in prison. His colleagues at BASF had testified on his behalf as character witnesses, emphasizing his important role in the invention of Periston (19). This apparently led to a relatively mild sentence; though a prisoner he was forced to work at the I. G. Farben Oppau works. After the war Schuster returned to Ludwigshafen and prior to retirement became an outstanding historian of the synthetic dye industry (20).

When the war ended, the Easton Central Research Laboratory employed 107 research workers, including chemists and physicists, 67 of whom had Ph.D.s. GAF manufactured dyestuffs and miscellaneous chemical products, including detergents, carbonyl iron powder, and resins; the Ansco Division manufactured photographic films, papers, and chemicals, as well as cameras; and the Ozalid Division produced sensitized materials and machines for printing and developing.

The December, 1945 monthly research letter at Easton provides a useful summary of activities directed at exploiting certain patents held as a result of the 1940 agreement (21):

These patents deal, to a very large extent, with the chemistry of acetylene and for new methods of handling acetylene under pressure and at high temperatures. Under these patents two products have been developed [that]... require the same general technique for handling acetylene under pressure.

Further research had been hampered under the wartime conditions, but it was subsequently placed on a systematic footing, particularly the polymerizations involving methyl vinyl ether, and other ethers.

Studies into the role of peroxides as initiators in vinyl polymerizations were conducted, and, as a result, the first polymerisations of vinyl pyrrolidone were carried out at Easton using hydrogen peroxide at 100° C.

The product was PVP. Information from Europe "on new method for synthesis of acrylic acid esters ... fits nicely with our work on the development of acetylene chemistry (21)." Infor-

mation had also arrived about Periston, the blood plasma substitute made from PVP.

As elsewhere, the research work was not without incident. In 1945 there was a massive explosion in the high pressure acetylene section (22):

It blew out windows and wrecked equipment in the research building... The blast buckled the ceiling of the basement and the floor of the first floor, knocking over and destroying analytical balances.

The cause was a miscalculation, namely addition of fifty times the required amount of catalyst.

Repe Chemistry in America

As a result of the successful acetylene research at Easton, in May, 1946 GAF announced that work had commenced on a new \$1,250,000 building at Linden that would serve as a semi-works and pilot plant for the manufacture of chemicals from acetylene. Opened in 1949, this was the first and probably only unit of its kind in the United



Hans Beller, at right, and Abraham Zoss, his chief assistant, at GAF Linden examine a sample of PVP. Photograph by Russell C. Aikins. From PVP. Polyvinylpyrrolidone. Preparation, Properties and Applications in the Blood Field and in Other Branches of Medicine, General Aniline & Film Corporation, New York, March 1951.



Linden factory of GAF, July 1947. The new high-pressure acetylene building is at center, closest to the camera. Courtesy of Newark Public Library.

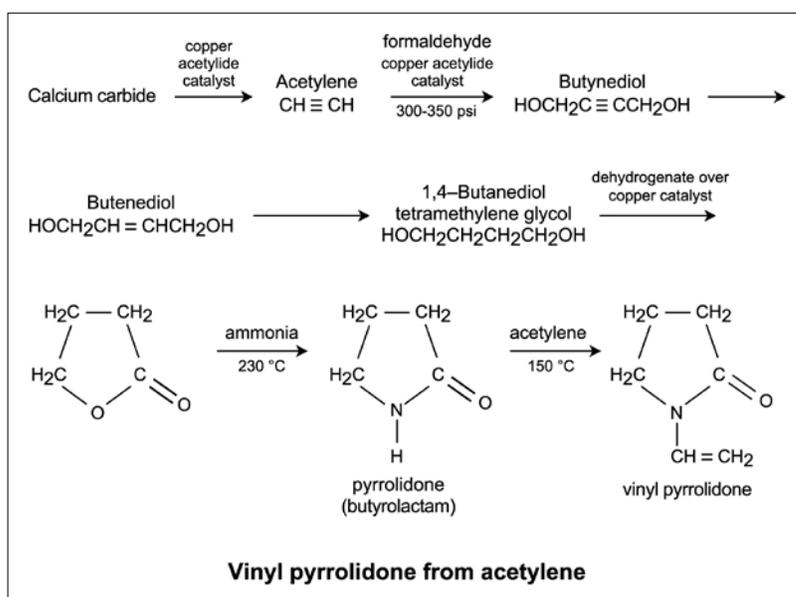
States. The two-story building was located on a vacant area at the southeast corner of the site. Some 640 piles supported the foundations. The building incorporated a reinforced explosion-proof stall for high-pressure acetylene experiments. The acetylene was produced from calcium carbide in a nearby building, since natural gas was then too expensive as a source.

The starting point for many of the new products was the reaction of acetylene under pressure with formaldehyde to form butynediol. This was reduced to butenediol and then to butanediol. During World War II, GAF produced two acetylene products for the military. One was Pollectron, poly(vinyl carbazole), also made in Germany as Luvican. It was useful as insulation for electronics and where high operating temperatures were employed. It was similar to polystyrene but exhibited improved heat resistance; mass polymerization gave almost clear glasslike castings. However, for peacetime use it suffered from high cost, lack of uniformity, poor color and poor mechanical properties. Nevertheless, copolymers of vinyl carbazole and styrene were found to have good molding properties. The other product was Koresin, also first developed in Germany.

This was a condensation product of acetylene and *p*-*t*-butylphenol. It was a very effective tackifier for GR-S synthetic rubber. John W. Copenhaver at Easton, a leading GAF expert in acetylene chemistry, and Maurice H. Bigelow, affiliated with Linden, undertook extensive investigations, including interviews of Reppe, in postwar Germany as members of an Allied commission. Later they wrote what would become the authoritative volume on the technology of acetylene chemistry (23).

The most important early product arising out of the acetylene work at Easton and Linden was PVP, originally discovered by Reppe's group at Ludwigshafen. A white powder, soluble in both alcohol and water, it was the basis of the valuable blood plasma extender.

Marketing of the vinyl derivatives and polymers was taken over by Jesse Werner, a former research chemist at Linden. In 1952, Werner was appointed director of commercial development, a post he held until 1959, when he was appointed vice president of the corporation. A GAF executive working closely with Werner was Juliette M. Moran, notable since she was one of



Flow chart for *N*-vinyl pyrrolidone (*N*-vinyl butyrolactam).

the first women to rise to a position of leadership in the chemical industry.

Moran had joined GAF at the end of 1943, since, as elsewhere, the shortage of male recruits during the war years hastened the admission of women into research and technical laboratories. Trained as an organic chemist, Moran was assigned to the GAF Process Development Department in New York, which in 1945 was transferred to Easton, where she became involved in administration. Subsequently she returned to New York, taking up a post with the marketing division, prior to becoming assistant to Werner. With Werner's support she was appointed, successively, vice-president, senior vice-president, and executive vice-president, followed by posts that led right to the top of the senior management team (24).

Werner, as part of his program for diversification away from dyes, and ably assisted by Moran, pushed the marketing of GAF's version of the blood plasma substitute (25). He also promoted the use of PVP in other medical applications. Though PVP underwent clinical trials in hospitals and was tested by the US military, it did not succeed commercially in medical fields as a blood substitute. One reason was that there was little perceived demand, since during World War II the Allied armies, unlike the Germans, organized the efficient collection of human blood on a vast scale and developed successful processes for handling plasma and other blood products.

However, the research did pay off in other ways. PVP formed transparent films on glass, plastics, and metals and found application in the formulation of cosmetics, particularly hair sprays. During 1949-1951, Herman A. Shelanski, a consultant to GAF, established through clinical trials that PVP combined with iodine was a useful germicide (26). GAF invested \$6 million in an acetylene chemicals plant at Calvert City, Kentucky, that came on stream in 1956. Linden's Hans Beller, who had earlier cooperated with Easton in acetylene research, was project director during the construction phase and the first plant manager. As in Germany, the technology was difficult and there were two serious explosions in the early years. However, GAF was the only producer of acetylene and its products in the United States, at least until the Dow-BASF process was introduced in 1958. The Calvert City plant lost money until 1962, after which the business became highly profitable. In 1965, after much legal wrangling over ownership, GAF was released from US government ownership and returned to the private sector, this time in American hands.

To fill the demand for the many new applications of acetylene products a second manufacturing unit was built at Texas City, Texas, in 1968 (27). There the acetylene was produced from petrochemical fractions. Another polymer based on PVP, known as Polyclar, used in production of beer and wine, was manufactured at Linden until the 1980s, and the copolymer Gafquat, for hair care products, was manufactured until 1991, half a century after Reppe acetylene chemistry was adopted at GAF.

ACKNOWLEDGMENTS

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MAUVE AND ITS ANNIVERSARIES*

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Introduction

In 1856, William Henry Perkin in London prepared the first aniline dye, later known as mauve. The eighteen-year-old inventor sought, but failed, to find a licensee for his process, and then embarked on manufacture, with the backing of his father and a brother. The opening of their factory and the sudden demand for mauve in 1859 foreshadowed the growth of the modern organic chemical industry. The search throughout Europe for novel colorants made scientific reputations and transformed the way in which research was conducted, in both academic and industrial laboratories. Accordingly, the sesquicentennial of mauve provides an opportune moment to review the early years of what became the first science-based industry and examine how its foundation has been celebrated through commemorative events in 1906, 1956, and 2006.

Background of Mauve

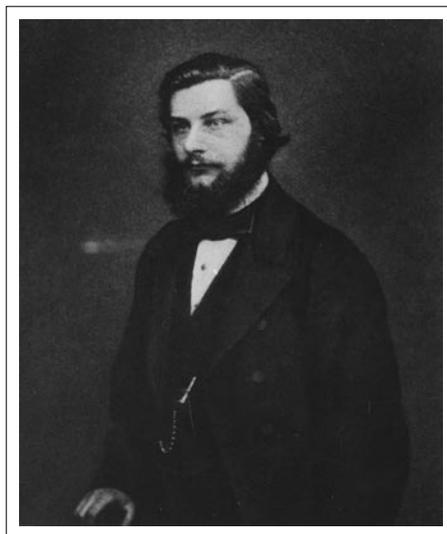
The story of aromatic amines begins at the Giessen laboratory of Justus Liebig, who in the 1830s investigated the

chemical constitution of the natural dye indigo, as well as other natural products. Of particular interest, however,

were the components of, and possible uses for, the vast amount of coal-tar waste available from coal-gas works and distilleries. Around 1837, Liebig's assistant A. Wilhelm Hofmann extracted several nitrogen-containing oils from coal tar and showed that of these bases the one present in greatest abundance was identical with a product earlier obtained from indigo as well as from other sources. It was soon known as aniline.

In 1845 Hofmann moved to London to head the new Royal College of Chemistry (RCC). There he continued his studies into aniline and its reactions. At that time, there were no modern structural formulae to guide chemists, only so-called type formulae. These indicated chemical constitutions and were

used as a system of classification. The related derivatives were drawn by stepwise replacement of hydrogens. Hofmann extended this to organic bases in general, by comparing aniline with ammonia. He suggested that the three hydrogens of ammonia could be replaced to give primary, secondary and tertiary amines, respectively. From this he developed what in 1850 he would call



*William Henry Perkin (1838-1907), in 1860.
Heinrich Caro (1834-1910), technical leader
at BASF, 1868-1889.*

the ammonia type theory. It was now possible to classify organic bases using a formula, that, as with the other type formulae, separated one atom, in this case nitrogen, with a bracket from other atoms and groups of atoms. Thus aniline was an ammonia derivative in which one hydrogen was replaced by what we now call an aryl

group. This was the state of knowledge in 1853 when William Henry Perkin (1838-1907) entered the RCC. Within two years, Perkin was undertaking chemical research and was appointed honorary assistant to Hofmann. In a laboratory set up at his home, Perkin undertook, with fellow student Arthur H. Church, further experimental work.

Mauve: The Discovery

Hofmann introduced to the RCC a new method for reducing nitrobenzene to aniline, based on the use of iron and glacial acetic acid as the source of reducing hydrogen, as described by André Béchamp in 1854. It was put to good use by several of Hofmann's students, including Perkin, whose interest in aromatic amines enabled him to create the first successful synthetic dye from aniline. This arose from interest in a synthetic quinine, much needed to control malaria among the British colonists. Hofmann had reasoned that quinine might be synthesized from coal-tar naphthalene. Perkin decided, instead, to start with the aromatic amino compound allyltoluidine, through oxidative condensation. The reaction, undertaken at home during the 1856 Easter vacation, failed. However, he wisely decided to repeat the experiment using aniline, the simplest aromatic amine. The result of treating it with dichromate was a mixture from which an alcoholic extract colored silk a brilliant purple that could not be removed by washing or exposure to sunlight. Perkin quickly recognised the potential as a dyestuff for fabrics. Samples were sent to the prominent dyer John Pullar & Sons, of Perth, Scotland, from where Robert Pullar, the son of the founder, wrote on June 12, 1856 (1):



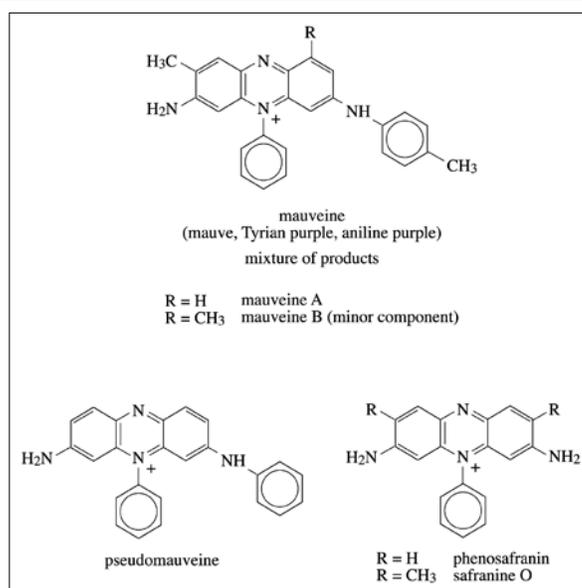
A. Wilhelm Hofmann and students, Royal College of Chemistry, around 1855. William Henry Perkin is in the back row, fifth from right.

If your discovery does not make the goods too expensive it is decidedly one of the most valuable that has come out for a very long time, this colour is one which has been much wanted in all classes of goods and could not be had fast on Silk, and only at great expense on cotton yarns.

By all accounts, purple was the supreme color of fashion in the high street just after the mid-1850s. The newer products, the semi-synthetic murexide and archil-derived French purple, were heralded as sensations in both the fashion world and scientific circles, even though the former colorant was not well suited to city atmospheres, and the latter was monopolized by a firm in France. These disadvantages would contribute to the success of the outstanding purple made from the waste of the coal-gas industry.

From late in 1858, the aniline purple was employed in calico or cotton printing, particularly in France. This was far more important than silk dyeing, but required the development of novel mordants (fixing agents), based on albumen or lactarine, as originally devised by Perkin and Pullar. Unlike the French, the British calico printers showed considerable resistance to the introduction of the aniline dye. Only after Perkin visited their factories and instructed them in the use of his colorant, at first named Tyrian purple, and its applications, was it quite generally adopted. By early 1859, it was gaining in popularity with the printers in Lancashire and Scotland. This enabled the aniline-derived colorant to become the main, if not overwhelming, color of fashion among the ladies of Britain and France. The English gave the aniline purple a new name, mauve. Perkin in 1863 called the major component mauveine. Its correct structure was established only in 1994 (2) (*See box*).

In 1859 an aniline red was discovered, also by treating aniline with an oxidizing agent. The preferred reagent was arsenic acid. The red colorant was known as fuchsine in France and magenta in England; and, following his



Structures for Mauveine A and Mauveine B.

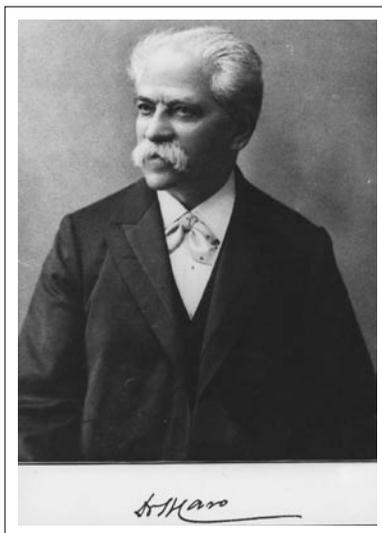
In 1863, Perkin gave his purple colorant a more scientific name, mauveine. He subsequently demonstrated that it consisted of a major and a minor component. Perkin established that the commercial dye was produced from a mixture of starting aromatic amines, and identified the major product as a derivative of *p*-toluidine and aniline. The minor component, according to Perkin, was from *o*-toluidine and aniline. The product from aniline alone he called pseudomauveine. Its structure was established by Otto Fischer and Eduard Hepp (1888, 1892, 1893), and by Rudolf Nietzki (1896). Remarkably, the early published structures for mauveine were not questioned until around 1990, when samples prepared according to Perkin's original recipe, perhaps dating from around 1906, were analyzed and shown to consist of what are now known as mauveine A (major component) and mauveine B (minor component), both derived from aniline, *o*- and *p*-toluidines. Otto Meth-Cohn and Mandy Smith published their structures, methylated homologs of pseudomauveine, based on comparisons with safranin and safranin O, in 1994 (Ref. 2). However, more recent studies by Micaela Sousa, M. J. Melo, A. J. Parola, and J. Seixas de Melo, in Portugal, in collaboration with Peter Morris at the London Science Museum, and Henry Rzepa at Imperial College, have led to the identification of at least one more component. Their investigations should enable further unravelling of the mystery of exactly what was the composition of Perkin's original mauve, and of the blue and red varieties that he and Heinrich Caro independently developed.

academic studies at the RCC, Hofmann gave its free base the scientific name rosaniline. The colorant-forming reaction worked because toluidines were present in the commercial aniline. In 1861, aniline red was converted into aniline blue; and in May 1863, Hofmann, working by analogy, transformed the red into violet dyes soon known as Hofmann's violets. In the meantime an aniline black colorant was isolated from the residue of a mauve reaction developed by the German colorist and chemical inventor Heinrich Caro, who worked in Manchester during 1859-1866.

At first the synthetic dye industry was based mainly in England and France, though the new discoveries were quickly copied in Germany and Switzerland. The outcomes of patent litigation in London and Paris led to the decline of the British and French industries, and, because of the absence of a comprehensive patent system in the German states, assisted the growth of the German dye industry (3). Patent suits and environmental difficulties did, however, encourage new ways of making aniline dyes. Thus from 1866, the hydrogen atoms of the amino group in aniline were replaced in industrial processes by alkylation and phenylation to provide intermediates,

the *N*-alkylated and *N*-phenylated anilines, respectively, that were to become important in dye manufacture. They enabled the circumvention of patent monopolies, since they could be converted directly into violets and blues, respectively. The processes also avoided the use of toxic arsenic acid to prepare aniline red, the original intermediate from which the blues and violets were obtained. Severe environmental problems arising from the use of arsenic acid brought about its replacement by nitrobenzene, which led to the discovery of the black colorant called nigrosine. John Lightfoot developed a process whereby a black was printed on cotton by applying aniline to the rollers of printing machines. Another aniline black was Frederick Crace-Calvert's emeraldine, which though a poor colorant is the basis of modern polyaniline chemistry.

From 1865, the industry that had originated in England and flourished for a time in France moved to Germany. The eventual leader was Badische Anilin & Soda-Fabrik, better known as BASF, founded in 1865 in Mannheim to manufacture aniline red and its derivatives, as well as other coal-tar dyes. Heinrich Caro had returned to Germany from England at the end of 1866 and acted as a consultant to BASF, before joining that firm in the fall of 1868. It had relocated to Ludwigshafen, on the west bank of the River Rhine, and the river served as both a waste sink and a means of transport for raw materials and finished products. Early in 1869, Caro became involved in industrialization of a process for synthetic alizarin, the commercially important colorant obtained from the root of the madder plant. The starting point was coal-tar anthracene, which was converted into anthraquinone, followed by sulfonation, then fusion with alkali under pressure to afford alizarin, as well as various coproducts, some that also became commercial dyes. Perkin independently discovered an almost identical process. Caro and co-inventors Carl Graebe and Carl Liebermann, who made good use of the Kekulé benzene ring theory in their studies on alizarin, filed a patent



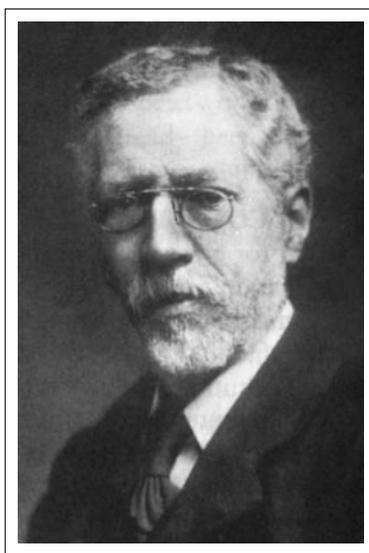
in London in June 1869, as did Perkin (4).

During the mid-1870s, Caro developed azo dyes, such as chrysoidine, and similar products he had worked with in Manchester, such as Bismarck brown and induline. These were based on coal-tar derived amino compounds. German chemists established the constitutions and structures of many of these compounds, including, in 1878, the aniline red. The latter was found to be a derivative of triphenylmethane, and once this was known numerous new products became possible, most of them invariably protected by the new German patent law of 1877. The

N-substituted anilines became important intermediates in the manufacture of both triarylmethane and azo dyes, which also expanded with the industrial availability of naphthylamines. In 1884 azo dyes based on the aromatic intermediate benzidine and its congeners were invented. These were the first synthetic dyes that adhered to fabrics without the need for a mordant. For this reason they were known as direct or substantive dyes.

Caro also introduced the industrial research laboratory as a formal business unit at BASF. Academic consultants, particularly Adolf Baeyer, played important roles as inventors for BASF and other German firms. Early collaboration between Caro and Baeyer led to the elucidation of the structure of alizarin (1874), and their joint interests in indigo enabled Baeyer to draw its structure in 1883. At the end of the 1880s, Caro oversaw the construction of a central research laboratory at Ludwigshafen, dedicated to research and development, and the important protection of BASF patents.

In 1897 BASF and Hoechst in Germany were the first firms to manufacture synthetic indigo. Four years later, René Bohn at BASF applied the indigo reaction conditions to an anthraquinone derivative and discovered the first of the anthraquinone (more correctly anthraquinonoid) vat dyes, also known as indanthrene dyes. The



Raphael Meldola (1849-1915), president of the Chemical Society, and organiser of the 1906 mauve jubilee events in London.

market for these relatively expensive vat dyes, noted for their resistance to fading under strong sunlight, was far greater in the United States than in Europe.

Toward the end of the 19th century, the German dye industry had embarked on diversification based on its coal-tar intermediates. These became important medicinal products, including Bayer's aspirin, which was made from the intermediate salicylic acid. Dyes were also used as models for products that attacked sites of infection within the body. By the turn of the 20th century, the dye industry, under German leadership, was acknowledged to be the leading science-based industry (5).

Anniversaries for Mauve 1906

In 1906 the importance of Perkin's discovery, particularly its far-reaching consequences, was widely acknowledged, with major commemorative events held in London and the United States. The leading figure in the organization of the jubilee events in London, called an international gathering, was Professor Raphael Meldola, president of the Chemical Society. It is interesting to consider for a moment how this came about. Though a great deal of archival material survives, it is not clear when the decision was made. The records of the Chemical Society are not very illuminating. We do know, however, that in February, 1906 various prominent and distinguished persons met in London and agreed that the occasion was worthy of celebration (6). However, well before that date, Meldola was already preparing the ground.

Raphael Meldola, dye chemist, educator, and lobbyist for science, was the grandson of a leader of the Sephardic Jewish community in London and well connected in English society (7). His many acquaintances were the elite of accomplished Englishmen and dominated the sciences

and arts. They included Charles Darwin, the writer Israel Zangwill, the artist Solomon J. Solomon, and William Henry Perkin. He was also on friendly terms with leading chemists elsewhere in Europe, particularly Heinrich Caro, who had retired from BASF at the end of 1889 (8). What is relevant here, at least from the perspective of celebration, is that Meldola was an active member of the Maccabaeans, a British Jewish society of professional men founded in 1891 to engage in philan-

thropic and cultural activities. Meldola was the only prominent professional scientist.

On December 16, 1905, at Meldola's instigation, the Maccabaeans hosted in London a remarkable event, a "Science Dinner" to which several leading non-Jewish scientists were invited. The almost two hundred guests included the chemists William Henry Perkin, Sir Henry Roscoe, Sir William Ramsay, Sir William Crookes, Professor Henry Edward Armstrong, and representatives of other areas of science, as well as the Chief Rabbi, and the Archdeacon of London, Canon Samuel Augustus Barnett (9). Toasts were drunk to "Science Institutions" and "Pure Science," and, among the various responses, Roscoe advised the audience that "Scientific men of the Jewish race had recently distinguished themselves in the world of Chemical Science (10)." He was, no doubt, referring to an illustrious cohort of German industrial and academic inventors that included Heinrich Caro, Adolf von Baeyer, and Carl Liebermann, all of whom had contributed to the emergence of the German dye in-



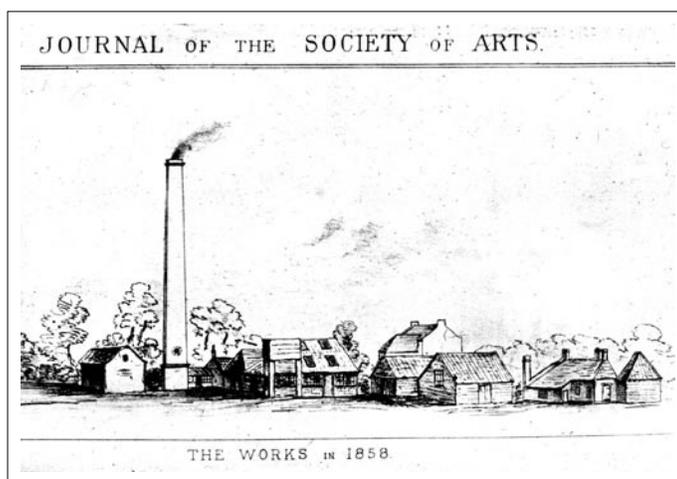
The banquet held on July 26, 1906 at the Hotel Métropole, London, in connection with the jubilee celebrations for the discovery of mauve by William Henry Perkin. Standing at the top table are Perkin (with beard) and next to him Raphael Meldola.

M56 Announcement for the Perkin Centenary Celebration, held in London during May 1956. Reginal Schoental Archive, Edelstein Center.

dustry. A few months earlier, Baeyer had received the Nobel Prize for his achievements in coal-tar color chemistry.

Meldola's gathering, a grand celebration of science, included representatives of the press, which meant extensive media coverage. Its success enabled Meldola over the following weeks to garner strong support for the coal-tar dye jubilee celebrations, aided by the fact that he possessed the gift of persuading those involved in pure and industrial science and affairs of commerce that it would be a memorable occasion. In this endeavor, he was soon corresponding with colleagues abroad, particularly Heinrich Caro, who was placed in charge of the German contingent. It was Caro who in a new year's card reminded Perkin that 1906 was the jubilee year for mauve. Within a few weeks Perkin was advised that proposals for the jubilee celebrations had been adopted.

On July 26, 1906, the English and foreign guests participated in the formal mauve proceedings, held in the theater at the Royal Institution, in London, and chaired by Meldola, who, along with many other gentlemen, wore a mauve necktie. Several wives of participants were dressed in mauve. Meldola, with due ceremony, unveiled a portrait by Arthur Stockdale Cope of the newly knighted Sir William Henry Perkin. Then greetings were read out from representatives of science and industry: Caro, on behalf of the German chemical industry association, presented a short address of congratulation to Perkin; Lord Kelvin, on behalf of the Royal Society, and others, also offered recitals of congratulation. Leo Baekeland, inventor of the new polymer bakelite, spoke for the United States. Meldola read out cablegram greetings received from all over the world, including from the American Perkin Committee, represented by Charles Frederick Chandler of Columbia University; Hugo Schweitzer, of the Continental Color and Chemical Co., agent for German dyes; Adolf von Baeyer, in Munich; Otto N. Witt, in Milan; Carl A. von Martius, who had worked with Hofmann in London and Caro in Manchester, and co-founded in 1867 the forerunner of AGFA; and Rufus Pullar, of the dyer in Perth that had first encouraged Perkin in 1856 (11). Sci-



The factory of Perkin & Sons, at Greenford Green, northwest of London, in 1858. From a sketch by William Henry Perkin.

gentlemen, including representatives of the press, attended a banquet held at the Hotel Métropole. Caro, the acknowledged most inventive genius in the realm of industrial organic chemistry, was among the guests of honour, sitting at the top table, close to Perkin and Meldola. Meldola, the master of ceremonies, proposed a toast to The Coal-Tar Colour Industry. (When Perkin lifted his glass it is not recorded what he drank, since he abstained from alcohol.) Roscoe saluted the foreign guests, particularly Caro (13).

The following day, the former Perkin works at Greenford Green, northwest of London, was visited by around 150 participants. Its total dereliction must have driven one point home more vividly than many of the speeches: in the first decade of the 20th century the chemical might of Germany was invincible. Maybe the visit appealed to Meldola through another of his great interests, namely, ancient monuments.

For Meldola and other English chemists, no doubt, Perkin fulfilled a deeply felt need to have at least one outstanding British hero from the glorious era of that new frontier, research-based industrial chemistry. This was particularly relevant in 1906, when the successor to Perkin's company, once Meldola's employer, collapsed. The British dye industry, it seemed, was in disarray, relying mainly on the struggling Holliday firm in Huddersfield, Levinstein, founded by the German immigrant Ivan Levinstein in the 1860s, and Clayton Aniline, established by Alsatian chemist Charles Dreyfus in the 1870s, both in Manchester. The mauve jubilee at least had some morale-boosting publicity value, even if it did not beget any profound improvement. It was an occasion for retrospect, with newspaper and journal reports often

entific addresses were given by August Bernthsen, of BASF, and Carl Liebermann, of the Technische Hochschule, Berlin. The praises and addresses of congratulation to Sir William Henry Perkin included presentation to him by Emil Fischer of the Hofmann Medal (12).

In the evening a "large and distinguished company" of around two hundred

dominated by opinions on why the British dye industry had declined.

In October 1906 William Perkin, having “braved the perils of a long ocean voyage,” was hosted by American chemists and industrialists, first by 400 at Delmonico’s restaurant, in New York, “a banquet of unusual proportions and completeness of detail,” that included “Saddle of Lamb Aromatic” and “Brussels sprouts with Chestnuts.” Prominent among the organizers of the event were, in addition to Schweitzer, US agents for German dye firms (14). A medal was founded “bearing Perkin’s name to be annually awarded to an American chemist (15).” William Perkin received the first gold impression. Then he went to Boston, where as Louis A. Olney later remembered, “we planned to outdo New York in our entertainment and celebration (16).” From Boston, Perkin, traveling with his wife and daughters, took a train to Washington, where they received an audience with President Roosevelt. America’s adulation could hardly be checked. The nation was clearly captivated with William Perkin, this modest individual—family man, teetotaler, and churchgoer—recalled from tranquil retirement to receive: a knighthood, that he declined at first; several medals, honorary doctorates, and accolades; and a silver tea service, engraved with the incorrect chemical structure for mauve. He was also compared with the likes of Thomas A. Edison. The white-bearded, aging scientist was now a larger than life international celebrity, commanding public respect and admiration (17). Newspapermen reported on his achievement with a mixture of sensation and fantasy, blended with some truth and a little alchemy. Mauve was a headline story, an epic to inspire and excite, the benefits of which were summed up by the *Detroit Sunday Times* (18):

Rainbows and Riches from Refuse: The Story of Coal Tar. How Chemical Wizards have drawn from a discarded product the most beautiful coloring, valuable drugs and given employment to Armies of Men.

Science and Industry in the United States

Unlike the British, the Americans were not celebrating a past glory, but the triumph of applied chemical science.

However, dyes were not part of the equation, since aggressive marketing and control of patents enabled Germany, and to a lesser extent Switzerland, to dominate the supply in colorants. More significant in 1906 America was the application of science in other areas of industry, particularly the electrical technologies, including electrochemistry and steel manufacture. There the Americans had made massive headways and were not only a threat to Britain, but also to Germany. Tellingly, American electrochemists scheduled their October 1906 meeting in New York so as to enable participants to join in the festivities at Delmonico’s.

The US entry into large-scale industrial aromatic chemistry took place almost a decade later as a result of the outbreak of war in Europe in 1914. Then, the United States, as a major consumer of dyes for its vast textile industry, was faced with severe shortages, since Germany requisitioned dyes for military uniforms, and the British blockaded transatlantic shipping. This forced the Americans to establish intermediate- and dye-making firms, such as Calco Chemical Company, at Bound Brook, New Jersey, founded in 1915 (19).

In May 1917 four chemical firms created the National Aniline & Chemical Company, later part of Allied Chemical & Dye Co. In the same year Du Pont at Deepwater Point, New Jersey, began production of indigo. Meantime, Hugo Schweitzer, co-organiser of the jubilee events in New York, disappeared from the scene after sending the German ambassador, Count von Bernstoff, a secret report on US tariffs introduced in 1916 and other matters related to the supply of dyes. Later he was variously described as the “head of every American German activity in this country and was the best chemist in the whole business,” by Joseph H. Choate, Jr., of the office of the Alien Property Custodian, and “chief secret-service agent of the German government, chief cook and bottle washer of the German government in this country” by American Chemical Society past president Charles Holmes Herty. Choate even cited Schweitzer’s secret service number, 963192637, though when asked about its significance wondered “whether it was a number of an automobile (20).”



Advertisement for Calco Chemical Company, Bound Brook, New Jersey, 1925

One of the most important outcomes of the American response was the organization of sophisticated, well equipped and well staffed research facilities dedicated to dye research. From the late 1920s the industrial research laboratories enabled diversification into synthetic resins and polymers, and in the 1930s into sulfonamide and other drugs. The development of synthetic fibers and massive expansion in printing on paper after the 1920s led to the modification of existing synthetic dyes to suit new needs and applications. During the 20th century the most important dyes classes were azo and vat dyes. Only one new structurally novel class of dye appeared, the phthalocyanine class, introduced by Britain's ICI in the 1930s.

1956

The Perkin centenary festivities in England took place during May 1956, with Sir Robert Robinson acting as chair of the Perkin Centenary Celebrations Committee (21). The Science Museum in London, in collaboration with ICI's Dyestuffs Division, arranged a special Perkin Centenary Exhibition in the Industrial Chemistry Gallery that included among the several dioramas a superb model of Perkin's factory (since lost in a flood). The exhibition, which ran from May 8 until July 17, was opened by Reginald P. Linstead, rector of Imperial College, who had established the structures of phthalocyanine dyes. ICI chose the centenary to announce the introduction of the first fiber-reactive (Procion) dyes that bond directly with the fabric. W. H. Cliffe, of ICI, and Laurence E. Morris, editor of *The Dyer*, produced the most detailed accounts yet of the history of Perkin & Sons. From the perspective of recording and publicizing chemical history, it is interesting that Morris expressed regret that "so little is being done to erect plaques on some of the buildings connected with Perkin." This included the site of his home in Sudbury, near Wembley, not far from Greenford Green. However, he noted, "Certain private citizens...acting through the Wembley Historical Society, have, however, decided that a plaque should be inserted

in the wall (or set in a cairn in the grounds) of Sudbury Methodist Church, which stands on the site of the New Hall, which Perkin built as a centre for some of his non-denominational religious activities (22)." Prominent among those engaged in the endeavor to establish a suitable plaque was keen historian of chemistry and of the locality, Harold Egan, the Government Chemist during 1970-1981 (23). It was through Dr. Egan that in the late 1950s this author was introduced to the history of Perkin's enterprise.

As was the case in 1906, the 1956 celebrations for mauve included high on the agenda the union of pure and applied science, though in 1956, in London at least, this was hardly directed toward novel dye discovery. Significantly, the 1956 festivities for mauve in New York surpassed those in England. The reason: by World War II, the United States had embarked on production of aromatics from petroleum, and after 1945, with the German chemical industry facing great difficulties, emerged as the world leader in dye manufacture, a position it would hold for over two decades.

During the week commencing September 10, 1956, several hundred leading scientists, industrialists, and other invited guests gathered at New York's Waldorf-Astoria Hotel to attend what was called the "Perkin Centennial 1856-1956," an event sponsored by the American Association of Textile Chemists and Colorists and memorialized in a substantial commemorative volume (24). The main historical papers were given by Sir Robert Robinson, Hans Z. Lecher, former research leader at American Cyanamid's Calco Division, and Sidney Edelstein, who two weeks earlier had published in the association's journal an account of the life of Sir William Henry Perkin (25). We may surmise that the celebrations and the prominence given to historical accounts of the rise of the dye and organic chemical industry, particularly at the US meeting, played a not insignificant role in Sidney Edelstein's decision to inaugurate also in 1956 the Dexter

**THE PERKIN
CENTENARY CELEBRATION**

7th to 10th May 1956

Patron H.R.H THE DUKE OF EDINBURGH K.G. K.T.
President SIR CYRIL HINSHELWOOD D.Sc. F.R.S.
(President of The Royal Society)
Chairman SIR ROBERT ROBINSON O.M. M.A. D.Sc. LL.D. F.R.S.

Sponsoring Bodies: The Royal Society - The Chemical Society - The Society of Chemical Industry
The Society of Dyers and Colourists - The Royal Institute of Chemistry
The Association of British Chemical Manufacturers

Perkin Centenary General Secretary: JOSEPH W. NICHOLLS F.C.I.S.
The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Reading 1, Yorkshire
Telephone 25138-9

In 1856 William Henry Perkin discovered Mauve. This historic event marked the birth of the synthetic dyestuffs industry and the greater part of the organic chemical industry of the world. From these small beginnings have sprung dyes and pharmaceuticals, textile and rubber chemicals, plastics and synthetic fibres, for Perkin's discovery turned organic chemistry from an academic study into a matter of world-wide industrial importance

The Centenary will be celebrated by Lectures and Social Functions in London on

<p>Monday 7th May <i>Evening</i> Principal overseas guests will be entertained by representatives of the Councils of the sponsoring bodies at 'Tallow Chandlers' Hall in the City of London, prior to the opening of the Conference</p> <p>Tuesday 8th May <i>Afternoon</i> Opening paper on <i>The Life and Work of Perkin</i> will be read by Prof. John Read M.A. F.R.S. <i>Evening</i> A Reception for all those attending the Conference, and guests, at Guildhall in the City of London by kind permission of The Rt. Hon. The Lord Mayor of London</p>	<p>Wednesday 9th May <i>Morning</i> A paper on <i>The Development of the Dyestuffs Industry</i> will be read by Clifford Paine Esq. B.Sc. <i>Afternoon</i> A paper on <i>The Theoretical Aspects of Dyeing</i> will be read by J. G. Evans Esq. M.Sc. Tech. <i>Evening</i> A Banquet will be held at The Drednower, Park Lane, London</p> <p>Thursday 10th May <i>Morning</i> A paper on <i>The Development of Organic Chemistry since Perkin's Discovery</i> will be read by Sir Alexander R. Todd M.A. D.Phil. D.Sc. LL.D. F.R.S. <i>Evening</i> A Perkin Dinner and Ball will be given by the London Section of the Society of Dyers and Colourists at The Waldorf Hotel, Aldwych, London (Tickets 4/5 each)</p>
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All the papers will be read in the theatre of The Royal Institution, Albemarle Street, London

The charges for those attending the Conference and other functions are:
Conference Registration Fee and Guildhall Reception £3 3 0, Banquet £3 3 0
There is available an inclusive charge of £5 10 0 for Registration, Reception and Banquet but the charge for an accompanying guest for the Banquet is £3 3 0 and for the Guildhall Reception £1 1 0
Applications indicating desired ticket requirements for Banquet, Reception and Lectures should be sent AT ONCE to the General Secretary of the Centenary and please state whether you will be accompanied by a lady when attending the Banquet and Reception

*Announcement for the Perkin Centenary
Celebration held in London during May 1956.
Regina Schoental Archive, Edelstein Collection.*

Award (Dexter Chemical Corporation Award in the History of Chemistry), now the Edelstein Award.

2006

William Perkin's pathbreaking discovery of mauve was remembered in 2006 through a series of gatherings organized by the Society of Chemical Industry (including a lecture at London's University College on March 23, believed to be the day and month in which Perkin made his discovery), the Royal Society of Chemistry, the Society of Dyers and Colourists, and the American Association of Textile Chemists and Colorists. Despite the various events, including Innovation Day at Chemical Heritage Foundation in September, when the SCI's Perkin Medal was awarded exactly a century after its inauguration, none of the festivities could compare to 1906, or to 1956, for that matter. In October, the RSC organized a special ceremony, appropriately at a community hall in Sudbury almost next to the site of Perkin's New Hall, before which the 1956 plaque had been set in the cairn. The National Portrait Gallery, in connection with its own sesquicentennial, placed on display the 1906 portrait of Perkin along with those of other prominent 19th-century British scientists and engineers. A few historical studies were stimulated by the 150th anniversary for mauve. Thus Peter Morris was encouraged to undertake an investigation into the provenance of various surviving samples of mauve and dyed fabrics, some stated to date from the time of Perkin's first experiments or the opening of his factory. Since only a piece dyed fabric (probably from 1856) and a scarf (around 1862) could be reasonably accurately dated, this called into question the labeling of museum artifacts, in this case samples of the colorant, suggesting that the Science Museum's "hitherto iconic specimen...[might need to be] relegated to the second division of chemical relics (26)."

Until the 1980s the anniversaries for both mauve and Perkin's birth had attracted great attention, as well as extensive participation from the chemical industries. Thus in 1988, on the occasion of the 150th anniversary of Perkin's birth, ICI sponsored widely publicized educational and commemorative programs under the title "Born to the Purple" (27). That this was not the case in 2006 is largely due to the fact that the dye industry founded by Perkin, the world's first high-tech science-based industry, has so little presence in Europe and North America. Environmental problems arising from the manufacture of colorants and the shift of the textile industry to Asia have caused the great dye firms to reinvent themselves as agrochemical and pharmaceutical corporations, casting

off long heritages that sometimes go back to the 1860s. Today the centers of production are India, China, Japan, and eastern Europe, while the main use for aniline is in the manufacture of polyurethane. Maybe that is why the SDC's Lahore Region annual conference "The Era of Colour 1856-2006" no doubt attracted at least as much attention as the events in Europe and North America.

ACKNOWLEDGMENT

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Future ACS Meetings

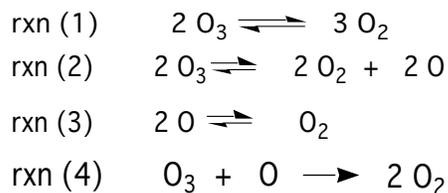
August 19-23, **2007**—Boston, MA
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 March 22-26, **2009**—Salt Lake City, UT
 August 16-21, **2009**—Washington, DC
 March 21-26, **2010**—San Francisco, CA
 August 22-27, **2010**—Boston, MA
 March 27-31, **2011**—Anaheim, CA
 August 28-September 1, **2011**—Chicago, IL
 March 25-29, **2012**—San Diego, CA
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THE HISTORY OF OZONE. V. FORMATION OF OZONE FROM OXYGEN AT HIGH TEMPERATURES (1)

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Introduction

In his 1884 book on the principles of mobile equilibria, van't Hoff (2) presented the generalization that, in an equilibrium system, an elevation of temperature would favor the endothermic reaction. Twenty years later, Nernst, as part of his efforts in developing the third law of thermodynamics (3), derived an expression for calculating the equilibrium constant for a reaction at any temperature. These ideas were expressed specifically in relation to ozone in a 1903 lecture by Nernst at the University of Göttingen as reported by Kremann (4). In agreement with van't Hoff, the formation of ozone was favored by increasing temperature. Nernst considered the equilibrium between two molecules of ozone and three of oxygen (rxn 1) to be composed of equilibria between ozone and oxygen plus atomic oxygen (rxn 2) and between oxygen and 2 atoms of oxygen (rxn 3); rxn 4 was not considered:



This report describes the proof that such an equilibrium exists at high temperature and the 35-year struggle

to establish the chemistry and the quantitative relationships involved.

Early Studies

Although Andrews and Tait (5) had reported in 1856 that ozone decomposed "instantaneously" at temperatures above 230° C, the formation of ozone from air or oxygen at higher temperatures was recorded nearly 50 years before Nernst's lecture. In fact, in the same year as Andrews and Tait's publication, Van der Willigen reported (6) that the gas above a platinum wire heated to redness by an electric current possessed a strong odor of ozone. Four years later Le Roux (7) confirmed this result by examining the gases exiting from a chimney containing an electrically heated platinum wire and added the observation that a positive starch-iodide test was obtained. Additional reports which appeared before Nernst's ideas include work by Saint-Edme (8), Böttger (9), Troost and Hautefuille (10), Helmholtz (11), Dewar (12), Elster and Geitel (13), and Brunck (14). Böttger was the first (see below) to employ an explosion for the high temperature conditions required to form ozone. Explosion of an oxygen-hydrogen mixture afforded a gas mixture which gave a positive starch-iodide (perhaps due to the presence of hydrogen peroxide, see below). Bichat and Guntz (15) were sufficiently enthusiastic about thermal formation of ozone to suggest that its formation in the silent discharge was not an electrical phenomenon at all; the function of electricity was simply to heat the apparatus. Ewell

reviewed the subject in 1909 and wrote (16):

The methods so far used are relatively inefficient but great improvements are expected in the near future.

We are still waiting.

While almost all of these experiments provided ambiguous identification of ozone (odor and starch-iodide paper, which could indicate nitric oxide or hydrogen peroxide as well as ozone), the work of Troost and Hautefeuille (10) is worthy of note. They seem to have been the first workers to realize the generality of the apparent paradox of formation of substances at temperatures much above their normal decomposition points. The distinction between thermodynamic and kinetic control of reactions had not arrived in chemistry at that time. Such thermal phenomena were observed in a number of inorganic systems. For example (rxn 5), silicon sesquichloride decomposed to silicon dichloride and elemental silicon on heating at temperatures well below 1000° C but regenerated the sesquichloride upon heating to about 1200° C and rapid cooling of the melt.



Troost and Hautefeuille also studied thermal formation of ozone from oxygen using the so-called hot-cold principle of Deville (17). The apparatus consisted of a ceramic outer tube which could be heated to high temperature by a flame and a water-cooled inner tube. Passage of oxygen through the annular space of a silver inner tube resulted in the formation of silver peroxide when the outer tube was heated to approximately 1200° C. When the silver tube was replaced by tubes of unreactive material in other experiments, examination of the apparatus after the heating was interrupted showed a strong odor of ozone, a positive starch-iodide test, and decolorization of indigo by the condensate on the outer wall of the inner tube. When water-cooling of the inner tube was omitted, no ozone was evident.

Acting on a suggestion by Warburg, Wartenberg (18) in 1910 reported the results of a study of the absorption spectrum of ozone in the region around 2537 Å at various temperatures up to 2000 K. He argued that ozone at high temperature was too unstable to survive cooling and that only by examining the hot gas directly would it be possible to obtain information on the presence of ozone. This in spite of the fact that, in 1906, Fischer and Marx (19) had measured ozone partial pressures greater than 1×10^{-4} atm in cooled samples of oxygen after passage over a Nernst glower at 2000 K. Such a concentration would most probably have been detected

in Wartenberg's experiments. These were performed using an oxygen-filled cell with a 10-cm light path in a heated oven; the spectrometer included a mercury vapor lamp as light source and a photocell to detect radiation between 2200 and 2500 Å. He obtained no evidence for the presence of ozone. The implications of this work were completely ignored by other workers, possibly because spectroscopy was not sufficiently established in the minds of most chemists at that time. Wartenberg himself drew no conclusions. The result lay dormant in the literature until 1932 when Harteck (see below) went back to such experiments using equipment of greater sensitivity than Wartenberg.

Formation of Ozone in Flames

Another source of ozone at high temperature was the flame; this might well involve both temperature and participation of reactive intermediates present in flames. The first report was published in 1867 by Pincus in an obscure source (20) and then reported briefly in *Annalen der Physik* in 1871 (21). He found that a flame of purified hydrogen and oxygen gave a condensate with a very strong smell of ozone. Neither Loew (22) nor Than (23) was aware of this work when both published their reports of ozone in flames in 1870. Loew's experiment was very simple; he blew a strong stream of air over a Bunsen flame into a beaker. Examination of its contents revealed the characteristic ozone odor, and the product liberated iodine from potassium iodide and gave a positive test for ozone with guaiacum paper. Than, using a similar procedure, reported that only flames of hydrogen-containing substances produced ozone while burning carbon did not. His intriguing explanation was that an oxygen atom was required for reaction with an oxygen molecule to give ozone; such atoms were not formed with carbon since its reaction with oxygen consumed an entire oxygen molecule. Than's procedure was adopted by Hofmann and Kronenberg (24) for a lecture demonstration.

Other reports during the 19th century of ozone in flames were due to Blochmann (25), Radulocoitsch (26), Cundall (27), Manchot (28), Loew (29), and Bose (30). Hofmann (24) described a lecture demonstration using the Than conditions.

The formation of ozone in flames seemed to some workers to offer a practical procedure for its preparation. What could be simpler than to blow air over a flame for instantaneous production of ozonized air? Patents were awarded in the 1870s to Loew (31), Rumine (32), Turner and Vanderpool (33), and Swan (34), among

others. Loew's patent described an apparatus in which a number of air inlets blew streams of air over a bank of Bunsen burners. In fact, the substances prepared in most, if not all, of these procedures were undoubtedly oxides of nitrogen and hydrogen peroxide.

C. F. Schönbein had a highly developed sense of smell which played a key role in his discovery of ozone (35). However, the literature provides many examples of erroneous identification of ozone based on odor by others who lacked Schönbein's olfactory talent. Furthermore, the starch-iodide test is not specific for ozone; it will give positive results with oxides of nitrogen and with hydrogen peroxide. Since odor and the starch-iodide test were often the only means for identifying the ozone produced in most of the work described above, it is not surprising that considerable criticism was directed toward the identification of ozone in thermal and flame reactions. Critics included Leeds (36), Ilosvay (37), and St Edme (8). In fact, Clement (38) claimed in 1904 that all of the early reports of ozone formation were due to the formation of low concentrations of nitric oxide. Engler (39), in his 1879-80 series of review articles on ozone chemistry, commented that it was unfortunate that the evidence for ozone formation was ambiguous but that the considerable number of reports lent some weight to the claims made. He also commented prophetically that there was a real possibility that oxygen atoms could be formed at high temperature and could then combine with O_2 molecules to form ozone which, of course, would be very short-lived under the conditions of reaction. Short-lived is the key word here.

By the beginning of the 20th century improvements in techniques and the possibility for testing Nernst's theoretical contribution led to intensive investigations of thermal equilibria of gases (oxygen, hydrogen and oxygen, nitrogen and oxygen, etc.). Nernst (with Jellinek) (40) succeeded in achieving good correspondence between experiment and theory in a study of the temperature dependence of the equilibrium constant in the system N_2 , O_2 , $2 NO$. This reaction was of considerable interest from the practical point of view as an approach to fixation of atmospheric nitrogen and was also investigated by Haber (41) and others.

Using the same procedures which were successful in the nitrogen-oxygen system, Clement (38), a doctoral student in Nernst's laboratory, made a valiant effort to study the oxygen-ozone equilibrium by blowing a very rapid (flow rates up to 1 m/s) stream of air over a Nernst glower (2200 K), an arc lamp (3000 K), or an electri-

cally heated platinum wire but obtained no evidence for ozone formation. As noted above, he concluded that all of the earlier experiments claiming ozone formation were incorrect. He abandoned thermal formation of ozone and went on to study its thermal decomposition for his doctoral thesis. His results indicated "that, at 1000 K, the concentration of ozone would be reduced by a factor of 1000 in 0.7 milliseconds," and the conclusion was that the decomposition of ozone at elevated temperature was too rapid to allow for its detection.

Proof of Ozone Formation at High Temperature

A concerted attack on the problem came from the laboratory of F. Fischer, with five publications on the subject appearing in 1906-7. A particular advantage was the emergence in 1902 of a simple analytical method for distinguishing qualitatively between ozone, nitric oxide, and hydrogen peroxide. This employed the "tetrabase paper" developed by Arnold and Mentzel and by Chlopik (42), which is prepared by absorbing an alcohol solution of p,p'-bis-dimethylaminodiphenylmethane on filter paper and drying. Exposed to gas vapors, this reagent gives a blue-violet coloration with ozone, a yellow color with nitric oxide, and remains colorless with hydrogen peroxide. While not as sensitive as starch-iodide paper, it provides a distinctive identification of gases present. Another, less sensitive procedure for identifying ozone in the presence of nitrogen oxides and hydrogen peroxide was reported by Manchot (28). Ozone vapors impinging on a silver surface maintained at 250° C led to formation of a black deposit of silver peroxide, whereas no effect was observed with nitric oxide or hydrogen peroxide at this temperature. Wartenberg (43) pointed out that the rapid decomposition of ozone molecules to molecular oxygen and oxygen atoms at this temperature meant that the active reagent was probably atomic oxygen.

In the first paper, by Fischer and Braehmer (44), the authors addressed the question of whether or not ozone is actually formed from oxygen in thermal reactions and in flames. They found (to this author's surprise), that devices such as an electrically heated platinum wire (protected from oxygen by a coating of zirconium and yttrium oxides) or a Nernst glower or various flames and arc lamps (possible photochemical as well as thermal reaction), if ignited and allowed to stabilize under ambient conditions, could then be immersed in liquid air or liquid oxygen without extinguishing their operation. One imagines that the procedure would be an exciting

one. Thus both extremely high and low temperatures could exist in very close proximity. Ozone (and oxides of nitrogen), if formed, would be cooled to very low temperature extremely rapidly. After most of the liquid had evaporated, any nitric oxide formed was filtered, the blue filtrate examined with tetrabase paper, and analyzed iodimetrically. Flames investigated included hydrogen, carbon monoxide, acetylene, hydrogen sulfide, sulfur, charcoal, and wood. In all cases, ozone was formed as well as traces of nitric oxide when liquid air was used; hydrogen peroxide was not observed unless the atmosphere was enriched in water vapor. Definite evidence for the presence of ozone was obtained with a Nernst glower operating at about 2000 K. A maximum ozone concentration of about 1 wt.% was obtained in the first work. One year later, Fischer and Marx (45) reported an improved version of the apparatus with which they obtained blue drops of ozone and a final concentration as high as 4%, much greater than predicted by theory. They suggested that a fractionation process was operative, perhaps due to the 71° difference in boiling point between ozone (bp -112° C) and oxygen (bp -183° C). Thus the formation of ozone at high temperature was definitely established.

Equilibration Studies

After the demonstration that ozone was indeed formed from oxygen at high temperatures, further work—until

the subject became dormant with the outbreak of World War II—was concentrated on efforts to establish equilibrium conditions and show that the Nernst relationship applied. Both Riesenfeld and Wartenberg (46) used the following expression (eqn 1) derived from Nernst's general treatment where 68,000 is twice the heat of dissociation of ozone (cf rxn 1) to calculate the equilibrium concentration of ozone, usually expressed as partial pressure of ozone (p_{O_3}) at one atmosphere total pressure.

$$K_p = 3 \log p_{O_2} - 2 \log p_{O_3} = 68,000/4.57 \cdot T + 1.75 \cdot \log T + 8 \times 10^{-5} \cdot T + 2.6 \quad \text{eqn 1}$$

E. H. Riesenfeld and Beja (47, 48) realized that the dissociation of oxygen into atomic oxygen (rxn 2) would be significant at high temperatures. The bond dissociation energy of oxygen was not known at the time (1920-23); unfortunately Riesenfeld and Beja assumed a value of 80 kcal/mol, significantly lower than the correct value (117.3 kcal/mol), to derive the partial pressure of atomic oxygen in equilibrium with oxygen at various temperatures. They then calculated the partial pressures of the three component mixture of atomic oxygen, oxygen, and ozone. The results are shown in the figure, where it can be seen that p_{O_3} reaches a maximum value of about 1.3×10^{-7} atm. at 3500 K and that atomic oxygen becomes the major component of the mixture at temperatures above about 4000 K. Eight years later Briner and Susz (49) recalculated using a value of 130 kcal/mol for the bond

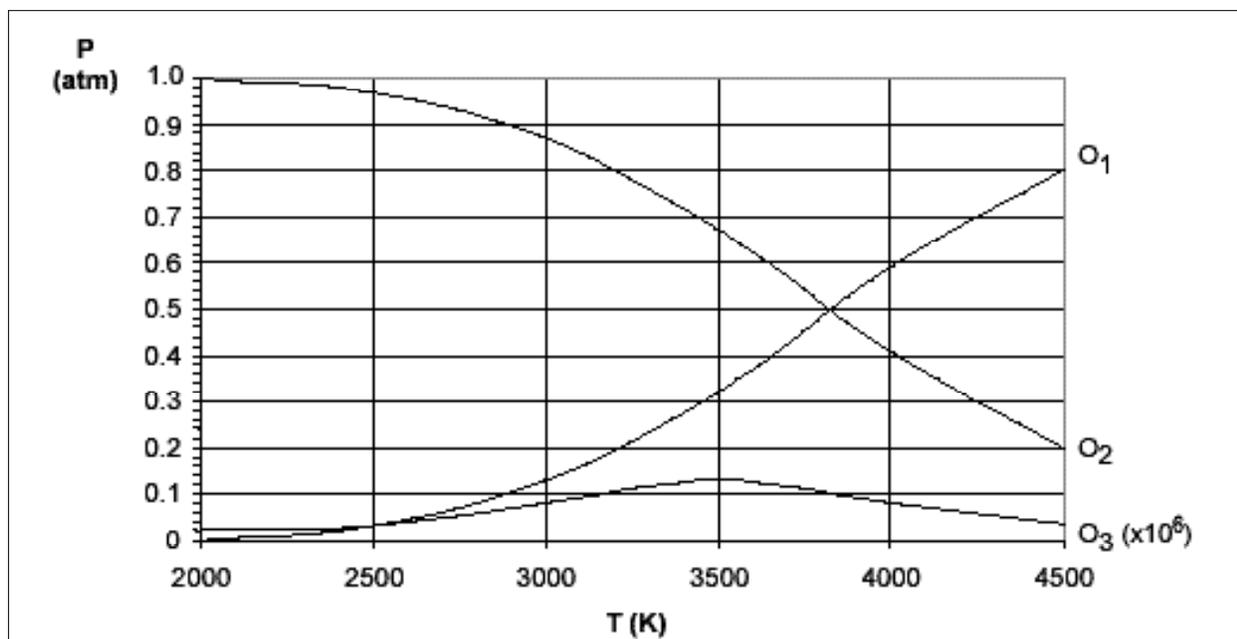


Figure. Calculated equilibrium partial pressures (total one atm) of atomic oxygen (O_1), oxygen (O_2), and ozone (O_3 , p_{O_3} shown is multiplied by 10^6) vs temperature (K) adapted from Riesenfeld and Beja (Ref. 47, 48).

dissociation energy of oxygen, again incorrect but this time on the high side. Finally, in 1935 (50), they used the correct value of 117.3 kcal/mol, whereupon their results paralleled closely those of Riesenfeld and Beja. The maximum partial pressure of ozone was calculated to be 2.2×10^{-7} atm at 3500 K, while partial pressures of atomic oxygen and oxygen were 0.24 and 0.76 atm., respectively, at this temperature.

A number of serious experimental difficulties were involved in the attempts to study such equilibria. These included: a) analysis for the low concentrations of ozone formed, which were sometimes at the limits of quantitative methods available at the time (cf for example 47, 48); b) the need for very pure, dry gases in order to ensure that hydrogen peroxide or oxides of nitrogen were not formed; c) technical problems involved in design and construction of suitable apparatus for an extremely short transition time between a very hot region and ambient or cooler temperature; and d) maintaining constant temperature and measuring temperature in the reactive region of the apparatus. The following methods used in these studies are discussed briefly and the results presented in Table 1; the last column, calculated partial pressure of atomic oxygen (pO), will be discussed later:

1. Blowing a very rapid stream of oxygen or air over a Nernst glower.

a. Analysis of ozone concentration as a function of time (19) (entry 1a). b. Analysis of ozone concentration as a function of temperature (51) (entry 1b). As noted earlier, this procedure had been used successfully by Nernst (with Jellinek) (40) to study the thermal equilibrium between nitrogen, oxygen, and nitric oxide. Calculated values for the yield of nitric oxide correlated well with experimental results over the temperature range 1800-3200 K. As noted earlier, Clement (38) concluded that the decomposition of ozone was too rapid for it to survive. Fischer and Marx (19) increased the gas flow rate to as high as 90 m/s and detected ozone in the product gas. The products of thermal reaction of air depend on the interplay of reaction rate constants. Ozone is formed and decomposed rapidly at high temperature, while nitric oxide is formed slowly and decomposes at a rate many orders lower in magnitude than ozone. Thus high flow rates favor ozone formation and survival, while slow flow rates favor formation of nitric oxide and destruction of ozone. This could be demonstrated nicely by varying the flow rate of air over a Nernst glower with tetrabase paper as an indicator, the color of tetrabase paper changing from yellow to blue as the flow rate was increased.

Entry 1a shows that varying flow rates did not significantly affect ozone formation. This was inferred as evidence that complete survival of ozone was occurring; otherwise the higher flow rates would have given significantly higher amounts of ozone. Note that pO_3 is approximately four orders of magnitude greater than the value calculated from theory. Entry 1b (51) demonstrates that pO_3 increases with increasing temperature as expected. When moist gas was used in these experiments, hydrogen peroxide could be detected; its reaction with ozone made quantitative studies unattractive. Temperature of the glower was determined optically.

2. *Immersion of an operating Nernst glower into liquid oxygen (44) (entry 2).*

This procedure has been discussed earlier. As can be seen from the table, pO_3 increased steadily with reaction time, giving values much larger than predicted by theory. Presumably the limitation on conversion is evaporation of the liquid oxygen; otherwise the method might even have practical value.

3. *Exploding ozone or ozone-oxygen mixtures (47, 48, cf ref. 9) (entry 3).*

Having developed techniques for safely isolating pure ozone (1) in the early 1920s, Riesenfeld and Beja were in the desirable position of being able to approach the ozone-oxygen equilibrium from the ozone side. Ozone itself and mixtures with oxygen can be exploded by a spark. The explosion temperatures were calculated from thermochemical data for ozone and for a series of mixtures with highly purified oxygen at 10% composition intervals; these ranged from 2880 K for pure ozone to 2397 K for a 1:1 mixture. The explosions were performed in a 127-cc heavy-walled flask with sealed platinum electrodes, providing the spark to initiate the explosion. A series of ozone-oxygen mixtures were prepared, exploded, and analyzed for ozone concentration by the iodimetric technique; this was shown to be just sufficiently sensitive for the very low ozone concentrations obtained. The results reported from mixtures ranging in explosion temperature from 2459-2880 K were scattered within the range $2-4 \times 10^{-8}$ atm.

4. *Rapid flow of oxygen through a heated capillary (entries 4a,b).*

Riesenfeld's last essay into thermal formation of ozone appeared in 1939 (52) and corrected earlier 1925 work (53). It involved directing a stream of oxygen at a rate of 1 m/s through 0.9-1.3 mm i.d. heated capillary

Table 1. Experimental and Calculated Results of Equilibrations of Oxygen, Ozone, and Oxyhydrogen Mixtures.

No.	Lit.	Method	T (K)	Conditions	pO ₃ (atm) Expt.	Calcd ^a	pO ^b (atm)
1a	c	Oxygen blast over Nernst glower	2000	Flow rate 30 m/s 57 96	3.2 x 10 ⁻⁴ 6.1 x 10 ⁻⁴ 3.5 x 10 ⁻⁴	1 x 10 ⁻⁸	5 x 10 ⁻⁴
1b	d	Oxygen blast over Nernst glower	2135 2310 2476	Flow rate 44 m/s	2.2 x 10 ⁻⁴ 3.9 x 10 ⁻⁴ 4.4x 10 ⁻⁴	1.4 x 10 ⁻⁸ 2.4 x 10 ⁻⁸ 2.8 x 10 ⁻⁸	1 x 10 ⁻³ 3 x 10 ⁻³ 8 x 10 ⁻³
2	e	Nernst glower in liquid oxygen	2000	25 min 50 125 360	7.8 x 10 ⁻⁴ 1.4 x 10 ⁻³ 3.1 x 10 ⁻³ 6.4 x 10 ⁻³	1 x 10 ⁻⁸	5 x 10 ⁻⁴
3	f	Explode ozone, ozone-oxygen mixtures	2148 2459- 2888	Varying ratios O ₃ :O ₂	<0.2 x 10 ⁻⁸ 2.4 x 10 ⁻⁸	3.5-8.4 x 10 ⁻⁸	
4a	g	Flow O ₂ through heated capillary	900 1000 1100 1400	Flow rate 2 m/s	1 x 10 ⁻⁷ 1 x 10 ⁻⁶ 2 x 10 ⁻⁶ 6 x 10 ⁻⁶	4 x 10 ⁻¹³ 3 x 10 ⁻¹² 1 x 10 ⁻¹¹ 4 x 10 ⁻¹⁰	6 x 10 ⁻¹² 2 x 10 ⁻¹⁰ 8 x 10 ⁻¹⁰ 4 x 10 ⁻⁷
4b	h	Flow O ₂ through heated capillary	<1273 1423	Flow rate 5-12 l/hr	5 x 10 ⁻⁷	4 x 10 ⁻¹⁰	5 x 10 ⁻⁷
5	i	Flow H ₂ + O ₂ through heated capillary	873 1150- 1273	Flow rate 660 cc/min	3 x 10 ⁻⁷ 2 x 10 ⁻⁶ 3 x 10 ⁻⁵	5 x 10 ⁻¹³ 2 x 10 ⁻¹¹ 9 x 10 ⁻¹¹	

a. Partial pressure of ozone calculated from equation 1. b. Partial pressure of oxygen atoms calculated from equation 2. c. Ref. 19. d. Ref. 51. e. Ref. 44. f. Ref. 47, 48. g. Ref. 52, 53. h. Ref. 54. i. Ref. 55.

tubes at temperatures ranging from 900 to 1400 K to a cooled region at the exit of the capillary and subsequent iodimetric analysis. Temperatures were measured optically. Once again, the experimental values were significantly higher than the calculated ones. This work was criticized by Wartenberg (54) (entry 4b), who claimed that the actual temperatures were as much as 400° higher than reported in the publication because of improper use of the optical pyrometer. In his brief 1940 paper Wartenberg reported, with minimal experimental detail, that he had repeated the Riesenfeld experiment with proper temperature measurement at flow rates of 5-12 l/hr. He was unable to detect ozone at temperatures below 1273 K but could measure the ozone concentration at 1423 K; pO₃ = 5 x 10⁻⁷ atm, three orders of magnitude greater than the calculated value.

5. Rapid flow of oxygen-hydrogen mixtures through a heated capillary (55) (entry 5).

The hydrogen-oxygen system ("oxyhydrogen") had been studied by numerous workers who had definitely established that hydrogen peroxide is formed in such flames or heated systems and found indications for ozone as well (56). The first detailed study of both products was reported in 1920 by Wartenberg and Sieg (55), who used a nonexplosive hydrogen-oxygen mixture (9 H₂:1 O₂ by volume), which flowed at rates between 600-1400 cc/min through a 1-mm i.d. quartz tube heated to temperatures between 600-1000° C. Rapid cooling afforded a condensate containing water and hydrogen peroxide that was weighed and analyzed for peroxide; the collected gases were shown to contain ozone by tetrabase paper and analyzed quantitatively by iodimetry. As can be seen in Table 1, the amounts of ozone formed were 5-6 orders of magnitude larger than the calculated values. It was concluded that ozone was formed by some additional mechanism, perhaps the thermal decomposition of hydrogen peroxide to give water and atomic oxygen (rxn 6), the

latter being the precursor of the ozone observed. rxn (6)
 rxn (5) $2 \text{Si}_2\text{Cl}_3 \rightleftharpoons 3 \text{SiCl}_2 + \text{Si}$

The amounts of hydrogen peroxide formed were larger than those of ozone; the reaction between ozone and hydrogen peroxide yielding water and oxygen was not taken into account, nor was the fact that a thermal reaction occurs between ozone and hydrogen (57).

Riesefeld (58) also investigated the hydrogen-oxygen system with a study of flames from very fine capillaries (0.2-0.4 mm i.d.) using varying ratios of hydrogen to oxygen. Water cooling of the gases formed resulted in condensation of water and hydrogen peroxide; the permanent gases were passed into KI solution for iodimetric analyses. With excess oxygen (molar ratio $\text{O}_2:\text{H}_2 = 3.3:1$) and a flow rate of 0.6 liter/hour, nearly equal partial pressures of ozone and hydrogen peroxide ($p\text{O}_3 = 18.8 \times 10^{-6}$ atm; $p\text{H}_2\text{O}_2 = 20.3 \times 10^{-6}$ atm) resulted, while under stoichiometric conditions (1 $\text{O}_2:2 \text{H}_2$ ratio, flow rate 5.85 liter/hr) there was a moderate increase in hydrogen peroxide ($p\text{H}_2\text{O}_2 = 38 \times 10^{-6}$ atm) and no detectable ozone formation. With excess hydrogen the partial pressure of hydrogen peroxide increased to 244×10^{-6} atm without any ozone formation. Riesefeld argued that these results negated Wartenberg's proposal that hydrogen peroxide was the precursor of ozone. However, this argument ignores the fact that ozone formation would not be possible without sufficient oxygen available for reaction with atomic oxygen; Riesefeld (59) later abandoned his objection.

Theory vs Experiment

From the results presented in Table 1 it is immediately obvious that entry 3, the explosion of ozone and of ozone-oxygen mixtures, is the only procedure that gave experimental results in approximate agreement with those calculated for $p\text{O}_3$ from eqn 1. We note that this is the only procedure that does not involve the initial presence of a large excess of oxygen. Unfortunately, the measured ozone partial pressures were at the limit of sensitivity of the iodimetric procedure used and were scattered over the range $2\text{-}4 \times 10^{-8}$ atm without any observable trend. Riesefeld and Beja expressed themselves as satisfied that they had achieved agreement between theory and experiment. The desirable addition of confirming experiments was never reported. It might, for example, have been possible to modify the procedure to provide larger amounts of ozone and thereby increase the precision of measurement.

The outstanding feature of all the other experiments, where equilibrium was approached from the oxygen side, is the absence of any correlation between eqn 1 and experimental values for $p\text{O}_3$. The latter are orders of magnitude larger than the calculated values in every case. The failure of a theory to give results that agree with experiment is often taken as a strong indication that something is wrong with the theory. In these cases, however, the opposite was true, perhaps because of the enormous influence Nernst had in his time. In all cases the authors concluded that the processes involved were not purely thermal ones or that the experimental procedures were faulty. The final conclusion (see below) is that the interpretation was faulty; experimenters were measuring a quantity different from what they thought.

Among the rationalizations presented to account for the observed results were the following. Riesefeld proposed that, in the experiments involving gas flowing rapidly through a heated capillary (entry 4), there was a wall effect which distorted the results. Both he and Wartenberg also suggested that the combination of translational and thermal energy involved in experiments with very high flow rates through capillary tubes could lead to ionization ("Ionenstoss"). Ionization was also proposed to occur with electrical devices such as Nernst glowers. In such cases, the ozone-forming process was suggested to be similar to that occurring in the silent discharge.

The breakthrough in understanding came with a 1932 paper by Harteck (60) following the 1910 paper by Wartenberg (18) on his failure to detect ozone absorption in heated oxygen samples by examination of UV absorption, as cited earlier. Harteck used a 100-cm cell at 2023 K with a slow flow of oxygen at one atm pressure. Using mercury lines at 2804, 2655, 2537, and 2482 Å and photometric analysis, he could detect no ozone absorption and set an *upper limit* of 4×10^{-6} atm for $p\text{O}_3$ at 2000 K contrasting with experimental values (see Table 1) greater than 1×10^{-4} atm. The conclusion was inescapable. The ozone measured, except in entry 3, was not formed in the hot section of the apparatus and, therefore, was not related to the thermal equilibrium between oxygen and ozone. Earlier workers had been barking up the wrong tree. Harteck derived an equation for calculation $p\text{O}$ at various temperatures, but the values he obtained for $p\text{O}$ were higher than the values observed experimentally for $p\text{O}_3$.

The results clearly implied that the ozone found experimentally is formed as the hot gas cools to its final temperature in the cooling section of the apparatus. This

gas contains a very small p_{O_3} , given by eqn 1, a very small p_O given by eqn 2, and oxygen itself at 1 atm. The reactions possible as the gas cools are those of atomic oxygen in the presence of O_2 and O_3 , namely dimerization (rxn 2), reaction with ozone (rxn 4), and addition to oxygen (rxn 1) to form ozone. Six years later Wartenberg (61), who earlier had dismissed the thermal cleavage of oxygen to atoms as unimportant, took the interpretation a step further by arguing that the reaction $O + O_2 \rightarrow O_3$ was diffusion controlled in the rapidly cooling gas. The relative rates of formation of the products would be determined by the relative amounts of each present. The enormous excess of oxygen at the temperatures employed meant that the almost exclusive reaction of O atoms would be the formation of ozone. If this were correct, ozone could be used as a label for oxygen atoms; p_{O_3} measured *experimentally* would be equal to p_O at the exit of the oven plus the negligible partial pressure of any ozone present. The situation would be more complicated at higher temperatures where p_O would be significantly larger. Interestingly, Riesenfeld, who was the first to suggest the importance of the dissociation of oxygen into atoms as a factor in the reactions at elevated temperatures, did not arrive at this interpretation of the results.

By 1938 spectroscopic measurements had established the value of 117.3 kcal/mol for the bond dissociation energy of oxygen. The partial pressure of atomic oxygen had been determined over a wide range of temperature and could be closely approximated between 1000 and 3000° C by the empirical equation 2.

$$\log(p_O) = -60,350/4.57 \cdot T + 3.466 \quad \text{eqn 2}$$

Wartenberg's 1938 experiment used highly purified oxygen flowing through a tube (22 cm long, 8 mm i.d.) in a heated oven which abutted directly on a water-jacketed metal capillary (0.5 mm i.d.) leading to a KI-starch solution for analysis. Reproducible values for p_{O_3} , shown in Table 2, were obtained at flow rates of 6 l/hr. The agreement between experiment and calculation is remarkably good.

Comparison with the results in Table 1 shows that there is also a reasonably good fit between calculated p_O and measured p_{O_3} except for entry 1b, where temperatures in the range 2100-2500 K were used. Here p_{O_3} values are an order of magnitude lower than p_O , possibly because some ozone was destroyed at the higher temperatures. The temperatures given in entry 4a were reportedly incorrect, as noted earlier.

To the best of our knowledge, there has been no further work on thermal formation of ozone since Wartenberg's 1940 paper (54). It would appear that the only type of procedure which could give information on the ozone-oxygen equilibrium is one in which the analysis is made on the heated sample of oxygen using an analytical method of sufficient sensitivity to measure the ozone concentration directly, as Wartenberg had suggested in 1910. This is what Harteck attempted by UV measurement with a one-meter path length; unfortunately, in that case the ultraviolet measurement was not sufficiently sensitive for the predicted p_{O_3} of about 1×10^{-8} atm. Apparently, the problem has been either too difficult or not of sufficient interest to tempt any investigators since



Ernst Hermann Riesenfeld, 1877-1957.
Photograph courtesy of Mrs. Harald Riesenfeld.

Table 2. Comparison of Experimental and Theoretical Results from Heating Oxygen Gas Followed by Rapid Coolinga.

No.	T (K)	Exptl. p_{O_3} b (atm)	Calc. p_O c (atm)
1	1283	0.1×10^{-6}	0.14×10^{-6}
2	1423	1.51×10^{-6}	1.53×10^{-6}

a. Flow rate 6 l oxygen per hour.

b. Measured values of partial pressure of ozone.

c. Calculated values for partial pressure of oxygen atoms at the given temperature, from eqn 2.

1940 although modern analytical methods could probably provide answers.

The only remotely related work we have found is that of Romanov et al. (and references therein (62)), who obtained ozone by passing air over heated crystals of magnesium and bismuth oxides. The result was explained on the basis of release of oxygen atoms from the crystals.

It is tempting to take a very critical attitude towards the progress of work described in this paper. If, for example, Wartenberg or other workers in the field had considered the implications of his 1910 failure to detect ozone in samples of oxygen heated to about 2000 K, the solution to the problem might not have had to wait over 20 years for correct interpretation. However, one should realize that these were formative years in physical chemistry and that the necessary information, in this case the quantitative dependence of oxygen dissociation upon temperature, was not available. A similar situation in pre-Schönbein ozone chemistry was the failure of van Marum (35) to decide that arcing air or oxygen produced a new compound. The tools to treat such a situation were not available in the 1780s.

Summary

A considerable number of early reports of formation of ozone by heating air and from a variety of flames were largely due to erroneous identification of nitric oxide as ozone by smell and starch-iodide test. However, despite the well known thermal instability of ozone, it was clearly established that it is formed from oxygen under these conditions. Detailed studies followed Nernst's work on the third law of thermodynamics, and a number of attempts were made to establish the equilibrium composition of the ozone-oxygen mixture as a function of temperature despite the considerable experimental difficulty involved. The only experiments which gave values compatible with theory were those in which the equilibrium was approached from the ozone side by use of explosions of ozone and oxygen-ozone mixtures; these were at the limit of sensitivity of the analytical methods available at the time. In all other experiments, amounts of ozone formed were far in excess of theoretical prediction. In fact, it was finally established that the quantity being measured when thermal reactions of oxygen were investigated was the concentration of oxygen atoms formed by thermal dissociation of oxygen molecules.

The presence of water vapor or its formation by combustion of hydrogen leads to formation of hydrogen peroxide in flames or upon heating moist oxygen. The oxyhydrogen flame produces hydrogen peroxide and also, if sufficient oxygen is present, ozone. The formation of ozone was suggested to proceed via the intermediacy of oxygen atoms formed by thermal decomposition of hydrogen peroxide.

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ABOUT THE AUTHOR

Mordecai B. Rubin is Emeritus Professor of Chemistry in the Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel. He can be contacted at chrubin@tx.technion.ac.il. Retirement is like a permanent sabbatical. A major interest for many years was organic photochemistry. Many years ago, as a young man in the laboratory of Professor William S. Johnson, he developed an apparatus for small scale ozonolysis which was dubbed the Rubin ozonator.

Workshop on Stahl and French Chemistry in the Late Eighteenth Century

Twelfth Congress of the International Society for Eighteenth-Century Studies (SIEDS)

Montpellier, France, from July 8 - 15, 2007.

The subject of this workshop is the relationship between the early 18th-century chemists in Europe and Stahl: for example, exchanges which seem to have existed between Stahl and the early French 18th century chemists; and similarities between Stahlian chemistry and Geoffroy's doctrine of affinities. We encourage historians of chemistry of this period to present their points of view and to exchange information to clarify the role of Stahl in the history of chemistry, when 18th-century European chemical thought was forming.

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Bernard Joly, Professeur de philosophie et d'histoire des sciences à l'université de Lille3

Rimi Franckowiak, Maître de conférences d'histoire de la chimie à l'université de Lille1

BOOK REVIEWS

The Chemical Promise: Experiment and Mysticism in the Chemical Philosophy, 1550-1800. Allen G. Debus, History of Science Publications, Sagamore Beach, MA, 2006; hardcover, xxv + 548 pp, ISBN 0-88135-296-9.

Allen Debus, winner of the 1987 Dexter Award in the History of Chemistry, has long been considered the world expert on the history of iatrochemistry, that peculiar blend of alchemical thought with medicine and pharmacy which characterized much of the 17th and late 16th centuries and whose most lasting impact on modern chemistry was perhaps its success in introducing chemistry into the university curriculum under the guise of service courses for students of medicine and pharmacy. Far more complicated than this brief characterization would suggest, iatrochemistry was also coextensive in its early phases with the reformation and the collapse of both church authority and medieval scholasticism—events which created something of an intellectual vacuum into which rushed not only the early stages of the mechanical philosophy but also the revival of a bewildering array of mystical and occult beliefs ranging from Neoplatonism to the doctrine of signatures.

The 26 essays reprinted in this volume attempt to guide the reader through this intellectual labyrinth and have been organized into four categories: The Alchemical Background, The Chemical Philosophy, Chemistry and Medicine in National Settings, and The Eighteenth Century and the Chemical Revolution. At first glance the reader will be somewhat puzzled as to the origins of the essays themselves as neither the table of contents

nor the individual essays carry a bibliographical reference indicating where the essays originally appeared. Eventually, however, one discovers that this information is instead embedded in Debus' introduction and reveals that, though two or three of the essays have been reprinted from easily accessible sources, such as *Isis* and *Ambix*, the vast majority originally appeared in the proceedings of relatively obscure French, German, Spanish, and Dutch publications, and that, in fact, one or two have never been previously published. Since tracking down these original sources would be a nontrivial task, it is a great convenience to have all of them collected together in a single and easily accessible book. The reviewer was particularly delighted to see that this collection included the 1986 essay "Chemistry and the Universities in the Seventeenth Century," which he has often found to be of great use in his own teaching and writing.

Potential readers can probably best judge the extent to which this book will be of interest by their reaction to the claim put forward by Debus in the final paragraph of the book's concluding essay, "History of Chemistry: Key to Modern Science," where he states, "I believe that Paracelsus is fully as important to our understanding of sixteenth century science as is Copernicus, and van Helmont should be studied with as much care as Galileo." If one is interested in the question "Who was important in determining the content and direction of 16th century science?" — and this is certainly a question that has interested Debus throughout his career—then this is probably an accurate claim. If, on the other hand, one is primarily interested in the question "What are the lasting contributions of 16th-century science to present

day science? — and this is the historical question which is of most interest to practicing scientists and the public at large—then such a claim is dubious in the extreme. The important point, however, is that neither response is correct or incorrect; the appropriate response depends rather on the question being asked. But even if, like the present reviewer, you fall into the second, rather than the first, of these camps, this book will probably be of interest, since to properly deal with the answer to the second

question, one must have an accurate knowledge of the answer to the first question, and Debus is probably the most congenial guide to that answer as he sticks to the historical subject at hand and seldom mars his writings with the strident revisionist rhetoric so characteristic of many of the younger historians of the alchemical and iatrochemical periods. *William B. Jensen, University of Cincinnati.*

Mendeleev on the Periodic Law: Selected Writings, 1869-1905. William B. Jensen, Ed., Dover Publications, Inc., Mineola, New York, 2005, 314 pp, ISBN 0-486-44571-2, \$19.95.

The German chemist Lothar Meyer once complained during a priority dispute with Mendeleev that few European scientists could be expected to be fluent in Russian. This is even truer today. Almost all of Mendeleev's writings on the periodic law, including archival material, were published in Soviet Russia. All in Russian, these very valuable texts, crucial especially for the study of the history of chemistry, have not been easily accessible to English-speaking readers. As William B. Jensen, the editor of this book, urges (pp 5, 160), a fresh English translation of such Russian collections of Mendeleev's writings on the periodic law is highly desired, but Jensen decided that such a project was beyond his ability and the scope of one book.

Therefore the writings in this collection are not fresh English translations of Russian originals. The editor uses the nineteenth century English, German, or French translations. This is partly due to Jensen's lack of knowledge of Russian. However, there is also another rationale. Even though Mendeleev learned German, French, and Latin in his school days and studied in Germany for two years, his knowledge of these languages was limited. He always wrote in Russian and asked his friends and

colleagues to translate his writings when necessary. All of Mendeleev's writings in languages other than Russian are translations. Therefore, the papers collected in this book also reflect the story of the reception of the periodic law by nineteenth-century chemists outside Russia. Furthermore, this book offers several episodes that show Mendeleev's poor knowledge of spoken foreign languages (the epigraph, pp 6, 154).

Jensen's selection comprises thirteen translated papers that appeared in European journals from 1869 to 1905. The papers are presented in roughly chronological order and divided into three groups, reflecting the period corresponding to the initial establishment of the periodic law (Papers 1-3, 1869-1871), a period of priority disputes and experimental confirmations (Papers 4-8, 1871-1886), and a final period of general acceptance for the law (Papers 9-13, 1887-1905).

Paper 1: "On the Relation of the Properties to the Atomic Weights of the Elements" [*Z. Chem.*, **1869**, *12*, 405-406]

Paper 2: "On the Correlation between the Properties of the Elements and their Atomic Weights" [*Zhurnal Russkogo Khimicheskogo Obshchestva*, **1869**, *1*, 60-77]

Paper 3: "On the Periodic Regularity of the Chemical Elements" [*Ann. Chem. Pharm.*, **1871**, *8* (Supplementband), 133-229]

Paper 4: “On the Question Concerning the System of Elements” [*Ber. Dtsch. Chem. Ges.*, **1871**, 4, 342-352]

Paper 5: “On the Application of the Periodic Law to the Cerite Metals: A Reply” [*Ann. Chem. Pharm.*, **1873**, 68, 45-63]

Paper 6: “Remarks Concerning the Discovery of Gallium” [*C. R. Séances Acad. Sci.*, **1875**, 81, 969-971]

Paper 7: “The Periodic Law of the Chemical Elements” [*Moniteur Scientifique*, **1879**, 21, 691-693]

Paper 8: “On the History of the Periodic Law” [*Ber. Dtsch. Chem. Ges.*, **1880**, 13, 1796-1804]

Paper 9: “The Periodic Law of the Chemical Elements” [*J. Chem. Soc.*, **1889**, 55, 634-656]

Paper 10: “On Argon” [*Nature*, **1895**, 51, 543]

Paper 11: “How I Discovered the Periodic System of Elements” [*Revue Général de Chimie Pure et Appliquée*, **1899**, 1, 211-214, 510-512; **1901**, 4, 533-546]

Paper 12: *An Attempt Towards a Chemical Conception of the Ether*, Longmans, Green & Co., London, 1904

Paper 13: “*The Grouping of the Elements and the Periodic Law*,” [*Principles of Chemistry*, Longmans, Green & Co, London, 3rd ed., 1905, Ch. 15]

When only German and French but no English translations were available, the editor himself translated those into English. (Papers 1, 4, 5, 8, 11). When English translations existed alongside their German or French versions, Jensen revised the English translations after a comparison with their German or French versions, since English translations were usually secondary and tertiary translations from German or French (Papers 2, 3, 6, 7). English versions translated directly from Russian originals are retained with minimum revisions, such as appropriating American spellings, rearranging footnotes as endnotes, and breaking apart “unending sentences” (Papers 9, 10, 12, 13).

There are some minor mistakes, because of Jensen’s unfamiliarity with the Russian language and literature

on Mendeleev in that language. The source of Paper 2 should be written as shown above. The Russian Chemical Society, founded in 1868, and the Russian Physical Society, founded in 1872, merged into the Russian Physical-Chemical Society in 1878, with individual Chemistry and Physics Sections, as proposed by Mendeleev. *Zhurnal Russkoe Fiziko-Khimicheskoe Obshchestvo* (used here in the grammatically incorrect form; the correct form is *Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva*) is the name of the journal of the combined new society, which did not exist in 1869. Paper 2, Mendeleev’s first paper on the periodic law, was read by the Russian chemist, Nikolai Menshutkin, not because Mendeleev was ill at the time (p 11), but because he was away inspecting cheese-making cooperatives for the Imperial Free Economic Society (see, for example, a well written first English biography of Mendeleev, Michael Gordin, *A Well-Ordered Thing*, 2004, p 30). Jensen writes that it is unclear from Walden’s bibliography whether Mendeleev ever completed his revision of the eighth Russian edition of *The Principles of Chemistry* (p 160 n.24). Mendeleev did complete it, the eighth edition appearing in 1906. As Jensen noticed, Mendeleev loved wordy footnotes, and this tendency went to extremes in *The Principles of Chemistry*. However, in the eighth edition, all the notes were separated from the main text and placed in the second half of the book [see this reviewer’s publication for the details, “D. I. Mendeleev’s Concept of Chemical Elements and the Principles of Chemistry,” *Bull. Hist. Chem.*, **2002**, 27, 4-16 (pp 10-12)]. In this way, the “typesetter’s nightmare” (p 157) was avoided.

This book is the product of Jensen’s lectures for the annual history of chemistry course for chemistry majors at the University of Cincinnati. His aim—provision of a single, easily accessible source for Mendeleev’s principal writings on the periodic law—has been successfully fulfilled. On the whole, this long overdue “English-language collection of Mendeleev’s most important writings” (p 5) on the periodic law is a most welcome contribution to the history of chemistry. *Masanori Kaji, Tokyo Institute of Technology, W9-79, 2-12-1 Ookayama, Meguro-ku, 152-8552 Japan*

De Re Metallica: The Uses of Metal in the Middle Ages, Robert Bork, Ed., Ashgate, Burlington, VT, 2005, xxii+401 pp. ISBN 0 7546 5048 0, \$99.95.

This volume is a collection of papers that examine metal objects and technical writings on metallurgy from Western Europe from the early Middle Ages to the Renaissance. *De Re Metallica*, not to be confused with Georgius Agricola's treatise with the same title, is divided into five sections: 1) "metal for secular display," that discusses metal bodily decoration and other personal metal objects; 2) metal objects that possess a religious significance; 3) "metals for everyday use;" 4) metals used in buildings and architecture; and 5) treatises about metal production. The final section is likely to be the most interesting to historians of science, because of its analysis of how metallurgical knowledge was conceived, explained, and transmitted. The detailed descriptions of metal objects and reconstructions of medieval technologies from the book's earlier archaeological and art historical sections also give us a richer understanding of the material history of medieval science. The level of scholarship in this work is high; the authors almost uniformly rely on careful examinations of physical and documentary evidence and refrain from speculative conclusions. The argumentation is precise and thorough. Someone hoping to gain a comprehensive knowledge of medieval metal production and other metallurgical topics, however, would be advised to turn elsewhere. General assessments are shunned in favor of investigations into particular objects, texts, and locales.

The first four articles of the first section consider bodily ornaments from early medieval northern Europe. Gale R. Owen-Crocker uses metal remnants found in fifth- to seventh-century Anglo-Saxon graves as a means to discuss wealth and its display in that society. Brooches, pendants, and other metal objects are often the only surviving artifacts of these graves and, therefore, offer important clues to the material culture of Anglo-Saxons. Thus Gabor Thomas applies ninth-century metalwork as evidence for determining the Northumbrian style of metalwork found in strap ends and concludes that Viking influence in Anglo-Saxon Northumbria was not as great as previously thought. Nancy L. Wicker discusses the social significance of bracteates found as pendants in Scandinavian graves from the Migration Period. Niamh Whitfield describes in detail a tenth-century "kite" brooch excavated from the Temple Bar West site in Dublin. Michèle Hayeur Smith continues the examination of

Scandinavian subjects by using experimental trials to recreate Viking Age mold-making techniques. The last two articles of the section change the geographical setting and move into the later Middle Ages. In one of the more fascinating articles of the volume, Elisabeth Antoine decodes the magical inscription on a signet ring owned by Guillaume de Flouri, a Frenchman who was the Viscount of Acre during the 1270s. John Cherry's piece closes the section by interpreting the metal decoration found on the Savernake Horn, a carved elephant's tusk from fourteenth-century England.

The following section limits itself to objects relevant to religious life that were composed of metal. The articles range widely through time and space. Michael Ryan concludes that, in Ireland in the years around 1000, as a result of economic factors, more effort was expended in decorating Eucharistic vessels than in architecture. Karen Blough analyzes a gold plated sculpture of the Virgin and Child that was likely commissioned by Mathilde, a Princess-Abess from Essen. Sally J. Cornelison, by deducing its originally intended location, skillfully reconstructs the inspirations for a bronze casket that Lorenzo Ghiberti made for the church of Santa Maria degli Angeli in Florence.

The third section is called "Mundane Metals: Metals for Everyday Use in War and Peace." Finding a common theme among these three disparate yet strong pieces is challenging. Kevin P. Smith describes how iron was produced at a farm in Háls, Iceland during the Viking Age, making sober estimates about the workforce, the scale of production, and methods and materials used. David Starley provides a starting point for further investigations into the materials and efficacy of quarrel-point arrowheads from late medieval England. And Julia Lea-Jones gives a detailed account of a water conduit built of lead during the fourteenth century in a Carmelite friary in Bristol, England.

While metal objects are often the only matter that survived in Anglo-Saxon graves and, therefore, essential to reconstructions of what is no longer extant, frequently the opposite prevails in medieval buildings, where stone has endured the centuries, but metal structures have corroded, are inaccessible, altered, or looted. It is in this light that the authors in the fourth section examine the employment of metals in medieval architecture, in both famous cathedrals and more modest structures. Carl F. Barnes, Jr. shows that Villard de Honnecourt was not an architect and that his interest in the role of metal in architecture was limited. Jennifer S. Alexander looks at

the use of lead, as well as other substances, in joints in medieval masonry, primarily in England. Sabine Lepsky and Norbert Nussbaum examine how lead was used in clamps, ties, joints, brackets, and window bars in a Cistercian Church in Altenberg, near Cologne. A. Richard Jones reconstructs the original ironwork in the highest parts of the Spire in Salisbury Cathedral through a careful consideration of both physical evidence and documentary sources. Phillippe Bernardi and Phillipe Dillmann wish to diminish the dichotomy between stone and iron skeletons in their treatment of the Papal Palace at Avignon. Charles R. Morscheck, Jr. shows how the various kinds of pegs, rods, templates, and rings gave structural strength to the seemingly stone Milan Cathedral.

The final section of *De Re Metallica* is dedicated to metallurgical writings. Ricard Córdoba de la Llave shows how a fourteenth-century Spanish vernacular treatise, the *Liber que enseña ensayar cualquier moneda*, explained the techniques needed to assay silver, a topic common among many vernacular arithmetic books of this era. Because of the ubiquity of debased coins during this period, assaying was of great value to both states and merchants. Córdoba de la Llave recreates the steps described in the treatise, demonstrating that assayers had not only numerous technical skills, honed through experience, but also used sophisticated methods of quantification and measurement in their practice. David E. Connolly gives a linguistic analysis of the “rhetorical

practice of restatement” (i.e., the use of “and” and “or”) in Ulrich Rülein von Kalbe’s *Bergbüchlein*, a theoretical and empirical account of metals that was printed repeatedly during the sixteenth century. In a separate article Connolly provides a detailed research bibliography on the *Bergbüchlein*, which, while useful, would benefit from the inclusion of alchemical treatises. Even if von Kalbe was at times dismissive of alchemists, he shared a theory of the creation of metals with them. Peter L. Siems summarizes the laws for the Schlackenwald (in present-day Czech Republic) tin mines enacted by Ferdinand I in 1548. He then discusses Ferdinand’s motivations and the effects these laws had on miners and their communities, judging that these laws probably improved working conditions slightly, changed the status of miners to that of paid workers instead of independent cooperatives, and did not greatly increase royal revenue.

The editor, Robert Bork, should be commended not only for bringing together a group of meticulously argued papers, but also for the quality of the book as a whole. Numerous figures and images clarify the articles and inform the reader. The copyediting is excellent; translations are written in a clear style, and the thorough index is more than welcome. These articles will be key for future research on the individual topics they treat and, in themselves, demonstrate the variety of ways that metal artifacts can be used as historical evidence. *Craig Martin, Oakland University.*

Creadores de la Ciencia Moderna en España y América: Ulloa, los Delhuyar y del Río descubren el platino, el wolframio y el vanadio (Creators of Modern Science in Spain and America: Ulloa, the Delhuyar and del Río discover Platinum, Tungsten and Vanadium). Manuel Castillo-Martos, Muñoz Moya Editores Extremeños, Seville, 2005, 293 pp.

The relationship and exchange of technological and cultural ideas between Spain and the American continent have been the focus of many books authored and edited by Manuel Castillo Martos; in this particular work, the chemistry of minerals is the central theme, and, more

specifically, both the role played by Spanish scientists on the discovery of platinum, tungsten (wolframium), and vanadium and the impact of these scientists on mineralogy in America and Europe.

The book is clearly divided into two halves. The first one takes up a third of the book and has a general character which positions the reader in the historical framework where the four scientists operated. The second part presents their respective contributions to the discovery of the above cited chemical elements alongside detailed biographical information on each of the four scientists.

The first part of the book is titled “Historical Framework where Ulloa, the Delhuyars and del Río Operated”

and it is divided into four unnumbered chapters; its purpose is to position the reader in the general, economic, commercial, political, social, ideological, and cultural environments of both Spain and the American Viceroyships during the 18th century. After this, the book turns to a description of the state of science on both geographical areas, focusing specifically on the chemistry of the time, and its effects on the historical development of Spanish and American mining and metallurgy. The description begins by displaying the evidence of not only the Iberian scientific backwardness (relative to that of its neighboring countries in the European framework), but also the even more obsolete state of the mineral processing techniques in the Viceroyships of New Spain (Mexico) and New Granada (Colombia). This situation was concurrent with the (often accidental) discovery of the great quantities of mines and mineral deposits located in these lands. This situation is presented alongside social considerations, such as the “criollo” feeling of rejection against everything related to the “motherland.” In the narrative there is a brief reference to the pioneer work of Proust as professor in the “House of Chemistry” in Segovia; the author considers this information relevant, given a publication by Proust on platinum, and this being one of the themes around which the book revolves.

The second part, titled by the author “The Creators,” presents separately similar information about the four scientists, who are, in the order of the book, Antonio de Ulloa (1716-1795), the brothers Juan José (1754-1796) and Fausto Fermín Delhuyar (1755-1833), and Andrés Manuel del Río (1764-1849). In addition to the biographical character of this information, the narrative places the characters inside the history of the discovery of the elements to which each of them was devoted, giving special emphasis on just one of these elements for each case in particular. For instance, in the case of Antonio de Ulloa, the author presents details of this scientist’s geodesic expedition to Peru and his stay in this and other American countries, along with the more relevant facts in the history of the metallurgy of platinum. These facts include the importance of platinum to the Spanish Crown, aspects related to its commercialization, and the role that different contemporary European scientists such as (among others) José Celestino Mutis, Pierre Joseph Macquer, Antoine Baumé, Andreas Sigismund Margraff, Jean Baptiste Boussingault, George le Clerc (count of Bufón), and none other than Antoine Lavoisier and Pierre Simon Laplace (who were the first to melt platinum using “dephlogisticated air”) had on the isolation and characterization of the properties of said element. The ties

among the different scientists in the book integrate the narrative and make it more interesting, as, for instance, when the author reveals details of the efforts of Fausto Delhuyar in obtaining malleable platinum. It is in this manner that the entire work is intimately connected, and so its reading should be done integrally and sequentially, and not by random chapter selection.

The presentation of the studies of the Delhuyar brothers raises the interesting scientific controversy between them and Karl Wilhem Scheele over the discovery of tungsten, along with the differing opinions that established this name over that of wolframium to represent the new element (Translator’s Note: the name wolframio is still used to represent tungsten in Spanish). The portion of the book devoted to Andrés Manuel del Río highlights his extensive relationships with the scientists of his time (who included one of the Delhuyar brothers, Fausto), his stay in New Spain, and his extensive scientific activity in the field of mineralogy, which led him to the isolation of vanadium in 1801 and a polemic over this point with the Swede Nils Gabriel Sefström (Friedrich Wöhler also played a role in this drama). This controversy centered on the identity of the actual discoverer and on the name that is universally accepted today (del Río had initially named the element eritronio). Through a detailed examination of the written publications of the implicated scientists as well as those of their contemporaries and analogously to what is done with Antonio de Ulloa, each one of the sections is complemented with a detailed analysis of the facts associated with the quantitative and qualitative analytical techniques utilized at the time for the discovery, characterization, and isolation of said elements.

The book concludes with the presentation of five appendices where the author supplies supplementary information of a more chemical and less historical character: the natural occurrence, properties, uses, and applications of each of the three elements. Throughout the work, the author includes numerous footnotes that refer the reader to the final part of the book where the entire bibliography is completely referenced. The quantity, quality, and relevance of the references demonstrate the high degree of erudition on the part of the author and the very adequate use of primary and secondary bibliographic sources.

In summary, this is a well executed work, written in a frugal but agreeable style, and with a rigid adherence to the facts, as suggested by the bibliography that was consulted during its production and writing. In the bibliography the reader will find information not widely circulated in historical publications but presented in a

clear and orderly manner, so that this will be enjoyed by not only those interested specifically in mining and metallurgy but also by those studying the relationship between Spain and its American colonies. The reading of this book may prompt the reader to consider two other books written by the author on very similar topics: *Mining and Metallurgy: Technological and Cultural Exchanges between America and Europe during the Spanish Colonial Period* (translator's title; actual Spanish title: "Minería y Metalurgia: Intercambio tecnológico y cultural entre América y Europa durante el periodo colonial español") and *Precious Metals: the Union of Two Worlds. Technology, Commerce, and Politics of Spanish-American Mining and Metallurgy* (translator's title;

actual Spanish title: "Metales preciosos: unión de dos mundos. Tecnología, comercio y política de la minería y metalurgia iberoamericana"). Distributed by the same publisher, these two works study the diverse factors in the Spanish and American framework that affected the technical and cultural activities of American mining and the extension and transfer of mining and commercial techniques to other materials such as gold, silver, or mercury. *Simón Reif-Acherman, School of Chemical Engineering, Universidad del Valle, Cali, Colombia.*
Translation by Dr. Gorka Peris; Research Associate, Department of Chemistry, Boston College, Chestnut Hill, MA 02467, USA.

A History of Chemical Warfare. Kim Coleman, Palgrave Macmillan, Houndmills, UK, New York, 2005, xxv + 164 pp, ISBN 1-4039-3460-6; paperback, \$26.95.

Although few of the books on chemical weapons listed in Kim Coleman's bibliography were published within the past few years, the topic does seem to be undergoing somewhat of a resurgence. While reading Coleman's book, I came across a review of two other books on chemical weapons in *Chemical Heritage* (vol. 24, No. 4, Winter 2006/7, pp 46-7), one newly published in 2006 and the other a 2005 reprint of a 1965 publication. Perhaps the increased fear of terrorists and of their use of weapons such as poison chemicals, biological agents, and "dirty" bombs against civilian populations has aroused renewed interest in these topics.

Coleman's book—much slimmer than the two mentioned above—offers a history of the development and use of chemical weapons throughout the 20th century. It begins by mentioning some historical precedents, including the military deployment of poison gases and fumes as long as 4,000 years ago, and also sets out the context for the discussion of later topics. The historical chapters cover chemical agents in WWI, the years

between the two world wars, WWII, the Cold War (including Korea and Vietnam), and the recent conflicts in the Middle East, Afghanistan, and the Gulf region. As expected, the author's attempts to write a history of the most recent conflicts—the Iran-Iraq war (1980-88), the war in Bosnia (1992-95), and the Gulf wars (1991 and 2003-present)—are less successful than her discussions of events from earlier periods.

In WWI all the combatants except the United States were signatories to the 1899 Hague Declaration, which prohibited "the use of projectiles the sole object of which is the diffusion of asphyxiating or deleterious gases" (p 9). This prohibition did not, of course, prevent their use in that war. First of all, they were available in large quantities. The significant growth of the chemical industry by the end of the 19th century made possible for the first time the production of large amounts of toxic chemicals for the battlefield. Also, it wasn't difficult to circumvent the Hague Declaration. The Germans developed a shell that contained not only a liquid tear gas, but also an explosive for producing shrapnel. In their well-known gassing of French troops with chlorine at Ypres in April, 1915, the Germans capitalized on Fritz Haber's suggestion of simply opening up canisters of gas when the wind was blowing toward the enemy trenches. Despite

the common misconception that the Germans were the first to deploy gas as a battlefield weapon in WWI—I certainly thought they did—the French actually were the first. In August, 1914 they fired tear-gas grenades filled with xylyl bromide at German troops without any significant effect.

For me, some of the most interesting material was the continued development of chemical weapons after WWI, especially the discovery of nerve gases in Germany despite the terms of the 1919 Treaty of Versailles that prohibited such research, as well as “the dog that didn’t bark,” i.e., the absence of chemical weapons in WWII even though both Allied and Axis countries had huge stockpiles and expected them to be used. With this material, Coleman finds her stride as a good storyteller, something she doesn’t always achieve.

The book’s final two chapters attempt to situate chemical weapons in today’s world, in terms both of terrorist groups and of current international agreements among nations. Again, the topics of these chapters are too close in time to lend themselves to historical treatment, and I think that Coleman succeeds less well in treating these recent events than in telling stories about the past and conveying their significance.

In general, I found Coleman’s writing both objective and well documented, especially in her examination of known and reported uses of chemical weapons throughout the 20th century. The one notable exception is her discussion of alleged US use of the nerve agent sarin in Southeast Asia in 1970 against American defectors and “also against American prisoners of war whom the [US] government decided would be a major embarrassment if they came home alive” (p 97). Unfortunately, Coleman offers no substantive evidence to support this allegation and gives a website as her only reference.

She then juxtaposes this allegation with yet another one concerning the suicide of a US Army sarin expert after a failed POW rescue mission in 1981. Her source for this is “Scott Barnes’ book,” which she neither identifies nor includes in her bibliography. The discussion continues with a quote from an unnamed source, who claims that the expert was probably murdered because of his knowledge of using sarin against American soldiers, and it concludes with the story of a CNN website on this topic, which mysteriously disappeared shortly after it was set up. This entire discussion is little more than innuendo and has the aura of a conspiracy theory with no documentation beyond websites, an unnamed book, and an anonymous source. The inclusion and presentation of this material seriously undercuts Coleman’s objectivity—perhaps fatally for some readers—but I was able to regain my confidence in her for the remaining pages.

While I learned a good deal from Coleman’s book, I obviously have some reservations about it. The author suffers a serious lapse in objectivity, and she sometimes provides a lot of details without necessarily weaving them into a compelling story. At the outset of the book I was troubled by the frequent lack of punctuation after introductory clauses and sometimes had to reread sentences for meaning. More troubling to me—as a former writing teacher—were the subject-verb disagreements. I found three on the first two pages, but either they disappeared or I stopped noticing them.

Even with the caveats mentioned above, I do recommend this book as a brief introduction to an important topic, one that unfortunately hangs over twentieth-century chemistry like a toxic cloud. *Richard E. Rice, P.O. Box 1210, Florence, MT 59833; charrice@juno.com.*

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