Captain Nemo's Battery

Assorted Chemical Annotations on
Science Fiction and Literature

William B. Jensen

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Dedicated to Jack Stocker

Who unintentionally started it all

Preface

Like my earlier collection of lectures dealing with humanism and skepticism (1), this volume is also a collection – albeit in this case of both published and unpublished essays. As with the previous collection, I have once again chosen to adopt the $8_{1/2}$" x 11" double column format usually reserved for journals and magazines because it allows for a much more intimate blending of text and illustration.

As a trained chemist I have always paid attention to any passing reference to chemistry or chemists that I have encountered over the years in my reading of imaginative fiction, whether in the form of classic literature or popular short stories and novels. And, as a chemical historian, I have never been able to resist the urge to track down the probable documentary background for these passing references. The resulting hobby is perhaps best thought of as a series of "chemical annotations" done at a sufficiently advanced technical level to prove intellectually satisfying to the trained chemist or teacher of chemistry, coupled with a level of detailed historical documentation sufficient to satisfy the most demanding of historians.

It has also long been my contention – some would probably call it a delusion or pretension – that these annotations and documentations would prove of interest to at least a small, but select, audience of my fellow chemists and teachers – a contention that appeared to be supported by the occasional appearance of similar articles by others in such publications as the *Journal of Chemical Education* (2-11) and *Chemistry in Britain* (12-15). However, little did I anticipate the obstacles and problems that I would encounter in my attempts over the years to bring these essays to the attention of the chemical community.

The first two essays in this collection date back to the 1970s and early 1980s when I was still a graduate student at the University of Wisconsin, as does the idea behind Essay IX. However, whereas Essays II and a precursor to Essay I were both published at the time, Essay IX was only outlined since the ever-present pressures of course work, research, and more serious chemical publications soon got in the way. Then followed a lull during which I was immersed in the pressures of my first three academic appointments at the University of Wisconsin, the Rochester Institute of Technology, and the University of Cincinnati, respectively.

Only in 1992, with the anxieties of securing tenure finally behind me, did an unexpected opportunity to resume my hobby present itself when Jack Stocker of the University of New Orleans invited me to participate in a major symposium on science fiction and chemistry at the Spring National American Chemical Society Meeting in San Francisco. This resulted in the writing of Essays III and IV and to an outline for Essays V. Stocker's intent was to have the symposium published by ACS Books as part of its standard symposium series and manuscripts for all three of these papers were duly submitted. However, when the galleys arrived disaster struck. I found that all of my chemical annotations, equations, and references – the very *raison d'etre* of the papers – had been deleted and the papers had been completely rewritten in short, choppy sentences by a young 22-year old English major just out of college who, though lacking any kind of chemical training, had been especially hired to edit the book.

It seems that the powers that be at ACS Books had decided that the Stocker book was their opportunity to enter the mainstream popular book market, though this necessitated removing as much chemistry as possible from the book in question. In fairness, I had some inkling that this move was in the works, as I had served on the editorial advisory board for a proposed history of chemistry series to be published jointly by ACS Books and the Beckman Center for the History of Chemistry in Philadelphia (now the Chemical Heritage Foundation) and had seen the representative from ACS Books repeatedly reject serious scholarly works on the history of chemistry with the complaint that they were not popular enough.

At one point she complained that what they needed was a chemical version of a popular science writer like Stephen Jay Gould or Lewis Thomas, though I quickly pointed out that these writers were well paid for their work and should such an imaginary person exist they would hardly be willing to give their writing away free to ACS Books in lieu of receiving proper compensation from a major publisher. I also pointed out that the only reason a professional society had any business maintaining a book publishing venture was to ensure the publication of specialist monographs of interest to its membership, but unlikely to be published by mainstream publishers.

In any case, I was outraged to have my work treated in this fashion and withdrew all three of my manuscripts from the book project, as well as having all of my copyrights returned to me. Stocker, however, had retained copies of my manuscripts and now proceeded to propose sending them to alternative authors so they could write replacement chapters to cover the

now missing topics of Jules Verne and H. G. Wells. Again outrage and threats of possible lawsuits were required to finally put this suggestion to rest. Only in 1998 – four years after the original symposium – did the Stocker book finally appear (16). Needless to say, not only did it not herald the entry of ACS Books into the popular book market, ACS Books itself ceased to exist not long afterwards, though it has more recently been revived once more and so far has restricted itself to the publication of symposia proceedings as given rather than imagined.

In the meantime, I continued to give lectures based on the manuscripts for both *Captain Nemos' Battery* (Essay III) and *Bug-Eyed Silicon Monsters* (Essay IV) at the invitation of dozens of college and university chemistry departments, and as an invited guest speaker at local ACS section meetings and at various symposia for college and high school chemistry teachers. And, as I had always suspected, both lectures proved to be highly popular. In addition, a second publication opportunity presented itself in 1997 with the appearance of the magazine, *The Chemical Intelligencer*. Modeled on the highly popular *Mathematical Intelligencer*, this magazine published popular historical and cultural articles, interviews, art, and puzzles of interest to the professional chemist and seemed an ideal medium for the kind of literary chemical annotation I enjoyed.

Indeed, the editor immediately accepted and published *Captain Nemo's Battery* and it was also used for the cover of the issue, but when I later informed him that I had at least four more similar manuscripts (Essays IV-VII) available for possible future use as space permitted, I was told that he could no longer accept such lengthy articles as he already had too many manuscripts in waiting and not enough space available in his magazine. I thought this extremely odd since even a cursory glance at the back issues of the magazine quickly revealed that between 50% and 60% of all the items published were written by the editor himself! Apparently either the publisher eventually noticed this oddity as well or the reading habits of the chemical community proved to be radically different from those of the mathematics community, since within a year or so the magazine suddenly ceased publication.

At this juncture I simply gave up and determined to allow the essays to accumulate with the thought of eventually publishing them in book form instead. During this period I wrote Essay VIII and finally completed, nearly 40 years after it was first conceived and outlined, Essay IX as well. However, by the time I finally got around to assembling the essays into a book I discovered to my dismay that, under the impact of the internet, the publication of paper-based monographs in chemistry had all but collapsed in the United States and all that was available were e-books, whereby I did all the writing, editing, layout work, and proofing and someone else got to control the distribution without performing even the minimal services of printing, binding, and advertising. In short, all they did was to post it on their website, something which I could do just as easily on my own – whence the following.

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Cincinnati, OH
November 2011

The Case of the Wrong Oxidation State

A Letter to the Editor

Almost 35 years ago, while still a graduate student at the University of Wisconsin, I wrote a brief letter to the editor of the *Journal of Chemical Education* (1):

A number of notes (2, 3) have appeared in this journal calling attention to novels and other fiction which might be of interest to the chemist or to the teacher looking for items to stimulate student interest in chemistry. In particular, mention has been made of Isaac Asimov's chemical detective novel, "A Whiff of Death" (4), and Dorothy L. Sayers' novel, "The Documents in the Case" (5). Recently I have come across a review of yet a third chemical detective novel in looking through a 1931 issue of "The Laboratory" (6). The novel in question is by T. L. Davidson and is entitled "The Murder in the Laboratory." The reviewer was quite enthusiastic, noting that the book "must have been written by a chemist with a flare for writing. It talks of beakers, balances, and methods of swings as smoothly as one chemist would to another." He concludes by declaring the novel a perfect solution to the problem of "what to give a chemist for Christmas."

Unfortunately, I have been unsuccessful in locating a copy of this book and would like to inquire whether readers of this journal might know something about it, or could suggest other fictional pieces which make clever use of chemical principles.

William B. Jensen

The Laboratory was a brief newsletter of between five and fifteen pages occasionally published by the Fisher Scientific Company of Pittsburgh – which was and still is a major supplier of scientific apparatus and chemicals. Though the primary purpose of this long-forgotten publication was to highlight the addition of new items of chemical apparatus and reagents to the company's product line, each issue also contained a feature article – frequently historical in nature – dealing with a general topic of interest to the professional chemist and/or teacher of chemistry. Why I was reading this publication was because I had inherited a large pile of old issues from my high school chemistry teacher when he retired my senior year. He had apparently thought the feature articles were interesting enough to save, and I had been scanning the issues
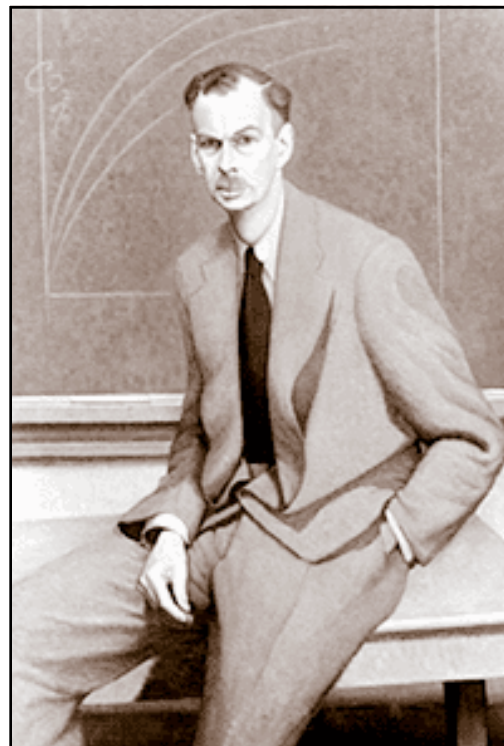

Figure 1. David Lansbourgh Thomson (1901-1964). A painting by Frederick B. Taylor, c. 1953.

trying to decide whether or not to donate them to the chemistry department library at Wisconsin when I chanced upon the book review in question.

My query received two responses, both in the form of personal hand-written letters – for these were the days before the advent of e-mail when even scientist were willing to occasionally and literally put pen to paper. The first was from one R. M. Baxter of Burlington, Ontario, and read (7):

I believe that T. L. Davidson, who wrote "The Murder in the Laboratory" was really the late David L. Thomson, who was formally Dean of Graduate Studies and Head of the Biochemistry Department at McGill University in Montreal.

I heard of this book when I was a graduate student in Professor Thomson's department in the 1950s, but I have never seen it. I suppose it has long been out of print, but perhaps the librarian at McGill might be able to tell you something about it.

If you should be able to locate a copy, I should be grateful if you would let me know.

The second letter, from Sidney Kasman of Chestnut Hill, Massachusetts, not only confirmed the information in the first letter, it also contained some further details (8):

"The Murder in the Laboratory" was written by David L. Thomson under the pen name of T. L. Davidson. He wrote the book as a graduate student in England to compete for a cash prize, which he won. I met the author, who is now deceased, and read his personal copy of the book while a graduate student in chemistry at McGill University between 1952 and 1954.

When I was at McGill, the author was Dean of Science. He did indeed have chemical training which accounts for the chemical facility displayed in the book. I still remember vividly an excellent lecture in biochemistry which he delivered on the primary, secondary, and tertiary structure of proteins.

The book was published in England and is now out of print. Possibly the library at McGill can provide additional information.

Though these small bits of information made my quest for this overlooked chemical detective novel seem all the more intriguing, the tentacles of the university's circa 1970 interlibrary loan system were unable – as implied in my letter to the editor – to locate a copy of the book for me to examine. And, not unexpectedly, the day to day pressures of other matters soon resulted in this piece of chemical trivia being filed away and forgotten until I chanced upon it again in 2007 when, prompted by an impending move of my office, I happened to clean out an old file cabinet. The computerization of the library system and the advent of the internet had by now greatly expanded the reach of interlibrary loan and now provided ready access to many biographical and historical items that would have been difficult to locate 30 years earlier, so I decided to apply both resources to my long forgotten mystery novel.

David L. Thomson

I was not disappointed. A search of the internet quickly led me to a history of the Department of Biochemistry at McGill University and to a painting of Thomson (figure 1) (9). Educated in biochemistry at Cambridge, Thomson joined the Department of Biochemistry at McGill in 1928 and served as its chair from 1941 to 1958 – the longest tenure of any chair since the department's founding in 1907 – as well as simultane-

ously serving as both Dean of Graduate Studies and Vice Principal of the University.

Primarily a teacher and administrator with little interest in hands-on laboratory research, Thomson had published a popular account of cell cytology in 1928 under the title of *The Life of a Cell* (10) and would leave – as suggested by Kasman's letter – an indelible impression on a generation of students (9):

Anyone familiar with biochemistry at McGill during the forties and fifties will, at the mere mention of Thomson's name, likely produce a positive and effusive response. Thomson became a legend with students primarily because his classes were not just a cut, but a mile, above the norm. Without a doubt, those who encountered Thomson were awed by the man's ability to share his knowledge in a lucid and captivating manner. His interests in science and culture were exceptionally broad and, according to those who knew him, he retained much of what he read. Moreover, he had a gift in the ability to explain new ideas in a thought-provoking as well as entertaining manner. Thomson continued to be the principal lecturer for all students in science and medicine and enthralled numerous classes of students for nearly 20 years, well into the 1950s. No other instructor in Biochemistry created the same excitement and enthusiasm for this subject at McGill. Many undergraduates became enticed to study biochemistry as a result of Thomson's lectures. In the pamphlet "McGill Medical Luminaries" he is described as having "a distinctive and arresting personality without rival at McGill."

The Forgotten Chemical Detective Novel

Similarly, consultation of the website for AbeBooks – an online international consortium of used book dealers – soon allowed me to locate and purchase my own personal copy of *The Murder in the Laboratory* (figure 2) and quickly revealed that it had indeed been a winner of "Messrs. Methuen's Detective Story Competition," but had taken second, rather than first place, as suggested by Kasman so many years ago. The second place prize had been for £150 and the judges had included the British author, A. A. Milne, best known as the creator of Winnie-the-Pooh, though the influential publication, *A Catalogue of Crime*, later begged to differ with the judges when it observed that "Davidson's work is far superior to that which won the first prize." First published in England by Methuen in 1929 and simultaneously in the United States by E. P. Dutton as part of "The Dutton Mystery of the Month" series, it was also eventually reissued by Newnes as an inexpensive paperback.

THE MURDER
IN THE LABORATORY

BY

T. L. DAVIDSON

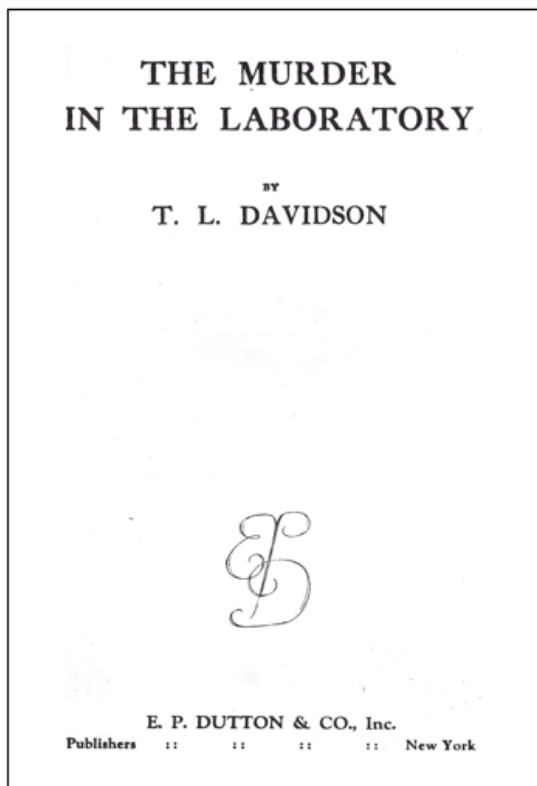E. P. DUTTON & CO., Inc.
Publishers :: :: :: :: New York

Figure 2. Title page of the American edition of T. L. Davidson's *The Murder in the Laboratory*.

The Murder in the Laboratory is not set in a chemistry department but rather in the toxicology department of a prominent medical school, and opens at 10:00 p.m. in the evening with an undergraduate named George Wroxham searching the halls of the largely deserted medical school building for the laboratory of one Walter Sheppery. Sheppery is working late at night on a series of tedious determinations of the arsenic content of pickles and during the waiting period between runs has agreed to tutor Wroxham in biochemistry. Initially unable to find Sheppery's laboratory, Wroxham instead encounters the laboratory of another late-night denizen of the building by the name of Martin Blythe who shows Wroxham to Sheppery's laboratory, where the two of them discover Sheppery dead on the floor with a bottle containing a solution of sodium cyanide, an empty pipette, and a beaker containing the pipetted sodium cyanide solution on the bench above him.

There is no doubt that Sheppery has died of cyanide poisoning and, at first glance, it appears that he had accidently swallowed some of the cyanide solution while pipetting it by mouth. However, Blythe notices that the door to Sheppery's analytical balance is open and that there are weights and a crucible still on the pans. Inspection of Sheppery's laboratory notebook reveals that he had begun recording the weight of the crucible but had suddenly stopped writing after the first digit. Why would he interrupt recording the weight in order to go to the other end of the laboratory and begin pipetting sodiium cyanide? In addition, though Sheppery had obviously been dead for only about 20 minutes when he was found, the lights to his laboratory were turned off when Wroxham and Blythe arrived. Why would he pipette sodium cyanide in the dark? In light of these discrepancies, Blythe quickly concludes that they are looking at a case of murder rather than an accident.

It turns out the Blythe, who is described as having a degree in chemistry rather than medicine, is in fact a well-known toxicologist and one of the stars of the medical school, and it is he who eventually solves the crime. However, the middle part of the novel is consumed in a rather tiresome search for clues and suspects outside of the medical school by Inspector Mellison of Scotland Yard, who has taken charge of the case, and who manages to misinterpret most of what he discovers. Only towards the end of the book does the story once again revert to the medical school, where Blythe has succeeded in solving the crime using data recovered there – a resolution which involves the use of pencils to record laboratory data and the construction of laboratory fume hoods.

Part of the resolution also requires the testing of various recovered items for traces of cyanide, a task which Blythe assigns to his laboratory assistant Russell (11):

Mellison came into Blythe's room at two o'clock sharp feeling slightly worried. He found Blythe and Russell engaged in some mysterious chemical operation ... "Now this is important, Mellison," he said. "Half the case hangs on this, so I want you to watch. These two test tubes contain prepared extracts from the two bits of paper, and I'm going to add this ferric chloride solution to them."

He did so, and the fluid in one of the test tubes turned blue, while the other remained colorless.

"The blue color – Prussian blue, actually," Blythe explained, "shows the presence of cyanide. It was present only in the piece of paper which was written on by the second pencil – the murder's pencil." ...

"Now these are extracts of the gloves you saw me cutting up this morning," he went on, "two from each glove, fingers in one and palm and back in the other. Have you got the numbers I gave you Russell?"

Russell pushed across a sheet of paper and stood watching intently as Blythe dropped in the brown ferric chloride. One of the tubes turned deep blue, one faintly greenish blue, the other two remained clear.
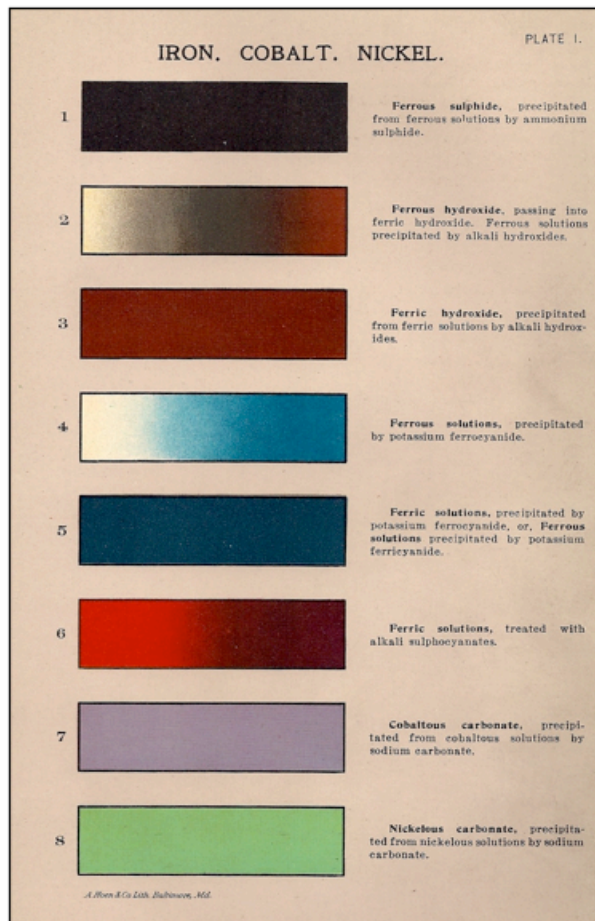
Figure 3. A typical color chart for selected precipitates of iron, cobalt and nickel from a period textbook for medical students. The color for both Prussian blue and Turnbull's blue is shown as strip 5.

"See that!" said Blythe, glancing at the paper. "The fingers of the left-hand glove were full of cyanide, and there was a little on the rest of the glove. The right-hand glove had hardly any, but I think I see traces in the extracts from the fingers.

Prussian Blue

The formation of Prussian blue was a standard toxicological test for cyanide (12). The resulting blue pigment (figure 3), which was first discovered in the 18th century, was originally made by reacting ferric chloride or iron trichloride with tetrapotassium hexacyanoferrate(II), otherwise known as potassium ferrocyanide, $K_4[Fe^{II}(CN)_6]$. The version produced in the cyanide test was probably the form known as "soluble" Prussian blue, though it is in fact a colloidal suspension of a solid precipitate. As originally described in chemistry textbooks, it was thought to correspond to the complex salt, potassium

iron(III) hexacyanoferrate(II) or $KFe^{III}[Fe^{II}(CN)_6]$. For many years a second blue pigment, known as Turnbull's blue, was also described in chemistry textbooks. Made by reacting ferrous chloride or iron dichloride with tripotassium hexacyanoferrate(III), otherwise known as potassium ferricyanide, $K_3[Fe^{III}(CN)_6]$, it was thought to correspond to the complex salt, potassium iron(II) hexacyanoferrate(III) or $KFe^{II}[Fe^{III}(CN)_6]$.

Both of these compounds are now known to be identical and are best described by the formula $K[Fe^{II}Fe^{III}(CN)_6]$. The change in the position of the left-hand square bracket is significant as no discrete octahedral complex anions are present but rather an infinitely extended 6/2 framework structure (figure 4) in which 50% of the cationic sites are occupied by Fe(III) ions and 50% by Fe(II) ions, and the K^+ ions are located in the interstitial cavities. The intense blue color is not due to d-d transitions but rather to a strong charge-transfer transition between the Fe(II) and Fe(III) sites. In the presence of excess Fe^{3+} ions an insoluble variation of Prussian blue is produced which is best described by the formula $Fe_4^{III}Fe_3^{II}(CN)_{18} \cdot xH_2O$. This has a more complex structure derived from that of the colloidal form.

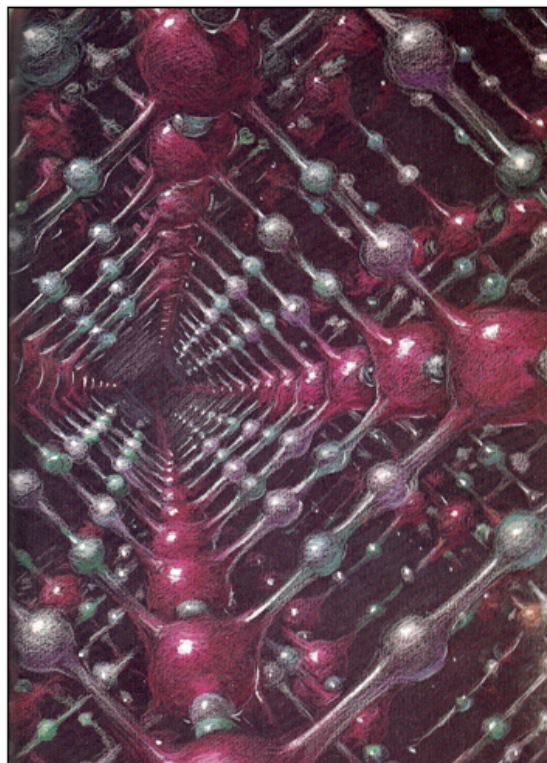Though the performance of the Prussian blue test for cyanide might be thought of as the chemical climax

Figure 4. An artist's rendition of the interior of the anionic lattice of colloidal Prussian blue.

of the novel, it is also unfortunately the one instance in which Thomson's chemical instincts failed him. As may be seen from its formula, the formation of Prussian blue requires the presence of both Fe^{3+} and Fe^{2+} ions. Consultation of period textbooks on either medicinal chemistry or toxicology reveals that the Prussian blue test was always performed using a mixture of ferric and ferrous ions, either in the form of the chlorides or the sulfates, followed by addition of potassium hydroxide and subsequent acidification with hydrochloric acid.

The K(OH) temporarily removed the the Fe^{3+} ions from solution by precipitating them as iron trihydroxide:

$$Fe(aq)^{3+} + 3(OH)(aq)^- \rightarrow Fe(OH)_3(s) \qquad [1]$$

and also ensured that any cyanide present was in the form of free CN^- ions rather than as neutral HCN molecules, thereby facilitating reaction with the Fe^{2+} ions to form the requisite hexacyanoferrate(II) complex:

$$Fe(aq)^{2+} + 6CN(aq)^- \rightarrow [Fe(CN)_6](aq)^{4-} \qquad [2]$$
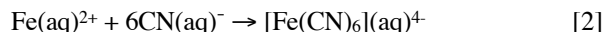
Acidification with HCl then once again released the Fe^{3+} ions, thereby allowing them to react with the $[Fe(CN)_6]^{4-}$ complex to produce a telltale precipitate of Prussian blue:

$$[Fe(CN)_6](aq)^{4-} + Fe(OH)_3(s) + 3H(aq)^+ + K(aq)^+ \rightarrow$$
$$K[Fe^{III}Fe^{II}(CN)_6](s) + 3H_2O(l) \quad [3]$$
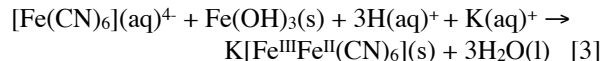
Some older textbooks report using ferrous sulfate alone in the first step. This often worked because ferrous salts are almost always contaminated with some ferric ions formed by air oxidation of their solutions, as shown by the gradual bluing of strip 4 in figure 3. But whether one used a mixture of ferric and ferrous salts or the ferrous salt alone, what is certain is that a solution of pure ferric chloride, like that used by Blythe in the novel, would not be able to form a precipitate of Prussian blue in the presence of cyanide ion. In short, Thomson had chosen the wrong oxidation state of iron for his cyanide test!

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Monsieur de Maupassant and Phosphure de Calcium

The Chemistry of Phosphure de Calcium

The other day, while idly thumbing through a rather thick volume of the collected short stories of the 19th-century French author, Guy de Maupassant (figure 1), my eye caught a paragraph designed to excite the interest of any full-blooded chemist worth his salt and, I suppose, his acids and bases as well. It read (1):

I had just finished my second term at college and had been particularly interested in chemistry and especially in a compound called phosphure de calcium which, when thrown in water, would catch fire and explode, followed by fumes of an offensive odor. I had brought a few handfuls of this compound with me, so as to have fun with it during my vacation.

"Phosphure de calcium" or tricalcium diphosphide, as it is now known to English-speaking chemists, was first made by George Pearson in 1792 by passing phosphorus vapor over quicklime heated to
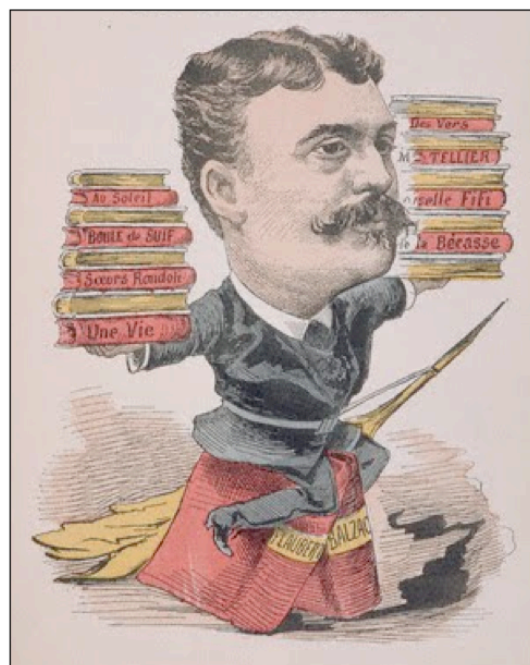

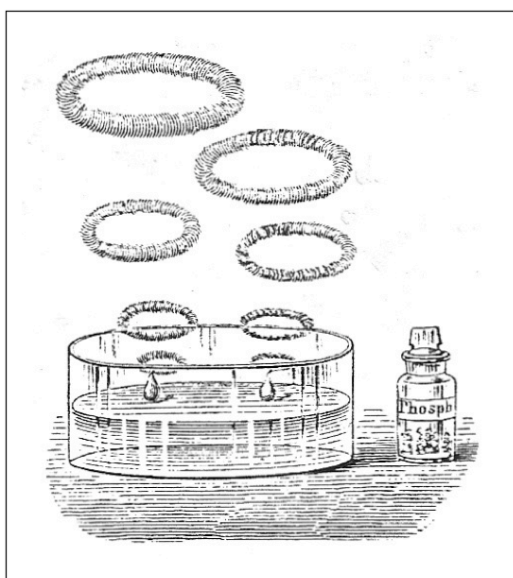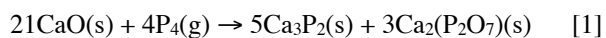Figure 1. A period caricature of Guy de Maupassant (1850-1893).

dull redness. The resulting product was a mixture of impure tricalcium diphosphide and dicalcium pyrophosphate (2):

$$21CaO(s) + 4P_4(g) \rightarrow 5Ca_3P_2(s) + 3Ca_2(P_2O_7)(s) \quad [1]$$

It was later made in a much purer form by P. Vigier by melting calcium and phosphorus together under petroleum (3).

When dropped in water, Ca_3P_2 hydrolyzes to give calcium dihydroxide and trihydrogen phosphide gas, otherwise known as phosphine or monophosphane:

$$Ca_3P_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(s) + 2H_3P(g) \quad [2]$$
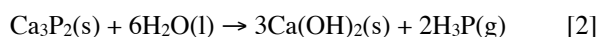
and the latter ignites on contact with air, generating characteristic circular rings of white tetraphosphorus decaoxide (figures 2 and 3):

$$4H_3P(g) + 8O_2(g) \rightarrow P_4O_{10}(s) + 6H_2O(g) \quad [3]$$

Figure 2. Characteristic smoke rings of P_4O_{10} produced by the hydrolysis of tricalcium diphosphide as depicted in R. Arendt, L. Doermer, *Grundzüge der Chemie und Mineralogie*, Voss: Leipzig, 1919, p. 288.
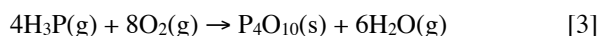
Figure 3. Characteristic smoke rings of P_4O_{10} produced by the spontaneous ignition of the hydrides of phosphorus generated by heating white tetraphosphorus in a concentrated KOH solution as depicted in J. H. Pepper, *The Boy's Playbook of Science*, Routledge: London, 1860, p. 171.

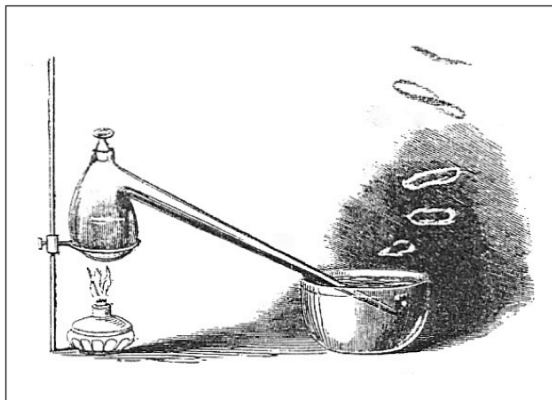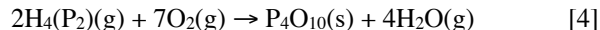As written, these reactions are actually oversimplifications, since it turns out that pure trihydrogen phosphide is not spontaneously flammable. Rather it is the minute traces of tetrahydrogen polydiphosphide or $H_4(P_2)$ gas, generated simultaneously by the hydrolysis reaction, that in reality cause the mixture to ignite:

$$2H_4(P_2)(g) + 7O_2(g) \rightarrow P_4O_{10}(s) + 4H_2O(g) \qquad [4]$$

This, in turn, probably results from the contamination of the Ca_3P_2 with dicalcium polydiphosphide, $Ca_2(P_2)$, a compound which, when pure, gives $H_4(P_2)$ as the primary product of its hydrolysis (4):

$$Ca_2(P_2)(s) + 4H_2O(l) \rightarrow 2Ca(OH)_2(s) + H_4(P_2)(g) \qquad [5]$$

This supposition is further supported by the fact that pure Ca_2P_3 has a blackish-violet appearance, whereas the product generated in equation 1 is reddish-brown, suggesting contamination with the brick-red polydi-
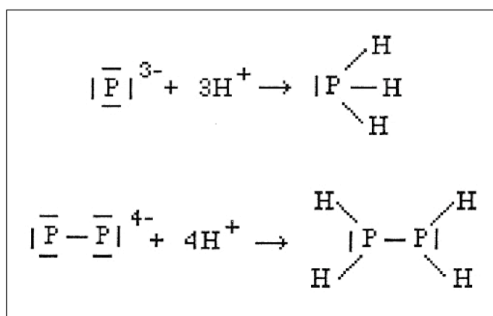

Figure 4. The structural interpretation of reactions 2 and 5 as phosphide anion protonations.

phosphide. In addition, Mg_3P_2, which has no corresponding $Mg_2(P_2)$ analog, does not give a spontaneously flammable product upon hydrolysis (5).

The structural interpretation of these reactions is also of some interest. Both Ca_3P_2 and $Ca_2(P_2)$ are so-called Zintl phases (i.e., compounds representing the transition from ionic to metallic bonding) and both their structures and hydrolysis reactions can be rationalized in terms of the generalized 8-N rule (6). If the compounds are formally treated as having pure ionic bonding involving positive calcium ions, on the one hand, and appropriately charged phosphorus atoms, on the other, then the phosphorus atoms will homocatenate to give covalently-bonded polyphosphide anions with structures similar to those of a neutral isoelectronic element.

Thus, in Ca_3P_2, the P atoms are formally P^{3-} anions. They are, therefore, isoelectronic with Ar atoms and should exist as isolated monoatomic phosphide anions in the solid compound. No complete crystal structure appears to have been done on Ca_3P_2 but the isoelectronic species Be_3P_2, Mg_3P_2, Sr_3P_2, and Ba_3P_2 all have structures consistent with this prediction and there is no reason to suspect that the calcium compound is an exception (7). Likewise, in $Ca_2(P_2)$ the P atoms are formally P^{2-} ions and are thus isoelectronic with Cl atoms. Consequently we would expect them to dimerize into polydiphosphide P_2^{4-} anions, paralleling the formation of diatomic Cl_2 molecules, an expectation which is again confirmed by the crystal structure (8). The hydrolysis reactions of the two compounds may, therefore, be viewed as direct anion protonations, as shown in figure 4.

Ignus Fatuus

The spontaneous ignition of H_3P and $H_4(P_2)$ gas generated by the decomposition of dead organic matter, particularly in peat bogs, swamps, and damp cemeteries, has been traditionally invoked to explain away the phenomenon of *ignis fatuus* (figure 5) or silly fire, also variously known as Jack-o'-lanterns, Will-o'-the-wisps, *feux follets*, corpse candles, and flying saucers (5), though the validity of this and other traditional rationales (e.g., electrical plasmas, combustion of methane, bioluminescence, etc.) has been recently challenged by Mills, who was, however, unable to suggest any satisfactory alternative (9).

The Practical Joke

Given the above chemistry and the knowledge that Maupassant's short story is entitled "A Practical Joke," it is not difficult to imagine what must follow. The nar-
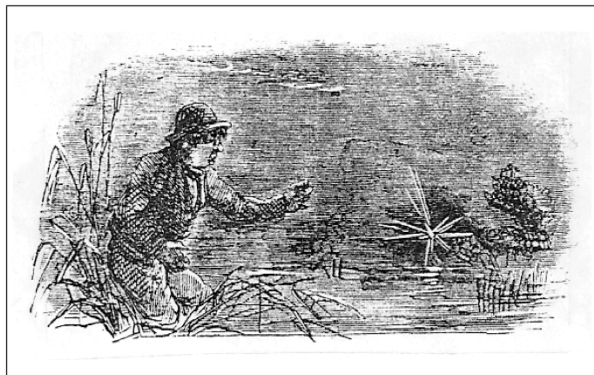
Figure 5. A 19th-century depiction of an unwary traveler being lured into a swamp by a Will-o'-the-wisp as found in J. H. Pepper, *The Boy's Playbook of Science*, Routledge: London, 1860, p. 172.

rator, home from school for summer vacation, is particularly irritated by one of his father's house guests (1):

An old lady named Mme. Dufour often visited us. She was a cranky, vindictive old thing. I do not know why, but somehow she hated me. She misconstrued everything I did or said, and she never missed a chance to tattle about me ... She wore a wig of beautiful brown hair, though she was more than sixty, and the most ridiculous little caps adorned with pink ribbons. She was well thought of because she was rich, but I hated her to the bottom of my heart, and I resolved to revenge myself by playing a joke on her.

Waiting until evening, the would-be jokester sneaks up to Mme. Dufour's rooms. Carefully drying the chamber pot and filling it with a handful of calcium phosphide, he then runs to his garret bedroom to await developments (1):

Pretty soon I heard everyone coming upstairs to bed. I waited until everything was still, then I came downstairs barefooted, holding my breath, until I came to Mme. Dufour's door and looked at my enemy through the keyhole.

She was putting her things away, and having taken her dress off, she donned a white wrapper. She then filled a glass with water and putting her whole hand in her mouth as if she were trying to tear her tongue out, she pulled out something pink and white which she deposited in the glass. I was horribly frightened, but soon found it was only her false teeth she had taken out. She then took off her wig ... kneeled down to say her prayers, got up and approached my instrument of vengeance. I waited awhile, my heart beating with expectation.

Suddenly I heard a slight sound; then a series of explosions. I looked at Mme. Dufour; her face was a study. She opened her eyes wide, then shut them again and looked. The white substance was crackling, exploding at the same time, while a thick white smoke curled up mysteriously toward the ceiling.

Perhaps the poor women thought it was some satanic fireworks, or perhaps that she had been suddenly afflicted with some horrible disease; at all events, she stood there speechless with fright, her gaze riveted on the supernatural phenomenon. Suddenly she screamed and fell swooning to the floor. I ran to my room, jumped into bed, and closed my eyes trying to convince myself that I had not left my room and had seen nothing.

"She's dead," I said to myself; "I have killed her," and I listened anxiously to the sound of footsteps. I heard voices and laughter and the next thing I knew my father was soundly boxing my ears.

Mme. Dufour was very pale when she came down the next morning and she drank glass after glass of water. Perhaps she was trying to extinguish the fire which she imagined was in her, although the doctor assured her that there was no danger. Since then, when anyone speaks of disease in front of her, she sighs and says: "Oh, if you only knew! There are such strange diseases"

Regrettably, standard biographies of Maupassant are silent on whether he ever received any formal chemical training, though they do point out that he was a realist and claim that he never wrote about anything he hadn't directly experienced for himself. Indeed, Mme. Dufour's reactions may not have been completely psychological in nature. Phosphine gas is highly toxic, causing cold sweats, weakness, extreme thirst, and, in large amounts, death by paralysis of the respiratory system. Mellor reports that one part of phosphine per 100,000 parts of air is fatal in 16-30 hours, 2.5 parts per 100,000 in 8.5-10 hours, and one part per 10,000 in 2.5-3.5 hours (5). Presumably, these data were obtained using white mice rather than summer house guests.

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Publication History

Captain Nemo's Battery

Chemistry and the Science Fiction of Jules Verne

The Father of "Scientifiction"

My high school English teacher always insisted that the first prerequisite of a good essay was a catchy title, and I flatter myself that my choice for this literary excursion is not half bad. Thus, it is with a great deal of reluctance that I must also immediately confess that it is misleading – misleading because of the existence of two very common and widespread myths about Jules Verne (figure 1).

The first and most fundamental of these is the myth that Verne wrote science fiction – indeed that he not only wrote it but actually invented the genre. This misconception appears to be due to none other than Hugo Gernsback, who in April of 1926 began publication of *Amazing Stories*, America's first science fiction pulp magazine. In his introductory editorial, Gernsback explained exactly what he meant by the kind of literature that he called "scientifiction" – a rather unmelodious term that has happily disappeared from the English lexicon (1):

By scientifiction I mean the Jules Verne, H. G. Wells and Edgar Allan Poe type of story – a charming romance intermingled with scientific fact and prophetic vision.

Figure 1. Jules Verne (1828-1905).

Later, Gernsback would single Verne out from this trio as the "patron saint" of the genre, and the masthead of the magazine would carry a drawing of Verne's tomb at Amiens as a symbol of his everlasting "immortality."

However, as Arthur Evans has shown in his book, *Jules Verne Rediscovered*, Verne never wrote science fiction – or at least not science fiction as the term is now understood (3). There are no alien monsters, no mysterious superforces, no time travel, no magic materials, and no heroines in skimpy futuristic attire in his novels. Rather, his works are a part of a tradition of French didactic writing known as the so-called "scientific novel" and were intended as a way of painlessly popularizing science for the lay public. They use an adventure story, combined with novel but not improbable applications of existing technology, as a framework into which are inserted sizable digressions on the facts of zoology, botany, geography, astronomy, phys-

ics, and occasionally even chemistry. In the course of his life, Verne would write over 60 of these novels.

The second common myth is that Verne wrote primarily for children and young adults. This is due to the fact that most English translations of his works have been butchered, with many of the didactic digressions on science – their very *raison d'etre* – having been either deleted or shortened to the point of becoming incomprehensible (3). It was only in the 1970s that Walter James Miller began publishing restored and annotated editions of some of Verne's classics, and it was the reading of Miller's restored edition of *Twenty Thousand Leagues under the Sea* (4) that first awoke my interest in Verne's use of chemistry.

Twenty Thousand Leagues under the Sea

First published in 1870, the novel opens with reports of

a strange sea monster that has been terrorizing shipping in both the Atlantic and Pacific oceans. The famous French scientist, Professor Aronnax (figure 2), who has been visiting the United States accompanied by his trusty servant, Conseil, agrees to join a U.S. expedition to hunt down the monster. As a result of the expedition's first encounter with the creature, Aronnax, Conseil, and a Canadian harpooner named Ned Land are thrown overboard and become the uninvited guests of Captain Nemo aboard his submarine, the *Nautilus*, which is, of course, the source of the reports of the sea monster.

The first digression on chemistry comes when Aronnax awakens after his first night as a prisoner on the *Nautilus* [4]:

I breathed with difficulty. The heavy air seemed to oppress my lungs. Although the cell was large, we had evidently consumed a great part of the oxygen it contained. Indeed, each man consumes, in one hour, the oxygen contained in more than 176 pints of air and this air, charged with a nearly equal quantity of carbonic acid [carbon dioxide], becomes unbreathable. It became necessary to renew the atmosphere of our prison and no doubt of the whole submarine boat. That gave rise to a question in my mind. How would the commander of this floating dwelling proceed? Would he
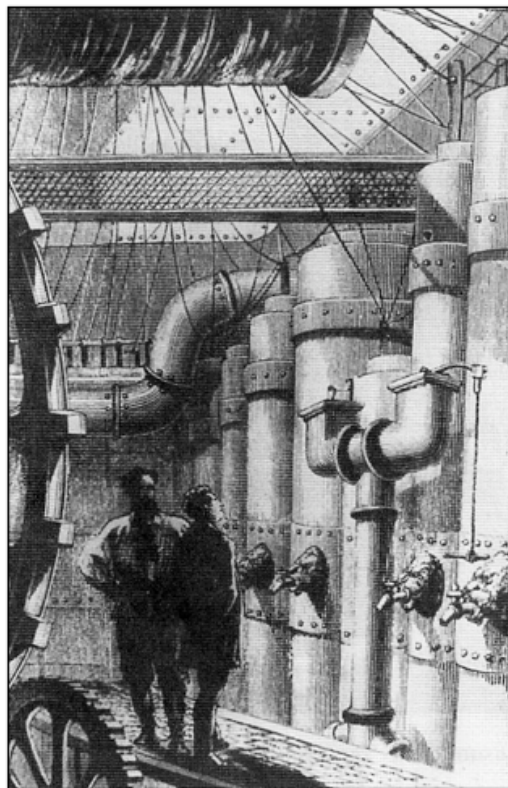

Figure 3. The engine room of the *Nautilus*.

obtain air by chemical means, in getting by heat the oxygen contained in chlorate of potass [potassium chlorate], and in absorbing carbonic acid by caustic potash [potassium hydroxide]?

In other words, Aronnax is proposing the use of the following standard reactions as a means of maintaining the air quality aboard the Nautilus (5):

$$2KClO_3(s) + heat \rightarrow 2KCl(s) + 3O_2(g) \qquad [1]$$

$$2KOH(aq) + CO_2(g) \rightarrow K_2CO_3(aq) + H_2O(l) \qquad [2]$$
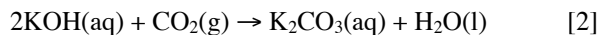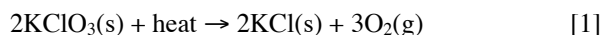
In the end, however, he decides that this chemical scheme is impractical and that surfacing every 24 hours, like a whale, to replenish the air supply would be best, which is in fact exactly what Nemo does.

The most interesting digression on chemistry, however, occurs when Nemo shows Aronnax the engine room of the *Nautilus* and they discuss how the submarine is powered (figure 3). This is also the part of the novel that has been most flagrantly misrepresented, since in Walt Disney's 1954 movie adaptation – starring James Mason as Nemo, Paul Lukas as Aronnax, Kirk Douglas as Ned Land, and Peter Lorre grotesquely miscast as Conseil – it is implied that the *Nautilus* is

Figure 2. Professor Aronnax (modeled by the artist Riou on Jules Verne as a young man).

powered by atomic energy and that Verne foresaw the nuclear age (6). However, Nemo is very explicit about the power source of his submarine (4):

There is a powerful agent, obedient, rapid, easy, which conforms to every use, and reigns supreme on board my vessel. Everything is done by means of it. It lights it, warms it, and is the soul of my mechanical apparatus. This agent is electricity.

We need to remember that in 1870 electricity was the power source of the future just as atomic energy was in 1954. And what is the source of Nemo's electricity? The answer is none other than chemical voltaic cells or batteries.

At the time Verne was writing, there were three important types of chemical voltaic cells (figure 4): the Grove cell, invented by the British chemist, William Grove, in 1839; the Bunsen cell, invented by the German chemist, Robert Bunsen, in 1841; and the dichromate or bichromate cell, apparently proposed by several different scientists in the period 1841-1842, including Bunsen, the German physicist Johann C. Poggendorff, and the Englishman Robert Warington (7, 8).

The Grove and Bunsen cells were both based on the same chemical reactions, namely, the oxidation of zinc at the anode:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E° = +0.76 \text{ V} \quad [3]$$

and the reduction of nitric acid at the cathode for a net cell potential of 1.72 V:

$$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow$$
$$NO(g) + 2H_2O(l) \quad E° = +0.96 \text{ V} \quad [4]$$
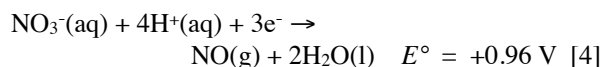
the colorless nitrogen oxide by-product quickly reverting to reddish-brown nitrogen dioxide on contact with air (9). The sole difference between the two was that Bunsen had replaced the expensive platinum cathode of Grove's original cell with an inexpensive one made of porous coke.

Grove or Bunsen cells would have been impractical on a submarine because of the necessity of venting the NO_2 fumes, so the best choice would have been the dichromate cell, which substituted the reduction of the dichromate anion for the reduction of nitric acid at the cathode:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow$$
$$2Cr^{3+}(aq) + 7H_2O(l) \quad E° = +1.33 \text{ V} \quad [5]$$
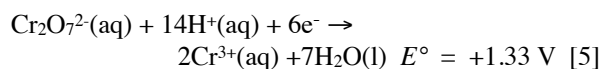
and in the process also increased the net standard potential of the cell from 1.72 V to 2.09 V (10).
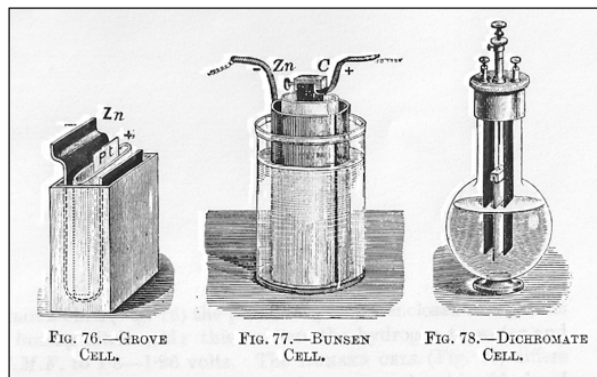

Figure 4. *From left to right:* Typical 19th-century Grove, Bunsen, and dichromate cells.

Nemo, however, has a fetish about obtaining all of his material needs from the ocean and, when Aronnax asks him where he gets the zinc for his batteries, he replies that he doesn't use zinc, but rather sodium metal extracted from seawater (4):

So it is this sodium that I extract from sea water, and of which I compose my ingredients ... Mixed with mercury, sodium forms an amalgam which can take the place of zinc in Bunsen batteries. The mercury is never consumed, only the sodium is used up, and that is supplied from sea water. Moreover, sodium batteries are the most powerful, since their motive force is twice that of zinc batteries.

Though Verne does not cite quantitative $E°$ values, it is interesting to note that use of modern data shows that Verne's estimate of the "idealized" relative strength of Captain Nemo's sodium/dichromate cell, versus that of the conventional zinc/dichromate cell, is accurate (i.e., 4.04 V versus 2.09 V) provided one uses the standard reduction potential for pure sodium metal [11]:

$$Na(Hg) \rightarrow Na^+(aq) + e^- \qquad E° = +2.71 \text{ V} \quad [6]$$

This strongly suggests that Nemo's cell was based on an actual experimental account published in the scientific literature of the period. Though I have not been able to trace the original reference, the most likely candidates for all of Verne's information on electrochemistry, as we will see in greater detail later, are the writings of the French electrochemist Antoine-Cesar Becquerel (1788-1878). In passing, it is also of interest to note that Antoine-Cesar was the grandfather of Antoine-Henri Becquerel, best known for his discovery of radioactivity in 1896 (12).

Aronnax then raises the question of how Nemo extracts his sodium (4):

I can see how sodium serves your needs. And there is plenty of it in sea water. But you have to manufacture it, to extract it. How? You could use your batteries to extract it, but it seems to me you would need more sodium for such equipment than it would be extracting. I mean, would you not consume more than you produce?

In short, Aronnax is suggesting that Nemo use his batteries to electrolyze seawater:

$$\text{electricity} + 2NaCl(aq) \rightarrow 2Na(Hg) + Cl_2(g) \qquad [7]$$
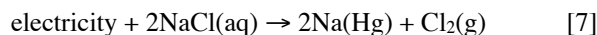
though he immediately realizes that such a process would violate the conservation of energy. Nemo replies:

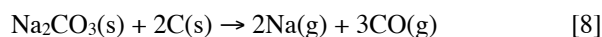*No, I do not use batteries, at least not for the extraction process. I use heat generated by coal.*

This answer is ambiguous but probably refers to the production of sodium via the carbon reduction of sodium carbonate, which was the standard method of manufacture in the 1870s (13):

$$Na_2CO_3(s) + 2C(s) \rightarrow 2Na(g) + 3CO(g) \qquad [8]$$

In keeping with his theme of "all from the sea," Nemo implies that he mines the necessary coal at the bottom of the ocean. However, the need to convert NaCl into Na_2CO_3, which requires use of either the Leblanc or the Solvay process, as well as the necessity of manufacturing the sulfuric acid and potassium dichromate required for the cathode reaction, strongly suggest that Nemo must have a land base somewhere to carry on these processes, and, as we will see later, this is indeed the case.

Note that not only is Nemo's claim of "all from the sea" chemically weak in this case, it is also geologically weak, as the coal that he mines on the bottom of the ocean is certainly not a product of the ocean itself but the result of the submergence of conventional land-based coal deposits formed from the decomposition of prehistoric land-based plant life. Indeed, in a later chapter entitled "The Submarine Coal Mines," Verne as much as admits that this is the case, though Nemo's submerged coal deposits are rather improbably located in the crater of an extinct volcano which is connected to the ocean via an underwater system of caves. Prior to large-scale industrialization and mining of coal in the eighteenth century, chunks of coal were often found along ocean beaches, where they were collected by women and children. Though this material was actually broken off from submerged shore-line coal outcroppings and washed ashore by wave action, it appeared to the common man to be a product of the

ocean and was consequently known as "sea coal." This incorrect association was still prevalent among the uneducated classes in the nineteenth century and is exploited by Nemo in the course of his discussion with Aronnax.

One final point of interest. When Nemo takes Aronnax for a walk on the ocean floor in one of his special diving suits, Aronnax asks Nemo what he uses to light his way in the blackness of the ocean abyss (figure 5). Nemo replies that he uses one of his special sodium batteries and a "Ruhmkorff apparatus" (i.e., an induction coil) connected to a special lantern (4):

In this lantern is a spiral glass which contains a small quantity of carbonic gas [carbon dioxide]. When the apparatus is at work this gas becomes luminous, giving out a white and continuous light.

What Nemo is describing is, of course, a Geissler tube – a sort of crude precursor of the fluorescent light (figure 6) – and this same contrivance is used to light the interior of the Nautilus. H. W. Meyer in his book, *A History of Electricity and Magnetism*, describes a similar device (14):

About the year 1895, D. McFarlan Moore of the United States began experimenting with long glass tubes filled
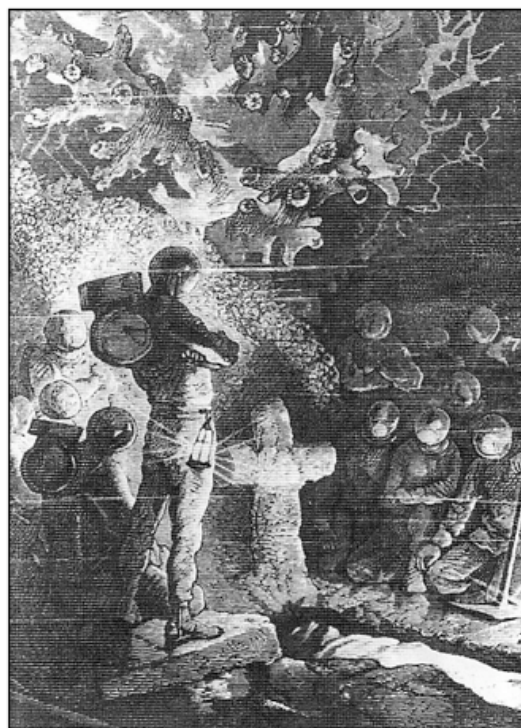

Figure 5. Captain Nemo's electric carbon dioxide lamps at work.

with carbon dioxide gas, which gave off a good quality white light when a current of electricity was sent through them at relatively high voltage. Beginning about the year 1904, many installations of such tube lighting were made, especially in stores.

So it would appear that Verne was prophetic about new applications of existing technology after all!

The Mysterious Island

This brings us to the sequel to *Twenty Thousand Leagues under the Sea*, the three-part novel *The Mysterious Island*, which was published in 1874, four years after *Twenty Thousand Leagues* (15). Set during the American Civil War, the story involves a group of Union prisoners held in Richmond, Virginia, who escape the city in March of 1865 in a Confederate observation balloon in the midst of a violent storm. The storm blows them west across the United States and out into the Pacific Ocean, where they crash on an uncharted island. Events eventually reveal that this island is one of Captain Nemo's land bases, hinted at in *Twenty Thousand Leagues*, but it is the first two parts of the novel that are of most interest to us.

Unlike the castaways in Johann Wyss's famous novel *The Swiss Family Robinson*, who have access to the cargo of their wrecked ship and are amply supplied with tools, provisions, guns, and domestic animals, the castaways in Verne's novel have only the clothes on their backs, the knowledge in their heads, and a single
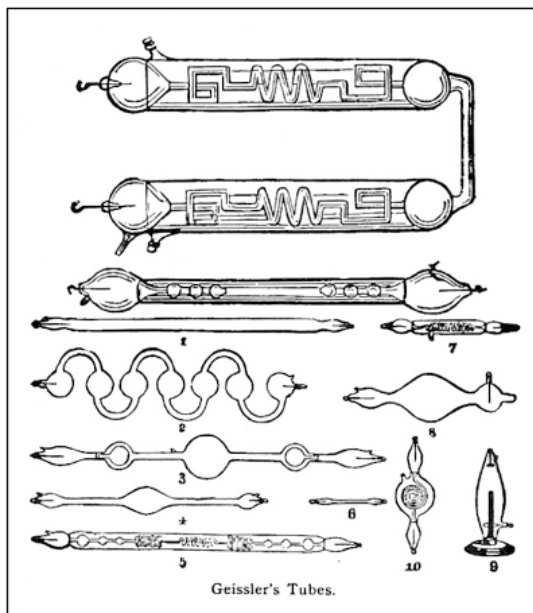

Figure 7. Cyrus Harding, the engineer-hero of *Mysterious Island*.

match – the wrecked balloon having been blown back out to sea (16). What follows might be appropriately called "The Chemical Swiss Family Robinson." It is a paean to the now defunct advertising phrase "better things for better living through chemistry" and a celebration of the engineer as hero.

The engineer in question is one Cyrus Harding (figure 7), and the worship of his fellow castaways is apparent from the beginning of the novel (15):

The engineer was to them a microcosm, a compound of every science, a possessor of all human knowledge. It was better to be with Cyrus Harding on a desert island than without him in the midst of the most flourishing town in the United States. With him they could want nothing; with him they would never despair.

The island itself, which the castaways name "Lincoln Island" in a display of patriotism, is of volcanic origin and is particularly rich in minerals. What follows is a partial chronology of the rise of "chemical man" on Lincoln Island, and it goes without saying that in each instance Verne inserts a short digression painlessly describing for the reader the chemistry involved.

Within eight days of their arrival (i.e., by the 31st of March) Cyrus Harding has discovered pyrites, clay, limestone, and coal deposits on the island. These materials are quickly put to use. Between the 2nd and 15th of April, the castaways manufacture bricks from fired

Figure 6. Typical 19th-century Geissler tubes.

clay and make mortar from stone and lime, the latter being produced by thermally decomposing limestone and slaking the resulting quicklime with water (13, 15):

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad [9]$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \qquad [10]$$
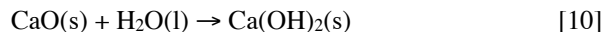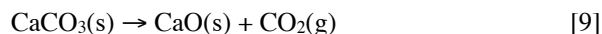
The bricks and mortar are then used to construct a pottery kiln (figure 8), which the castaways use to fire crude pots, dishes, etc.

By the 17th of April, Harding has added niter (KNO_3) and iron ore to his mineralogical discoveries and begins the construction of a large bellows using the skin of a dead seal and clay pipe manufactured in the pottery kiln. Between the 21st of April and the 5th of May, the resulting forced-air furnace is used, along with the iron ore and the coal discovered earlier, to produce iron and steel (figure 9):
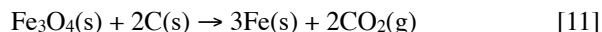
$$Fe_3O_4(s) + 2C(s) \rightarrow 3Fe(s) + 2CO_2(g) \qquad [11]$$

which is then employed to make crude saws, hammers, nails, axes, hatchets, chisels, spades, and pickaxes.

Between the 7th and 18th of May, Harding extracts green vitriol ($FeSO_4 \bullet 7H_2O$) and alum from schistose

Figure 9. The castaways make iron and steel.

pyrites and soda (Na_2CO_3) from the ashes of marine plants. He then uses the soda to produce soap and glycerin by saponifying the fat of a dugong that has been mysteriously killed after attacking the castaway's pet dog, Top:

$$Na_2CO_3(s) + H_2O(l) \rightarrow$$
$$2Na^+(aq) + OH^-(aq) + HCO_3^-(aq) \quad [12]$$

$$C_3H_5(OOCR)_3(s) + 3OH^-(aq) \rightarrow$$
$$C_3H_5(OH)_3(l) + 3RCOO^-(aq) \quad [13]$$

$$RCOO^-(aq) + Na^+(aq) \rightarrow Na(OOCR)(s) \qquad [14]$$
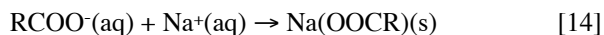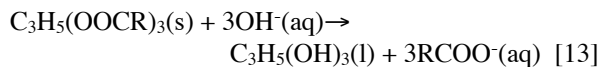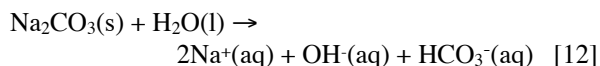
Given that Harding has already manufactured slaked lime (equations 9-10), it is surprising that he doesn't use it to convert his soda into caustic soda (NaOH):

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \rightarrow$$
$$2NaOH(aq) + CaCO_3(s) \quad [15]$$
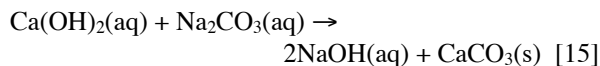
since this would have made a much more effective saponifying agent:

$$C_3H_5(OOCR)_3(s) + 3NaOH(aq) \rightarrow$$
$$C_3H_5(OH)_3(l) + 3Na(OOCR)(s) \quad [16]$$

Figure 8. The castaways make pottery.
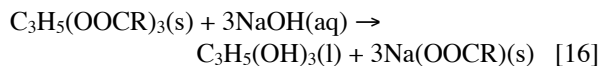
On the 20th of May, Harding, using chemical apparatus made in the pottery kiln, manufactures sulfuric acid via the destructive distillation of the green vitriol:

$$2FeSO_4 \cdot 7H_2O(s) \rightarrow$$
$$H_2SO_4(l) + Fe_2O_3(s) + 13H_2O(l) + SO_2(g) \quad [17]$$
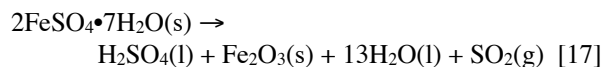
He then uses this, along with the niter discovered earlier, to produce concentrated "azotic acid" (nitric acid):

$$H_2SO_4(l) + 2KNO_3(s) \rightarrow K_2SO_4(s) + 2HNO_3(l) \quad [18]$$

and this, in turn, is used, in combination with the sulfuric acid and glycerin, to make nitroglycerin (figure 10), which is subsequently used for various large-scale engineering projects on the island:

$$C_3H_5(OH)_3(l) + 3HNO_3(l) \rightarrow$$
$$C_3H_5(NO_3)_3(l) + 3H_2O(l) \quad [19]$$
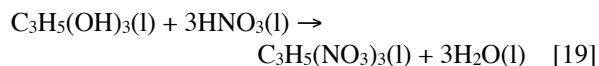
On the 5th of June, Harding manufactures candles from seal fat, lime, and sulfuric acid and, finally, to round out their first year on the island, he extracts sugar from a local variety of the maple tree on the 25th of August.
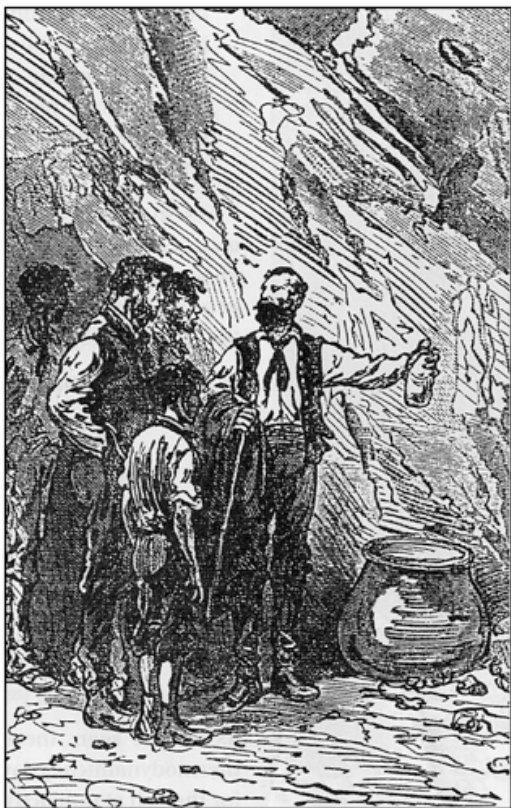
Figure 10. "It's nitroglycerin!"

In early January of their second year on the island, Harding uses his supply of sulfuric and nitric acids, in combination with native plant cellulose, to manufacture pyroxylin or guncotton. On the 28th of March, he makes glass using sand, chalk produced from limestone, and soda extracted from seaweed, and in January of their third, and last, year on the island, he decides to build an electric telegraph in order to facilitate communication between the various outposts that the castaways have established. This brings Verne back to the subject of electricity and chemical batteries. In this case, his choice is an unusual acid/alkaline battery invented in 1820 by the French physicist and electrochemist Antoine Cesar Becquerel, whom we met earlier in connection with Captain Nemo's sodium cell. Verne describes Becquerel's cell in great detail and in terms which strongly suggest that he has read Becquerel's original account (17, 18):

Cyrus Harding, after mature consideration, decided to manufacture a very simple battery ... in which zinc only is employed [obtained from the lining of a sea chest in which Captain Nemo has anonymously left supplies for the castaways]. The other substances, azotic [nitric] acid and potash [potassium carbonate], were all at his disposal. The way in which the battery was composed was as follows, and the results were to be attained by the reaction of acid and potash on each other. A number of glass bottles were made and filled with azotic acid. The engineer corked them by means of a stopper through which passed a glass tube, bored at its lower extremity, and intended to be plunged into the acid, by means of a clay stopper secured by a rag. Into this tube, through its upper extremity, he poured a solution of potash, previously obtained by burning and reducing to ashes various plants, and in this way the acid and potash could act on each other through the clay [see figure 11].

Cyrus Harding then took two slips of zinc, one of which was plunged into the azotic acid, the other into the solution of potash. A current was immediately produced, which was transmitted from the slip of zinc in the bottle to that in the tube, and the two slips having been connected by a metallic wire, the slip in the tube became the positive pole and that in the bottle the negative pole of the apparatus. Each bottle, therefore, produced as many currents as, united, would be sufficient to produce all the phenomena of the electric telegraph.

As in the case of Verne's paraphrase, Becquerel's own account of his cell tells us little about its chemistry other than the fact that dioxygen gas is generated at the anode, probably via the reaction (18):

$$4CO_3^{2-}(aq) + 2H_2O(l) \rightarrow$$
$$4HCO_3^-(aq) + O_2(g) + 4e^- \quad E° = -0.62 \text{ V } [20]$$
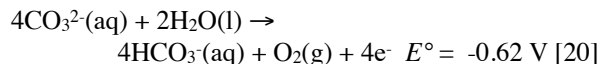
while Benjamin, who refers to it as the "Becquerel Oxygenated Gas Cell" in his 1893 treatise on the voltaic cell, claims that the cathode reaction corresponds to the reduction of the concentrated nitric acid to ammonium nitrate (19):

$$10H^+(aq) + NO_3^-(aq) + 8e^- \rightarrow$$
$$NH_4^+(aq) + 3H_2O(l) \quad E° = +0.88 \text{ V } [21]$$
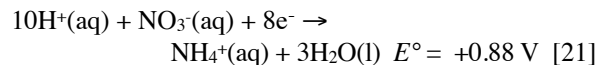
As can be seen, these half-reactions give us a thermodynamically favorable net potential of only +0.26 V for the cell at unit activities.

I must confess, however, to having certain reservations about representing the cathode reaction in terms of equation 21, since Latimer reports that the reduction of nitric acid to nitric oxide, as observed in the case of the Grove cell, is slightly more favorable (20):

$$4H^+(aq) + NO_3^-(aq) + 3e^- \rightarrow$$
$$NO(g) + 2H_2O(l) \quad E° = +0.96 \text{ V } [22]$$
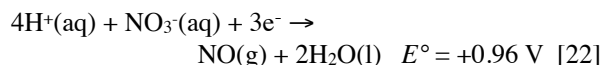
This would give us a favorable net potential of around +0.34 V at unit activity.

In his original account, Becquerel used platinum, rather than zinc, for his electrodes, and a quick replication of the cell in my laboratory, using a saturated potassium carbonate solution and 16 M nitric acid, gave a potential of around +0.87 V, provided that one used either platinum or nichrome wire electrodes, though I could observe no gas evolution at either electrode. This is not bad agreement given the enormous deviations from unit activities. Unfortunately, Verne's substitution of zinc in place of platinum for his electrode material appears to be the source of a serious defect in his scheme, since I found that all attempts to use zinc for the electrode in the nitric acid half-cell led to its rapid destruction, regardless of how dilute the acid (21).

Though Verne does not explicitly spell out his reasons for choosing this rather unusual cell, it appears to be related to the fact that the castaways have access to a continuous supply of only one metal – iron. As a consequence, they are unable to construct batteries based on the chemical difference between two metal electrodes, since that would lead to the net consumption of their strictly limited supply of zinc from the lining of the sea chest. Verne emphasizes this circumstance when he discusses their substitution of iron for lead in making shot for their guns and iron for copper when making the wires for their telegraph. If this is, in fact, the true reason for Verne's choice of a cell having two identical metal electrodes, then it is elegant testimony
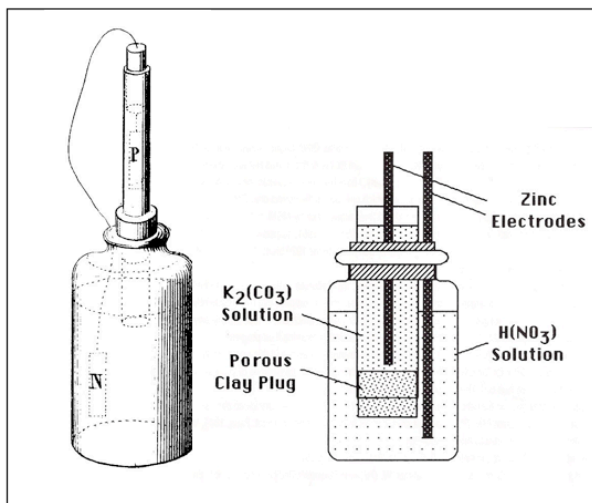
Figure 11. *Left:* Becquerel's original acid-alkali cell. *Right*: a reconstruction of the modified acid-alkali cell as described by Cyrus Harding in *The Mysterious Island*.

to the care with which he planned the scientific details of his novels, even though, as already indicated, he negated this advantage via his ill-advised substitution of zinc in place of platinum.

Based on his comments in both *Twenty Thousand Leagues under the Sea* and *The Mysterious Island*, there is little doubt that electricity was Verne's favorite choice as the power source of the future. Nevertheless, he was not unaware of society's ultimate dependence on fossil fuels, and at one point in *The Mysterious Island* he has the castaways discuss the possibility of a future energy crisis. A castaway by the name of Gideon Spilett begins this discussion by asking Harding how he is able to square the consequences of such a crisis with his habitually optimistic view of mankind's technological future (15):

But now, my dear Cyrus, all this industrial and commercial movement to which you predict a continual advance, does it not run the danger of being sooner or later completely stopped ... by the want of coal, which may justly be called the most precious of minerals.

Harding agrees but is not upset, as he foresees a future in which coal will be replaced by an alternative fuel (15):

Water ... but water decomposed into its primitive elements ... and decomposed, doubtless, by electricity which will then become a powerful and manageable force, for all great discoveries, by some inexplicable law, appear to agree and become complete at the same time. Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which

constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. Some day the coal-rooms of steamers and the tenders of locomotives will, instead of coal, be stored with these two condensed gases, which will burn in the furnaces with enormous caloric power. There is, therefore, nothing to fear. As long as the earth is inhabited it will supply the wants of its inhabitants, and there will be no want of either light or heat as long as the productions of the vegetable, mineral, or animal kingdoms do not fail us. I believe that when the deposits of coal are exhausted we shall heat and warm ourselves with water. Water will be the coal of the future.

In this selection Verne exploits the known difference in the heats of combustion per unit mass of dihydrogen gas versus carbon:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
$$\Delta H = \text{-142.93 kJ/g } H_2 \quad [23]$$

$$C(s) + O2(g) \rightarrow CO_2(g)$$
$$\Delta H = \text{-32.79 kJ/g C} \quad [24]$$
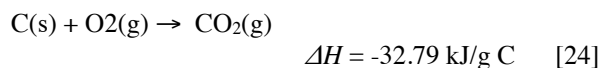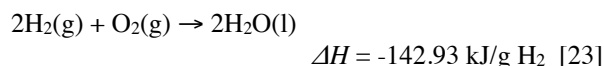
but unhappily fails to tell us how we are going to generate the electricity necessary to electrolyze all of this water in the first place.

Other Examples

Several of Verne's other novels also contain brief digressions on chemistry (22). Thus, in his famous account of space travel, *From the Earth to the Moon* (1865), he discusses the manufacture of aluminum using the Deville process, the manufacture of guncotton, and various chemical schemes for generating dioxygen gas and for absorbing carbon dioxide aboard his proposed spacecraft. In his equally famous novel, *Journey to the Center of the Earth* (1864), he discusses various chemical theories of volcanism and makes use of the same carbon dioxide Geissler lamps later used by Captain Nemo in *Twenty Thousand Leagues*. Likewise, Captain Nemo's sodium cell makes a second appearance in the 1886 novel, *The Clipper of the Clouds* – this time as the power source for a lighter-than-air craft called the "Albatross," which is commanded by a Nemo-like clone by the name of Robur. In the short story *Dr. Ox's Experiment* (1874), Verne once more returns to the subject of various alternative methods of generating dioxygen gas and the effects of increased dioxygen concentrations on the physiological and psychological behavior of living organisms, while in the novel, *The Southern Star Mystery* or *The Star of the South* (1884), he deals with the synthesis of artificial diamonds. But none of these chemical digressions come close to rivaling the chemical versatility of the castaways in *The Mysterious Island*.

In February of 1873, while still in the process of planning the details of *The Mysterious Island*, Verne wrote a letter to his friend and publisher, Pierre-Jules Hetzel, in which he referred to his new project as a "roman chimique" – a chemical romance – and confessed that he had been spending his time doing background research "among Professors of Chemistry and in chemical plants" (23). Surely, it is time that chemists and teachers of chemistry return the compliment and spend some time with Verne enjoying what must surely be the only known example of that most elite of literary genres – the *roman chimique*.

References and Notes

1. Quoted in J. Gunn, *Alternate Worlds: The Illustrated History of Science Fiction*, A&W Visual Library: Englewood Cliffs, NJ, 1975, p. 120. See also S. Moskowitz, *Explorers of the Infinite: Shapers of Science Fiction*, Hyperion Press: Westport, CT, 1974, Chapter 19.

2. A. B. Evans, *Jules Verne Rediscovered: Didacticism and the Scientific Novel*; Greenwood Press: Westport, CT, 1988. Though intended for adults and far better researched, Verne's novels actually have more in common with such juvenilia as the Tom Swift series than with modern science fiction.

3. A good example of a butchered version of *Twenty Thousand Leagues* can be found in A. K. Russell, Ed., *Jules Verne, Classic Science Fiction: Three Complete Novels*, Castle Books: Secaucus, NJ, 1981. Though care was taken in this collection and in its earlier companion volume (A. K. Russell, Ed., *The Best of Jules Verne: Three Complete Novels*, Castle Books: Secaucus, NJ, 1978) to reproduce all of the 19th-century French illustrations to the novels, most of which had been deleted from the original English editions, similar care was not taken with the text. As a consequence, the version of *Twenty Thousand Leagues* which it reprints is missing virtually all of the technical passages found in the version given in reference 4 and which I quote in this article.

4. W. J. Miller, Ed., *The Annotated Jules Verne: Twenty Thousand Leagues under the Sea*, Crowell: New York, 1976, pp. 54-55, 75-77, 100.

5. Verne refers to these reactions again in a later chapter entitled "Want of Air" in which the *Nautilus* becomes trapped under the polar ice and the crew is caught in a frantic struggle to free her before they die of suffocation.

6. In addition to the 1954 Disney film, there are two earlier silent-film versions of *Twenty Thousand Leagues Under the Sea*, one made by Universal Studios in 1916 and the other by the French director George Melies in 1907.

7. For historical background on these batteries, see (a) L. Dunsch, *Geschichte der Elektrochemie*, Deutscher Verlag für Grundstoffindustrie: Leipzig, 1985; pp. 56-57; (b) A. Ritter von Urbanitzky, *Electricity in the Service of Man: A Popular and Practical Treatise on the Applications of Electricity in Modern Life*, Cassell: London, 1886, pp. 106-115; (c) T. Lowry, *Inorganic Chemistry*, Macmillan: London, 1931, pp. 208-209; (d) P. Benjamin, *The Voltaic Cell: Its Construction and Capacity*, Wiley: New York, 1893; and (e) J. T. Stock, "Bunsen's Batteries and the Electric Arc," *J. Chem. Educ.*, **1995**, *12*, 99-102.

8. There seems to be considerable confusion in the literature as to who actually invented the dichromate cell. Kevin Desmond, in his reference work, *A Timetable of Inventions and Discoveries* (Evans: New York, 1986), claims that it was invented by Heinrich Ruhmkorff in 1855; Dunsch (reference 7a) attributes it to Robert Bunsen in 1842; Benjamin (reference 7d) claims that it was developed by Johann C. Poggendorff the same year; and Stock (reference 7e) claims that it was mentioned in passing by Bunsen in 1841 and discussed in detail by Robert Warington in 1842. Of these four authors, only Stock provides original literature citations to support his claims.

9. The potentials quoted correspond to unit activities. In practice, the nitric acid in the cells was much more concentrated, and Benjamin (reference 7d) reports actual operating values of 1.60-1.90 V for the Grove cell and 1.93-1.96 V for the Bunsen cell, whereas Lowry (reference. 7c) reports values of 180-1.96 V for the Grove cell.

10. The potentials quoted correspond to unit activities. In practice, the solutions were much more concentrated. Benjamin (reference 7d) reports actual operating values of 1.92-2.2 V for the dichromate cell, whereas Lowry (reference 7c) reports a value of 2.0 V.

11. The "idealized" potentials quoted are based on unit activities. The actual voltage of Nemo's sodium cell would depend on the activity of the sodium in the amalgam. The value of 1.957 V for the sodium amalgam half-cell reported by Dietrick et al. (H. Dietrick, E. Yeager, F. Hovorka, *The Electrochemical Properties of Dilute Sodium Amalgams*; U.S. Office of Naval Research, Technical Report 3; Western Reserve University: Cleveland, OH, 1953) would give an overall value of 3.29 V for the cell, which is only about one and half times that of the dichromate cell. This suggests that Nemo was using very concentrated amalgams in his cells.

12. The only nineteenth-century estimates reported by Benjamin (reference 7d) for the half-cell potentials of sodium amalgams are those originally reported by Antoine-Cesar Becquerel and his son, Alexandre-Edmond Becquerel, in their 1855 volume *Traité expérimental de l'électricité et du magnetismé*. These range from 2.303 to 2.334 V, which again gives an net potential that is only about one and half times that of the standard dichromate cell.

13. A nineteenth-century account of the chemistry underlying all of the manufacturing processes described by Verne in both *Twenty Thousand Leagues under the Sea* and *The Mysterious Island* can be found in *The Encyclopaedia of Chemistry, Theoretical, Practical, and Analytical as Applied to the Arts and Manufactures* (2 volumes; Lippincott: Philadelphia, 1879) under the entries for sodium, pottery, cement, iron, steel, soap, alum, sulfuric acid, nitric acid, nitroglycerin, candles, sugar, guncotton, and glass.

14. H. W. Meyer, *A History of Electricity and Magnetism*, MIT Press: Cambridge, MA, 1971, pp. 174-175.

15. J. Verne, *The Mysterious Island*, Burt: New York, no date; pp. 57, 90, 94-95, 96, 107-113, 124-126, 126-127, 145-146, 162-163, 225-226, 234-235, 250-252, 311-312. This is one of many inexpensive rip-off editions of Verne. Other English translations of this novel use the name Cyrus Smith, rather than Cyrus Harding, for the engineer hero. Unfortunately, I have been unable to examine a French edition and so cannot tell which rendition is the correct one. *The Mysterious Island* has been filmed three times: once by MGM in 1929, and twice by Columbia Pictures, in 1951 and 1961, respectively. Captain Nemo was played by Lionel Barrymore in the 1929 production and by Herbert Lom in the 1961 production.

16. Later in the novel, the resources of the castaways are further augmented by accidental finds of supplies that have apparently washed ashore from wrecked ships but which are, in fact, provided by Captain Nemo, who has been secretly observing their progress.

17. There are some obvious confusions in this quote, which again reflect the low quality of most English translations of Verne's novels emphasized by Miller in reference 4.

18. A. C. Becquerel, *Traité de physique considérée dans ses rapports avec la chimie et les sciences naturelles*, Didot: Paris, 1844; Vol. 2, pp. 300-301.

19. Benjamin (reference 7d), p. 267.

20. W. Latimer, *Oxidation Potentials*, 2nd ed., Prentice-Hall: Englewood Cliffs, NJ, 1952, p. 93. For consistency, this reference has been used to calculate all other thermodynamic values cited in the article.

21. Verne may have been misled by Becquerel's remark in reference 18 that the potential of his cell could be increased by substituting zinc for platinum at the anode. He may not have realized that a similar substitution would not work for the cathode, nor that the increase in the potential is due, in the case of the anode substitution, to oxidation of the zinc.

22. I have discussed several of these in greater detail in the essays "Sir Humphry Davy and the Hollow Earth: The Geochemistry of Journey to the Center of the Earth" and "Tom Swift Among the Diamond Makers: Synthetic Diamonds in Fact and Fiction" to be published in future issues of *The Chemical lntelligencer*.

23. Quoted in C. N. Martin, *La vie et l'oeuvre de Jules Verne*; Michel de l'Ormeraie: Paris, 1978; p. 200.

The Chemistry of Bug-Eyed Silicon Monsters

The Rise and Fall of an Analogy

Carbon and silicon were not always regarded as isovalent analogs of one another. The great Swedish chemist, Jöns Jakob Berzelius (figure 1), who was the first to isolate silicon as a simple substance in 1823, thought that it most resembled boron (1, 2). This assignment was based on the fact that both elements formed acidic, nonvolatile oxides which could act as glass formers, and on a similarity in the appearance of the simple substances themselves, both of which had been prepared only as highly-impure, amorphous, nonmetallic powders. This analogy was further reinforced by errors in the determination of their atomic weights, which assigned the analogous formulas, BO_3 and SiO_3, to their respective oxides, in sharp contrast to the formulas, CO and CO_2, assigned to the oxides of carbon. With the gradual correction of atomic weights and the equally gradual substitution of "stoichiometric type" or valence, in place of acidity and electronegativity, as the preferred basis for chemical classification, silicon was reassigned as an analog of carbon.

In 1857, the German chemist, Friedrich Wöhler (figure 2), discovered silicon tetrahydride (SiH_4), the stoichiometric and structural analog of methane (CH_4), and the logical starting point for speculations on an alternative organic chemistry based on silicon rather

Figure 2. Friedrich Wöhler (1800-1882).

than carbon (3). Ironically, however, Wöhler did not consider this possibility until 1863 and then only as a result of a faulty interpretation of his experimental data. Having obtained, via the hydrolysis of magnesium silicide, a series of apparent compounds of silicon, hydrogen and oxygen, he found it very difficult to assign them exact formulas. Possibilities suggested by his analytical data for one of these compounds included $Si_8H_4O_6$, $Si_6H_3O_4$, $Si_{12}H_6O_8$, etc. Since the only compounds that Wöhler knew of having equally complex formulas were the organic compounds of carbon, he concluded that, regardless of which of these choices ultimately proved correct, it would correspond to (4):

... a result of great interest in that it can be viewed as a compound constructed after the manner of an organic substance in which silicon plays the role of carbon in the organic material. Perhaps it can serve as the type for an entire series of similar bodies, and there would then exist the prospect of a special chemistry of silicon, similar to that which exists in the case of carbon.

Figure 1. Jöns Jakob Berzelius (1779-1848).

With the gift of hindsight, we would suspect that Wöhler's organic analogs were in fact nothing more than poorly characterized samples of silicic acid in various stages of dehydration.

Though the preparation and isolation of the pure silicon hydrides would show little further progress until the work of Alfred Stock in the 1920s, other classes of silicon compounds were soon discovered which proved to be more promising sources of inspiration for an alternative organosilicon chemistry than were Wöhler's poorly-characterized silicate sludges. Already in 1844, the French chemist, Jacques-Joseph Ebelmen, had successfully prepared a number of alkoxide derivatives of silicon having the general formula $Si(OR)_4$ (5), and in 1863 the French-American team of Charles Friedel and James Mason Crafts synthesized the first alkyl derivative – tetraethylsilane, $Si(C_2H_5)_4$ (6). This work was continued by Friedel (figure 3), and especially by the German chemist, Albert Ladenburg (figure 4), throughout the last quarter of the 19th century, so that by 1916 the Swedish chemist, Artur Bygden, could list several hundred organosilicon compounds in his monograph *Silicium als Vertreter des Kohlenstoffs' organischer Verbindungen* (7).

In summarizing the early work on organosilicon chemistry, it is important to realize that the carbon-silicon analogy was used in two different ways by 19th- and early 20th-century chemists. The first of these usages, which we will call the "strong analogy,"

Figure 4. Albert Ladenburg (1842-1911).

was the claim that it should be possible to build up a silicon analog of organic chemistry containing no carbon whatsoever. In other words, just as one constructs conventional organic chemistry from the hydrocarbons by preparing an almost limitless number of oxygen and nitrogen derivatives, so one should also be able to prepare large numbers of homocatenated polysilanes and their corresponding oxygen and nitrogen derivatives (or, for the more adventuresome, their isovalent sulfur and phosphorus derivatives). This is, in fact, the prospect hinted at by Wöhler, and discussion of the possibility of silicon-based life in the popular science literature and among science-fiction writers is always based, either explicitly or implicitly, on claims for the validity of this strong analogy.

The second usage, which we will call the "weak analogy," was the more modest claim that it should be possible to modify or perturb conventional carbon-based organic compounds by substituting isolated carbon centers with silicon. Here, quite naturally, the emphasis was placed on the substitution of key carbon atoms corresponding to optically-active centers, functional groups, etc. The question of Si-Si chains arose in this context only in connection with the analogs of those functional groups corresponding to C-C multiple bonds.

Examination of Bygden's monograph shows that virtually all of the work on organosilicon chemistry

Figure 3. Charles Friedel (1832-1899).

done in the 19th and early 20th centuries was based on the weaker of these two claims. The vast majority of the compounds listed by Bygden were simple substitution products of the tetralkylmonosilanes, and in almost all cases they were assigned structures based solely on the assumption that an analogous stoichiometry with a corresponding carbon compound automatically implied an analogous structure. Yet among popular writers, this work was often quoted as evidence for the validity of the stronger analogy.

The English-speaking reader can best catch the spirit of this tactic by reading a popular lecture given by the Irish chemist, James Emerson Reynolds, in 1873, summarizing the early results obtained by Friedel and Ladenburg. Reynold's provocative title, "On Alcohols from Flint and Quartz," not only reveals how literally the strong carbon-silicon analogy was taken, but also that the art of attracting an audience with a less than forthright seminar title has an ancient and honorable history (8).

In 1899 the British organic chemist, Frederick Stanley Kipping (figure 5), began an intensive study of organosilicon compounds (in the sense of the weak analogy just outlined) that would eventually span nearly four decades. Perhaps the most important contribution to come out of this work was Kipping's discovery of a new class of organosilicon oxygen derivatives known as the silicones. Like his predecessors, Kipping, in his early work, naively assumed that analogous stoichiometry automatically implied analogous structure. Consequently when he prepared a class of compounds having the general formula R_2SiO, he naturally thought that he had discovered the alkyl silane analogs of the ketones R_2CO – hence his use of the name "silicones" – a term equaled in the annals of chemical nomenclature for its misleading implications only by Lavoisier's equally naive assumption that the composition of sugars and starches implied that they were literally hydrates of carbon (9).

However, by the time Kipping delivered his 1936 Bakerian Lecture on "Organic Derivatives of Silicon," summarizing his life's work, time and experience had considerably dampened his earlier enthusiasm for the possibility of a silicon-modified organic chemistry (10):

Even after a very short experience, it was evident that corresponding derivatives of the two elements in question showed very considerable differences in their chemical properties; it may now be said that the principal, if not the only, case in which they exhibit a really close resemblance is that of the paraffins and those particular silicohydrocarbons containing a silicon atom directly united to four alkyl radicals. But of far greater importance in any general comparison of car-

Figure 5. Frederick Stanley Kipping (1863-1949).

bon compounds with the organic derivatives of silicon is the fact that many, if not most, of the more important types of the former are not represented among the latter. Apparently this is not merely a consequence of the insufficient experimental investigation of silicon derivatives but is due to the fundamental differences in the properties of the atoms of silicon and carbon ...

In other words, after 40 years of research, Kipping had come to the conclusion that even the weak from of the analogy was defective, and subsequent work would soon show that his pessimism was fully justified.

As it turns out, the structures and chemistry of the silicones, silicols and other oxygen derivatives of the alkyl and arylsilanes are best viewed from the standpoint of inorganic chemistry as progressively depolymelized derivatives of silica in which one or more bridging Si-O-Si bonds per silicon center have been formally replaced by terminal or capping R- or RO-groups:

$$2(R\text{-}) + (\text{=}Si\text{-}O\text{-}Si\text{=}) \rightarrow 2(\text{=}Si\text{-}R) + (\text{-}O\text{-}) \qquad [1]$$
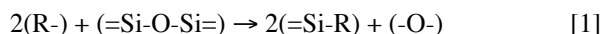
rather than from the standpoint of organic chemistry as simple substitutional analogs of the ketones, alcohols, etc. Indeed, this process parallels that observed in the purely inorganic realm when one depolymerizes silica via reaction with metal oxides, a process which leads
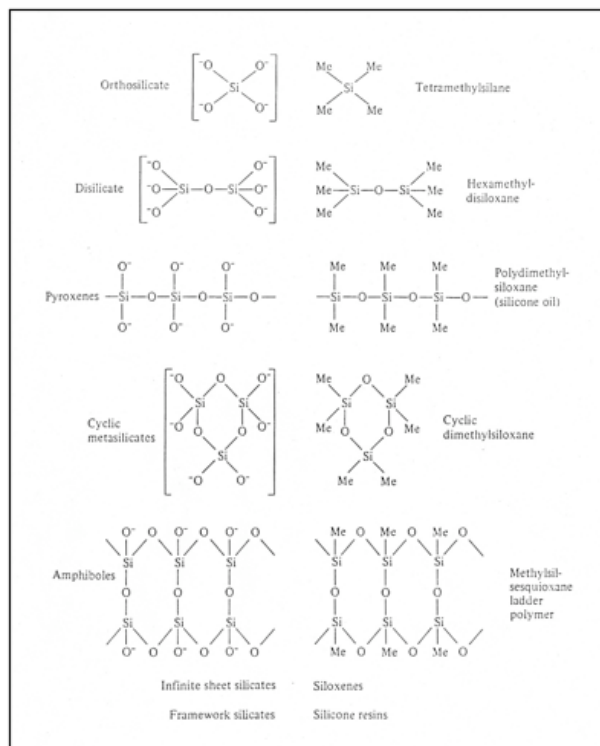
Figure 6. The analogy between the depolymerization of silica via capping with O^{1-}, as found in the silicates, versus capping with alkyl groups, as found in the alkylsiloxanes.

to the formation of layer, chain, ring and isolated silicate anions, as well as silicate glasses of varying viscosity (figure 6). This may be "formally" viewed as the replacement of oxygen bridges by terminal $(O-)^{1-}$ groups, which are isolobal with the alkyl and aryl groups used in relation 1:

$$2(O-)^{1-} + (=Si-O-Si=) \rightarrow 2(=Si-O)^{1-} + (-O-) \qquad [2]$$
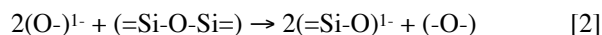
Though silicon has an extremely interesting and highly diversified chemistry, that chemistry is uniquely its own and is not just a simple (please, excuse the pun) carbon copy of that of carbon.

By 1946, when Eugene Rochow's (figure 7) classic monograph, *An Introduction to the Chemistry of the Silicones*, appeared, not only had these facts concerning the organosilicon oxygen derivatives been established, but the work of the Braggs in X-ray crystallography had shown the total absence, in the purely inorganic domain, of any similarity between the structures of carbon dioxide and the carbonates, on the one hand, and the structures of silicon dioxide and the silicates, on the other; and Alfred Stock's (figure 8) work on the silanes in the period 1916-1923 had totally undermined the strong form of the analogy by showing that the

hydrides of silicon were highly sensitive to air and moisture and strictly limited in their propensity to undergo homocatention – in short, that they were about as unlike the alkanes as one could imagine (11). The chemist's naive faith in a simple silicon analog of organic chemistry in both its weak and strong forms was dead, and Rochow provided the funeral oration (12):

In these and in the many other ways in which silicon differs markedly from carbon, the differences arise from the larger size of the silicon atom, with the correspondingly greater screening of its nuclear charge. Therefore, any attempt to force silicon into the framework of classical organic chemistry or to predict the reactions of silicon purely by analogy with those of carbon compounds is likely to fail because of this fundamental difference ... If the reader has any doubt about this point, let him attempt to predict the behavior of the hydrides of silicon from a consideration of the hydrocarbons.

That more recent authors still agree with this evaluation is apparent from the remarks of the American chemist, Grant Urry, made nearly a quarter of a century after the publication of Rochow's monograph (13):

Figure 7. Eugene George Rochow (1909-2002).

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It is perhaps appropriate to chide the polysilane enthusiast for milking the horse and riding the cow in attempting to adapt the successes of organic chemistry in the study of polysilanes. A valid argument can be made for the point of view that the most effective chemistry of silicon arises from the differences with the chemistry of carbon compounds rather than the similarities.

From Silicon Chemistry to Silicon Life

Based on this brief outline of the rise and fall of the chemist's belief in the possibility of a silicon-based organic chemistry strictly analogous to that of carbon, to what extent did chemists further speculate on the possibility of a silicon-based biochemistry capable of serving as the basis of a silicon life-form? Quite surprisingly, given the widespread belief among science fiction fans that this was a common fantasy of chemists, I have found few examples of such speculations in the chemical literature and none before the turn of the 20th century. The earliest example I could locate occurs as an appendix in a monograph entitled *Researches on the Affinities of the Elements and on the Causes of the Chemical Similarity and Dissimilarity of Elements and Compounds* published in 1905 by the British chemist, Geoffrey Martin, who later in his career would, interestingly enough, become a coworker of Frederick Stanley Kipping (14).

The major premise of Martin's monograph was that the pattern of properties for the elements in the periodic table was pressure and temperature dependent and that it was possible to "equalize" the properties of two elements, especially if they were in the same group, by comparing them under widely different physical conditions. In particular, Martin postulated a "critical temperature and pressure" for each element's chemical compounds. This corresponded to an upper limit on their stabilities and represented the conditions under which they displayed a maximum in their reactivity. After first observing that carbon-based life was limited to a small temperature-pressure range, Martin wrote (14):

I suggest that the temperature range of animal life is probably nothing more or less than the range of the critical temperature of decomposition of a series of certain very complex carbon compounds which are grouped together under the name "protoplasm," the external pressure of the atmosphere coinciding roughly with their critical pressures of decomposition.

Given this assumption, the next step was obvious:

We are therefore justified in asking whether there is any other element which at some other temperature could

Figure 8. Alfred Eduard Stock (1876-1946).

play the part now played by carbon at ordinary temperatures in living organic matter?

as was Martin's answer to his rhetorical question:

Silicon is such an element ... There probably exists for silicon, as well as for carbon, a transition or critical temperature range whereat a large number of unstable silicon compounds are capable of momentary existence, a higher temperature rendering their existence impossible, while a lower temperature would make the compounds stable. At this transitional temperature the complex compounds would be capable of a continual metathesis, and thus give rise to the phenomenon of life; only in this case all forms of life would have as the determining element not carbon, but silicon. Seeing that in the case of carbon this temperature occurs when many of its compounds are in a semi-fluid condition, and near their decomposing point, we should expect the corresponding temperature for silicon compounds to occur when they, too, are in a pasty or semi-fluid condition.

Last, but not least, Martin connected his speculations with the geological history of the earth, which he assumed had been formed via the gradual cooling of an originally molten mass:

Have we any evidence which supports the view that living matter did not start originally with carbon, hydrogen, oxygen, and nitrogen as its fundamental elements, but started with elements of far higher atomic weights, such as silicon, phosphorus, and sulphur, of which only vestiges now remain in the protoplasm? It must be remembered that our evidence could only be indirect; such life could have thrilled to an enormous extent in the white hot molten siliceous matter which covered the earth's surface in by-gone ages, and yet have left no traces of its existence behind; for when such forms of life died, their bodies would but blend again into the molten rock, in the same way that a jelly-fish dies and blends into the ocean of salt water without leaving a vestige behind ...

Similar ideas were expressed four years later by the Irish chemist, James Emerson Reynolds, whom we encountered earlier, in a popular lecture entitled "Recent Advances in Our Knowledge of Silicon and Its Relations to Organized Structures" (15):

We can conceive of the existence of similar groupings of other analogous elements forming other protoplasms capable of existing within much greater ranges of temperature than any plants or animals now known to us have to withstand. For example, we might imagine a high temperature protoplasm in which silicon takes the place of carbon, sulfur of oxygen and phosphorus of nitrogen, either wholly or in part.

Reynolds had made no reference to such musings in his 1873 lecture on silicon analogs of organic compounds, mentioned earlier, nor in his 1893 lecture on the same subject, which he presented to the Chemical Section of the British Association for the Advancement of Science as part of his presidential address for that year (16), and their appearance in his 1909 lecture leads to some interesting historical speculation. For though Reynolds failed to raise the issue of silicon life forms in 1893, a young British biology teacher, who summarized Reynolds' presidential address for the S*aturday Review* in 1894, did (17):

... at very much higher temperatures this immobility of silicon compounds might be exchanged for a vigorous activity ... [and] at temperatures above the points of decomposition of the majority of the carbon-nitrogen compounds, a silicon-aluminium series may conceivably have presented cycles of complicated syntheses, decompositions, and oxidations essentially parallel to those that underlie our own vital phenomena ... And if we are to admit the possibility that the chemical accompaniments of life were rehearsed long ago and at

Figure 9. A young H. G. Wells (1866-1946).

far higher temperatures by elements now inert, it is not such a very long step from this to the supposition that vital, subconscious, and conscious developments may have accompanied such a rehearsal. One is startled toward fantastic imaginings by such a suggestion: visions of silicon-aluminium organisms – why not silicon-aluminium men at once? – wandering through an atmosphere of gaseous sulphur, let us say, by the shores of a sea of liquid iron some thousand degrees or so above the temperature of a blast furnace.

The name of the young biology teacher was Herbert George Wells, or H. G. Wells (figure 9), as he is now universally known. He had recently abandoned the teaching of biology for the more lucrative career of a free-lance writer and would publish his first major science fiction novel, *The Time Machine*, the very next year. Did Wells send Reynolds a copy of his review and did it play a role in shaping Reynolds' explicit discussion of hypothetical silicon life forms in his 1909 lecture? Unfortunately, we can only speculate on this possibility, though it is of interest to note that Wells himself never saw fit to make his "fantastic imaginings" on this subject the theme of one of his science fiction stories.

The High-Temperature Fallacy

The early speculations of Martin, Wells, and Reynolds are typical examples of what I call the "high temperature fallacy." This approach uses the stoichiometric analogy of one class of compounds (the hydrides) to argue that silicon can take the place of carbon in organic chemistry (the chemistry of the hydrocarbons and their derivatives) in the strong sense of the carbon-

silicon analogy, and then proceeds to substitute a second unrelated class of compounds (the silicates) in place of the original, while continuing to assume that the analogy remains unimpaired. More particularly, this fallacy, by taking silicon dioxide or silica, rather than silicon tetrahydride or monosilane, as its archetype for the behavior of silicon compounds, comes to the conclusion that, if silica can withstand higher temperatures than carbon-based materials, then the same must be true of all other silicon compounds, and that consequently silicon-based life, if its exists, can do so only at high temperatures.

Yet another example of this approach can be found in the poem, "The Silicon Man," which appeared in a popular 1915 text by Elwood Hendrick, entitled *Everyman's Chemistry*. Since this is not the most sterling example of English poetry to see the light of day, I've taken the liberty of editing out most of the less inspired verses (18):

I saw a glowing silicon man
Within my chamber fire,
And heard him cry in agony
"More fuel, or I expire!"

"I am," said he, "John Silicon,
And I am so constructed
That silicon's my substitute;
My carbon's all deducted."

"My tissues, nerves, and viscera
Show this phenomenon:
That just as you of carbon are
I am of silicon."

At ordinary temperature
His soul was frozen dead
And only resurrected when
The flames were blazing red.

"My needs," said he, "are very few;
I want no meat nor bread,
And if you feed the fire well
You'll never find me dead."

Though Stock's work on the polysilanes, which destroyed the major premise of this flawed syllogism, should have put an end to this view of possible silicon life-forms, it is, in fact, still alive and well among writers on popular science, where it is now reinforced by the revised interpretation of the silicones as organic derivatives of silica, despite the fact that this revision invalidates their original interpretation as analogs of carbon-based organic compounds (19). This persis-

Figure 10. Lawrence Joseph Henderson (1878-1942).

tence is, in my opinion, ultimately traceable, not just to a misuse of the analogy between silicon and carbon in the periodic table, but to an ancient and deep-seated human fascination with blurring the lines separating living and nonliving matter – with the time-honored superstition that minerals, rocks, and even the earth itself, may be primitive living organisms with infinitely slow metabolic rates.

The Biologist and Biochemist Also Disagree

If one turns from the writings of the chemist to the speculations of the biologist and biochemist on the origins of life and looks for comments on the possibility of silicon-based life, one finds that the statements take on a decidedly negative tone. Examination of twenty 20th-century books on this subject (20-39) showed that either the authors did not consider this possibility worthy of discussion or were quite skeptical of such suggestions (40). Much more attune to the requirements of metabolism, transport, replication and repair necessary to sustain a living organism, they were much less inclined to be enamored of superficial analogies of stoichiometry and valence implied by an excessively naive reading of the periodic table.

A good example of this critical attitude is the classic 1913 volume, *The Fitness of the Environment*, by the Harvard physiologist, Lawrence J. Henderson (figure 10), which was written one year before the nonmo-

lecular structure of quartz was established by Bragg using X-ray crystallography. Commenting on the problems inherent in imagining the use of silicon compounds in living systems, Henderson wrote (41):

From time to time loose discussion has arisen among chemists as to the possibility of substituting another element for carbon in the organic cycle. Such speculations have never been serious, but they have at least demonstrated that very few elements, probably only silicon and perhaps boron can even be imagined in such a role. It has moreover just been shown [i.e., earlier in the book] that only carbon among the elements, and carbon itself only in conjunction with hydrogen, has the power to form the skeletons of compounds numerous, complex, and varied like those of organic chemistry. But apart from this conclusion, it is certain that silicon and boron cannot be mobilized like carbon. Quartz, the oxide of silicon, is the most inert and immobile of rocks; the oxide of boron is only less available as a movable constituent of the environment, and there is no other stable compound of either element that can be compared with carbonic acid [i.e., carbon dioxide] for its mobility.

What Henderson is emphasizing here is the fact that all known living organisms are dynamic, open systems which require a continuous flow of matter and energy for their maintenance. Transport (or mobility, to use Henderson's phrase) of the material components always involves the use of solutions or gases and it is the negligible solubility and volatility of the oxides of silicon and boron, as compared to that of carbon dioxide, that almost immediately eliminates these elements from practical consideration as carbon substitutes.

The Silicon Monster in Science Fiction

Henderson's observations about the lack of mobility of silicon dioxide versus carbon dioxide form the basis of one the earliest and most famous examples of a silicon-based life form in the annals of science fiction – Stanley G. Weinbaum's short story, "A Martian Odyssey," which was first published in 1934, about 20 years after Henderson's book (42). Its author was a 32-year old chemical engineer (figure 11) trained at the University of Wisconsin who had begun writing science fiction only a few months earlier and who would tragically die 15 months later of throat cancer at age 33 (43).

The story itself concerns Dick Jarvis, a chemist connected with a successful space mission to Mars, who runs into trouble when his one-man scouting rocket develops engine trouble and he is forced to walk 1800 miles back to the mother ship. Of course, he is
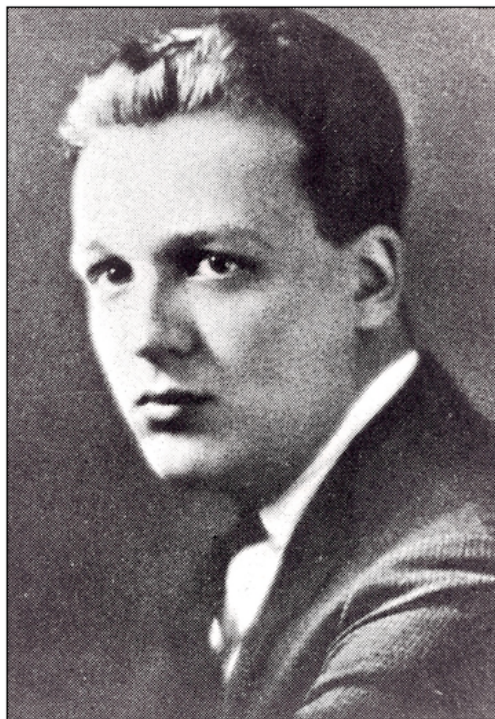
Figure 11. Stanley Grauman Weinbaum (1902-1935).

rescued by another member of the crew before he covers this distance but not before he meets an intelligent bird-like alien named "Tweel" and the two of them encounter a variety of curious life forms in their trek across Mars (figure 11).

In the course of their journey they come upon a series of brick pyramids of ever-increasing size. In each case the capstone is broken off and the pyramid is empty. Eventually, however, they encounter one with the cap in place. As they are examining it, the top tier of bricks begins to shake and heave, and (42):

A long silvery-grey arm appeared, dragging after it an armored body. Armored, I mean, with scales, silver-grey and dull-shiny. The arm heaved the body out of the hole; the beast crashed to the sand, It was a nondescript creature [figure 12] – body like a big grey cask, arm and a sort of mouth-hole at one end; stiff, pointed tail at the other – and that's all, No other limbs, no eyes, ears, nose – nothing! The thing dragged itself a few yards, inserted its pointed tail in the sand, pushed itself upright and just sat. Tweel and I watched it for ten minutes before it moved. Then, with a creaking and rustling – oh like crumpling stiff paper – its arm moved to the mouth-hole and out came a brick! The arm placed the brick carefully in the sand and the thing was still again. Another ten minutes – another brick. Just one of Nature's brick layers.

Figure 12. Jarvis and Tweel on their trek across Mars.

Jarvis soon realizes that he has encountered a silicon life-form (42):

The beast was made of silica! There must have been pure silicon in the sand, and it lived on that. Get it? We, and Tweel and those plants out there, and even the bipods are carbon life; this thing lived by a different set of chemical reactions, It was silicon life ... We're carbon and our waste is carbon dioxide, and this thing is silicon and its waste is silicon dioxide – silica. But silica is a solid, hence the bricks. And it builds itself in, and when it is covered, it moves over to a fresh place to start over.

At one point in the story the ship's biologist questions Jarvis' conclusions, asking him how he knew it really was a silicon-based creature, and Jarvis snaps back, "Because I'm a chemist!" This may be, but it is also apparent from Jarvis' description of the creature as taking nourishment through its so-called tail and removing its waste products through its so-called mouth, that he is no biologist since his description of the creature is obviously (and I hope you will excuse my vulgarity, but the phrase is so appropriate that I cannot pass it up) "ass-backwards" and that he has actually encountered a species that has to shit the proverbial brick every ten minutes.

Though one of the first science fiction stories to sport a silicon-based life form, Weinbaum's tale still remains one of the best – at least in the sense of having some contact with the realities of chemistry. In sharp contrast, in many stories which have appeared since the publication of Weinbaum's classic, the chemistry is either unspecified or just down right wrong. Indeed, one of the best examples of the wrong category is the short story "The Devil in the Dark," which served as an episode of the original Star Trek series (44). This featured a silicon life-form called a "Horta" (figure 14) which spends its time instantaneously cutting man-sized tunnels through silicate rock by spitting out its own blood. This, in turn, supposedly consists of a rather improbable mixture of *aqua regia* and hydrofluoric acid, which the author of the story not only imagines is capable of instantaneously dissolving rock but also, when necessary, human bodies. Quite obviously, neither the author nor the screen writer had ever done a silicate analysis as they have no concept of the either the volume of liquid required (the creature is about half the size of a man) nor the rate at which hydrofluoric acid and silica react. Likewise, no attention is given to the enormous volumes of silicon tetrafluoride gas which are necessarily produced by the creature as a result of its tunneling operations in what appears to be a normal oxygen - water environment suitable for human beings, Under these conditions, the silicon tetrafluoride should partly hydrolyze back to hydrogen fluoride and silicon dioxide:
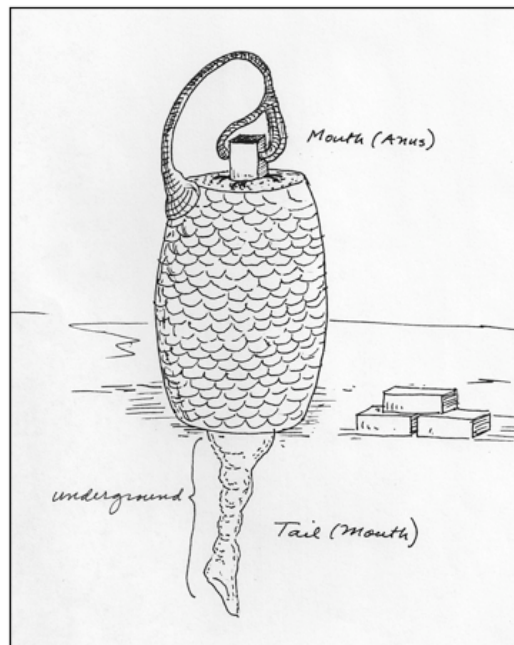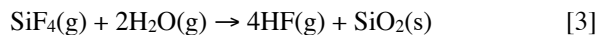
$$SiF_4(g) + 2H_2O(g) \rightarrow 4HF(g) + SiO_2(s) \qquad [3]$$

Figure 13. The author's interpretation of Weinbaum's "brick layer."

Figure 14. Captain Kirk confronts the Horta.

Yet Captain Kirk, Mr. Spock, and Bones run around in the resulting HF-SiF$_4$ clouds with no apparent ill effects. Other elementary errors also abound: at one point Spock announces that teflon is made by reacting fluorine with silicon, the author repeatedly confuses the terms silicon and silica, and part of the resolution of the story rests on the mistaken impression that *aqua regia* doesn't dissolve platinum.

Another defect common to most stories dealing with silicon creatures is a failure on the part of the author to postulate both a geochemical history and a contemporary environment that are compatible with the evolution of such life forms. Thus Weinbaum assumed a pure silicon layer beneath the sandy surface of Mars, even though he also assumed an oxygen-rich atmosphere – a rather unlikely thermodynamic combination to survive the rigors of planet formation – and no explanation is given for where the Horta gets the materials necessary to generate the enormous volumes of hydrofluoric, nitric, and hydrochloric acids needed for its tunneling operations.

Finally, few authors appreciate the delicate interplay between form and function in living organisms and consequently they make no allowance for growth, repair and replication of their silicon creatures. What they are really describing are manufactured items made of the sorts of materials that an engineer would select in building a robot or android. Thus we are told that the Horta's internal organs are made of teflon – nice to hold acids, but lacking any type of chemical functionality and hence any mechanism for repair, growth or replication.

Yet More Chemistry

In closing, I would like to return again to the question of why silane chemistry is not the simple parallel of

organic hydrocarbon chemistry in the strong sense of the carbon-silicon analogy implied by science fiction writers and by a naive freshman chemistry reading of the periodic table. In explaining the observed differences, at least four points of are interest (45-48):

1. Comparison of the hydrogen derivatives of carbon and silicon shows that the silicon hydrides or silanes are thermodynamically unstable with respect to disproportionation to their elements at STP but are kinetically metastable up to about 500°C (52). Cycloalkanes, alkenes, alkynes, and aromatic derivatives of carbon are likewise thermodynamically unstable but kinetically metastable with respect to disproportionation, whereas the alkanes and their oxygen derivatives are thermodynamically stable. This point is emphasized in the graph in figure 15 which clearly shows the metastability of the cycloalkanes, alkenes, alkynes, and aromatics, and the corresponding thermodynamic stability of the alkanes and oxygen derivatives of the hydrocarbons.

2. The hydrocarbons and their derivatives are all thermodynamically unstable but kinetically metastable with respect to oxidation and hydrolysis at STP. Silanes, on the other hand, are both thermodynamically
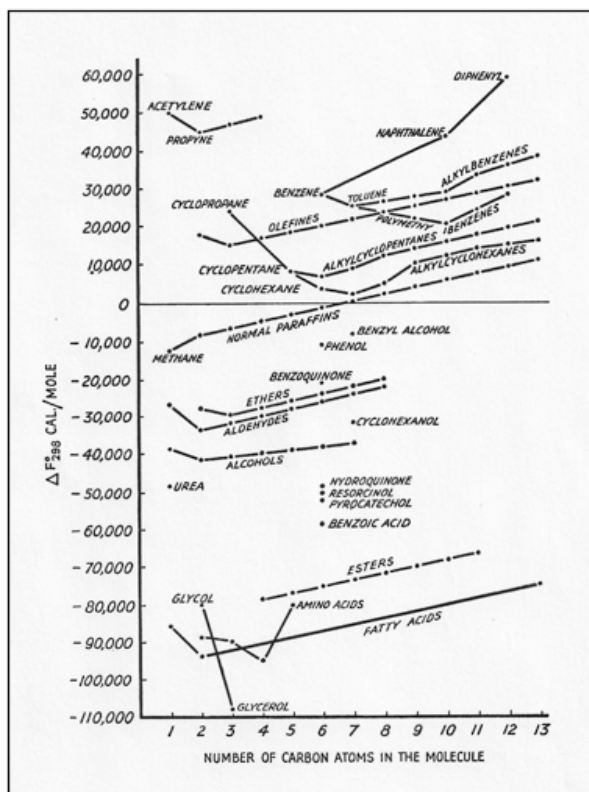

Figure 15. The thermodynamic stability of the hydrocarbons and their derivatives at STP.

and kinetically unstable. With the exception of pure monosilane, the silanes spontaneously ignite on contact with air and all of them rapidly hydrolyze in slightly basic water.

3. It has not been possible to synthesize derivatives of unsubstituted silanes containing functional groups strictly analogous to those found among the derivatives of the hydrocarbons, most notably those containing analogs of either C=C multiple bonds or C=O multiple bonds, both of which play a key role in the synthetic reactions used to build up complex carbon chains.

4. Most conventional electronegativity scales give the order C > H > B > Si, which means that the polarity of the C-H bond is the reverse of that of the B-H and Si-H bonds. In effect, boranes and silanes are hydrides, whereas hydrocarbons are "carbides." Consequently alkanes and silanes generally respond differently to substituent effects and to attacking reagents (12).
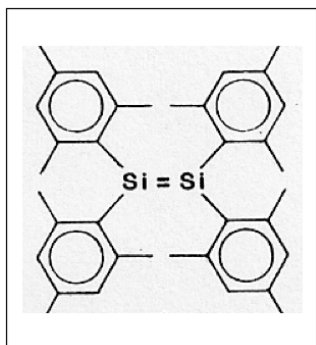
The role of C=C multiple bonds in point 3 can be further emphasized by comparing the energy change which accompanies the conversion of a C=C double bond into the equivalent number of C-C single bonds:

$$E_{C=C} - 2E_{C-C} = -82 \text{ kJ/mol} \qquad [4]$$

a result which clearly suggests that C=C double bonds are kinetically metastable. Presumably not only are Si=Si double bonds thermodynamically unstable relative to the equivalent number of Si-Si single bonds, they are kinetically labile as well, since to date no one has succeeded in making a simple unsubstituted silene:

$$E_{Si=Si} - 2E_{Si-Si} < 0 \text{ kJ/mol} \qquad [5]$$

This surmise is further supported by the well-publicized synthesis of the first Si=Si double bond in 1981 by West, Fink and Michl using large sterically hindering mesityl groups to induce kinetic metastability (49):

In a similar manner, the role of C=O double bonds in point 3 can be further emphasized by comparing the energy changes which accompany the conversion of C=O versus Si=O double bonds into the equivalent number of single bonds (45):

$$E_{C=O} - 2E_{C-O} = +88 \text{ kJ/mol} \qquad [7]$$

$$E_{Si=O} - 2E_{Si-O} = -282 \text{ kJ/mol} \qquad [8]$$

As may been seen, the C=O double bond is thermodynamically stable with respect to the C-O single bond, whereas the reverse is true of its silicon analog, and it is this key difference which, in turn, accounts for the difference in the molecularity of carbon dioxide versus silicon dioxide, for the difference in their transport properties emphasized more than 80 years ago by Henderson, for the waste disposal problems encountered by Weinbaum's Martian "brick layer," and for the high temperature fallacy which characterized early speculations on silicon life-forms.

All of these facts converge to a single question:

Why are most hydrocarbons and their derivatives kinetically metastable at STP with respect to such reactions as disproportionation, oxidation, hydrolysis and polymerization, whereas the corresponding silicon analogs are not?

The usual answer involves the assumption of an associative transition state for these reactions in which the coordination sphere of carbon and silicon is expanded to five:

$$B' + AB_4 \rightarrow [B'-AB_3-B] \rightarrow AB_3B' + B \qquad [9]$$
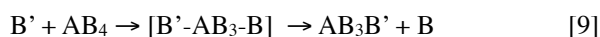
This, in turn, is assumed to require octet expansion on the part of carbon and silicon and the use of outer d-orbitals. Since these are energetically much more accessible in silicon than in carbon, this fact supposedly accounts for the lower activation energies observed for the silicon compounds and for their lack of kinetic metastability (45).

However, in 1982 Dewar and Healy published a paper giving the results of a detailed MNDO calculation for S_N2 displacement reactions at tetrahedral carbon and silicon centers (50). Their results showed an activation barrier corresponding to the formation of the pentacoordinate intermediate for carbon, but none for silicon, even though no outer d-orbitals were included in the basis set. Indeed, the pentacoordinate intermediate for silicon actually appeared as an energy minimum (figure 16). As a result of these calculations, the authors concluded that the activation barrier for carbon

Figure 16. Energy profiles for S_N2 displacement reactions at carbon (a and b) and at silicon (c).

came largely from the increase in the ligand-ligand repulsions which accompanied the expansion of the carbon coordination sphere from four to five. On the other hand, these repulsions were f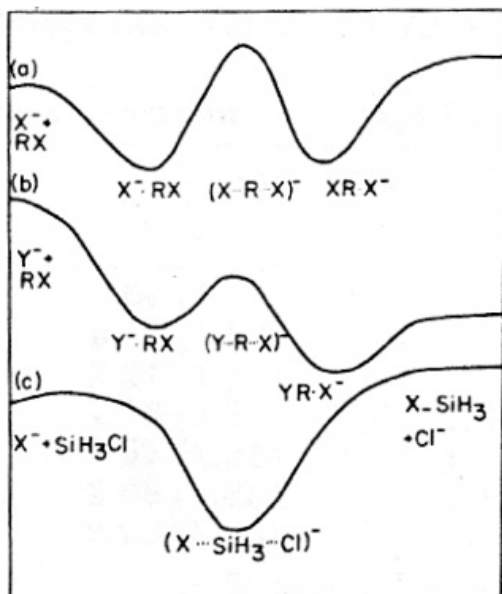ound to be much less important in the case of silicon because of its larger size, and, indeed, were actually outweighed in this case by the favorable energy changes which accompanied the formation of the new bond to the incoming ligand. Other theoreticians, most notably Werner Kutzelnig, have also opted for this explanation in the case of the closely-related problem of the so-called hypervalent compounds formed by the heavier p-block elements (e.g., PCl_5, SF_6, etc.), preferring a model based on multicentered 3c-4e bonds and reduced steric crowding to one which uses traditional 2c-2e bonds and outer d-orbitals for octet expansion (46, 51). Thus, we have ironically come full circle, and have arrived again at Rochow's 1946 statement.

Put colloquially then, the reason for the observed differences in the reactivity of carbon and silicon compounds can be ultimately traced to a difference in the size of their respective atoms. The small size of carbon results in kinetic metastability, which can be manipulated via changes in reaction temperature, solvent environment and the use of catalytic agents, and which leads to the isolation of a wide range of "metastable" compounds with reactive functional groups. By way of contrast, the larger size of silicon results in kinetic lability, leading to thermodynamic control of its reactions and to the isolation of only a few highly stable

compounds which are best characterized as relatively unreactive "thermodynamic sinks."

Of course, in light of the work of West, Fink and Michl on the Si=Si double bond, mentioned earlier, one might argue that one could engineer both the necessary kinetic control and the necessary functional groups into the chemistry of silicon via the use of large sterically hindering ligands, and indeed an increasing number of examples of this technique have been discovered, including many cases of the successful substitution of single, sterically-protected, carbon centers with silicon in conventional organic compounds, dyes, and natural products (52). However, this approach is best characterized as a perturbation on conventional carbon-based organic chemistry (i.e., our original weak analogy). As such, it does not correspond to the literal, naive silicon parallelism of an organic chemistry sans carbon (i.e., our original strong analogy) which inspired the silicon-life forms of the science fiction writer in the first place,

As compensation for this loss of innocence, it is at least worth pondering the irony that so large a difference as that which differentiates a living organism from a dead rock should find its ultimate explanation in so small a difference as that which differentiates the size of a carbon atom from that of a silicon atom.

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Update

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Recent theoretical calculations have also called into question the existence of a classical double bond in the silenes strictly analogous to that found in the carbon-based alkenes, indicating instead that the actual bond order is closer to 1.2 and that there is some lone pair electron density on each of the Si atoms leading to a nonplanar arrangement of the attached ligands. See:

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V

From Cavorite to Carolinum

Chemistry and the Science Fiction of H. G. Wells

The English Jules Verne

In his autobiography, the English author, Herbert George Wells (figure 1) or H. G. Wells, as he was universally known, complained about the way in which he had been characterized by the literary critics during the early stages of his career as a novelist (1, 2):

Literary criticism in those days had some odd conventions. It was either scholarly or with scholarly pretensions. It was dominated by the medieval assumption that whatever is worth knowing is already known and whatever is worth doing has already been done ... Anybody fresh who turned up was treated as an aspirant Dalai Lama is treated, and scrutinized for evidence of his predecessor's soul. So it came about that everyone of us who started writing in the nineties was discovered to be "a second" somebody or other. In the course of two or three years I was welcomed as a second Dickens, a second Bulwer Lytton and a second Jules Verne.

Given his apparent dislike for such literary comparisons, Wells would doubtlessly be distressed to discover that the public's propensity to lump him with the likes of Jules Verne has, if anything, increased, rather than decreased, with the passage of time.

Superficially, at least, this propensity would appear to have ample justification. Currently, both authors have almost instant name recognition as "founding fathers of classic science fiction" not only among devotees of the genre, but among the public at large. In both cases this reputation is based on only a small portion of their total literary output. In both cases this "small portion" consists of novels which were written early in their careers. And, in both cases, the novels in question were later given widespread publicity as a result of having been transformed into movies that often bore only the most superficial resemblance to the written originals (and, in the case of Wells, some would also have to include the notoriety generated by Orson Welles' famous 1938 radio adaptation of *The War of the Worlds*).

For Verne, this select list of novels would have to include *Journey to the Center of the Earth (1863), From the Earth to the Moon (1865), Twenty Thousand Leagues Under the Sea (1870),* and *Around the World*

Figure 1. A caricature by David Low of H. G. Wells (1866-1946) as he appeared later in life.

in Eighty Days (1873) – a list that represents only four of the more than 60 novels which Verne wrote during his lifetime – all of them during the first ten years of his career as an author (3). The corresponding list for Wells would have to include *The Time Machine* (1895), *The Island of Dr. Moreau* (1896), *The Invisible Man* (1897), *The War of the Worlds* (1898), *The First Men in the Moon* (1901), and *The Food of the Gods* (1904). Again, all six of these novels were written during the first decade of Wells' career as an author, and they represent only a small fraction of the more than 120 books which he published during his lifetime (4).

Support for these selections can be found from an examination of the current edition of *Books in Print*.

Figure 2. Jules Verne (1828-1905) as caricatured by the French artist André Gill in 1874 for the cover of the magazine *l'Eclipse*.

plots generally combine an adventure and/or romance story with novel, but not improbable, extensions of existing technology and with sizable digressions on the facts of geography, zoology, botany, astronomy, physics, and chemistry. Verne almost never invokes the suspension of established scientific law – there are no alien monsters, no mysterious power sources, and no super materials. Indeed, only a small fraction of the novels involve the theme of space travel and can be classified as true "science fiction," as that term is now understood.

By way of contrast, the imaginative fiction of Wells is much closer to the spirit of current science fiction. His novels are almost always predicated on the violation of one or more of the known laws of science and involve an imaginative exploration of the consequences of that violation. The use of established scientific theories and facts is quite marginal and the larger message, if any, is generally either sociological or political, rather than scientific. Most frequently it takes the form of an exploration of the ability of scientific and technological advances to disrupt the existing social structure, generally in a manner totally unforeseen by the scientists themselves, and the consequences of this disruption for the establishment of the kind of tepid socialism that was favored by Wells since his days as a student at South Kensington.

Interestingly, both Verne and Wells were well aware of these differences. Thus, when asked his opinion of Wells in a 1903 interview, Verne (figure 2) was quick to deny any similarities (6):

... I do not see this possibility of comparison between his work and mine. It occurs to me that his stories do not repose on very scientific bases. No, there is no rapport between his work and mine. I make use of physics. He invents. I go to the moon in a cannon ball discharged from a cannon. He goes to Mars [sic] in an airship which he constructs of a metal which does away with the law of gravitation. Ça c'est tres joli, but show me this metal. Let him produce it.

And Wells made a similar point in 1934 in the preface which he wrote for the first collected edition of his best science fiction novels (7):

These tales have been compared with the work of Jules Verne and there was a disposition on the part of literary journalists at one time to call me the English Jules Verne. As a matter of fact there is no literary resemblance whatever between the anticipatory inventions of the great Frenchman and these fantasies. His work dealt almost always with actual possibilities of invention and discovery, and he made some remarkable

This shows that 31, or roughly 50%, of Verne's novels are still available in English translation. In sharp contrast to the single edition listed for most of these novels, nine editions of *Journey to the Center of the Earth* are listed, two editions of *From the Earth to the Moon*, 14 editions of *Twenty Thousand Leagues Under the Sea*, and 15 editions of *Around the World in Eighty Days*. In the case of Wells, 33, or roughly 28%, of his books are currently in print, again mostly as single editions. However, 14 editions of the *The Time Machine* are listed, five of *The Island of Dr, Moreau*, ten of *The Invisible Man*, eleven of *The War of the Worlds*, two of *The First Men in the Moon*, and two of *The Food of the Gods*. In addition, one also has to take into account the dozen or so collected editions of Wells' best science fiction novels and short stories that are listed, most of which reprint one or more of these six novels.

However, as my earlier use of the qualifier "superficially" implies, this apparent similarity between Verne and Wells does not hold up under closer scrutiny. As noted elsewhere, Verne's books were actually part of a French tradition of didactic writing known as the so-called "scientific novel" (5). Intended as a way of painlessly popularizing science for the lay public, their

forecasts. The interest he invoked was a practical one; he wrote and believed and told that this or that thing could be done, which was not at that time done. He helped his reader to imagine it done and to realize what fun, excitement or mischief would ensue. Many of his inventions have "come true." But these stories of mine collected here do not pretend to deal with possible things; they are exercises of the imagination in a quite different field ... They are all fantasies; they do not aim to project a serious possibility; they aim indeed only at the same amount of conviction as one gets in a good gripping dream. They have to hold the reader to the end by art and illusion and not by proof and argument, and the moment he closes the cover and reflects, he wakes up to their impossibility.

These differences in emphasis also take on a certain irony when placed in a biographical context. Verne, who had been forced to study law by his father, had no formal scientific training. Wells, on the other hand, had won a scholarship in 1884 to attend the newly-founded Normal School of Science in South Kensington in order to be trained as a secondary science teacher. Wells was initially inspired by his brief contact with Thomas Huxley, during his first year of the three-year training program, but quickly became disillusioned with the uninspired teaching of Huxley's colleagues. This disillusionment, coupled with extreme poverty and the emotional turmoil of his first love affair with his cousin, Isabel Wells, resulted in his almost flunking out by the end of the third year. Though this undistinguished academic performance effectively debarred Wells from further pursuing a research career in science, he was able to obtain a series of teaching posts at several third-rate private schools, and he also managed to obtain a B.Sc. degree in 1890 with first-class honors in zoology. As a result of his teaching activities, he published a two-volume *Text Book of Biology* in 1893 and coauthored a volume on *Honors Physiography* the same year. In 1930 he again returned to his training in biology and published a massive, popular account of contemporary biology for the lay public entitled *The Science of Life*, which was coauthored by Thomas Huxley's grandson, Julian Huxley, and Wells' own son, George, who was also trained as a biologist (8).

The irony in all of this is, of course, the fact that Verne, the nonscientist, attempted to educate the public on the facts and theories of science and tried to dispel common misconceptions about these facts and theories, whereas Wells, the trained scientist, did not and, indeed, often exploited and reenforced popular misconceptions about science in order to create the "suspension of reality" necessary for his imaginative "fantasies" – a lapse that Wells was more than willing to admit (7):

For the writer of fantastic stories to help the reader to play the game properly, he must help him in every possible unobtrusive way to domesticate the impossible hypothesis. He must trick him into an unwary concession to some plausible assumption and get on with his story while the illusion holds ... Hitherto, except in exploration fantasies, the fantastic element was brought in by magic, Frankenstein even, used some jiggery-pokery magic to animate his artificial monster. There was trouble about the thing's soul. But by the end of the last century it had become difficult to squeeze even a momentary belief out of magic any longer. It occurred to me that instead of the usual interview with the devil or a magician, an ingenious use of scientific patter might with advantage be substituted. That was no great discovery. I simply brought the fetish stuff up to date, and made it as near actual theory as possible.

Just how far Wells was willing to push his theory of "science as modern magical fetishism" will become apparent in what follows.

The Diamond Maker

Though the nature of Wells' scientific training meant that most of the scientific references in his novels and short stories were biological in nature, he does, from time to time, make passing references to chemistry. Indeed, one of the most explicit of these occurs in a tale called "The Diamond Maker" which appeared in an early collection of his short stories, *The Stolen Bacillus and Other Incidents*, first published in 1895. However, since the theme of synthetic diamonds is the subject of a later essay in this book, we will leave a discussion of its contents until then and instead move on to the chemical references to be found in some of Wells' more famous full-length novels.

The Invisible Man

Wells' third major science fiction novel, *The Invisible Man: A Grotesque Romance*, was published in 1897 and deals with the activities of a man named Griffin, who describes himself as a former medical student at University College-London, "almost albino, six feet high and broad, with a pink and white face and red eyes – who won the medal for chemistry," and who has discovered a process to render himself invisible (9). The novel opens with Griffin's invisibility already an accomplished fact and with a description of many of his adventures while in that state. These eventually reduce him to the status of a fugitive and force him to seek shelter in the house of a certain Doctor Kemp, whom, as it fortuitously turns out, he had briefly known at University College. It is to this

unwilling host that Griffin first reveals the history and secret of his process (9):

I came on the stuff first at Chesilstowe I went there after I left London. You know that I dropped medicine and took up physics ... light fascinated me Optical density! The whole subject is a network of riddles – a network with solutions glimmering elusively through. And being but two-and twenty and full of enthusiasm, I said, "I will devote my life to this. This is worthwhile." ... I had hardly worked and thought about the matter six months before light came through one of the meshes suddenly – blindingly! I found a general principle of pigments and refraction a formula, a geometrical expression involving four dimensions. Fools, common men, even common mathematicians, do not know anything of what some general expression may mean to the student of molecular physics ... it was an idea that might lead to a method by which it would be possible, without changing any other property of matter – except, in some instances, colors – to lower the refractive index of a substance, solid or liquid, to that of air – so far as all practical purposes are concerned.

This personal introduction is followed by a lengthy, but credible attempt, on the part of the invisible man to explain the difference between transparency or lack of color, on the one hand, and refractive index, on the other, and the role which these two properties play in rendering an object visible or invisible (9):

Visibility depends on the action of the visible bodies on light. Either a body absorbs light, or it reflects it, or does all these things. If it neither reflects nor refracts nor absorbs light, it cannot of itself be visible. You see an opaque red box, for instance, because the color absorbs some of the light and reflects the rest, all the red part of the light, to you. If it did not absorb any particular part of the light, but reflected it all, then it would be a shining white box. Silver! A diamond box would neither absorb much of the light nor reflect much from the general surface, but just here and there, where the surfaces were favorable, the light would be reflected and refracted, so that you would get a brilliant appearance of flashing reflections and translucencies, – a sort of skeleton of light. A glass box would not be so brilliant, not so clearly visible, as a diamond box, because there would be less refraction ... From certain points of view you would see quite clearly through it. Some kinds of glass would be more visible than others, a box of flint glass would be brighter than a box of ordinary window glass. A box of very thin common glass would be hard to see in a bad light, because it would absorb hardly any light and refract and

reflect very little. And if you put a sheet of common white glass in water, still more if you put it in some denser liquid than water, it would vanish almost altogether, because light passing from water to glass is only slightly refracted or reflected or indeed affected in any way. It is almost as invisible as a jet of coal gas or hydrogen is in air. And for precisely the same reason!

Aside from the incorrect use of the word "color" in the second sentence to describe the thing which absorbs light rather than the effect of that absorption, this is not a bad summary of the contents of a typical introductory physics textbook of the period.

The invisible man now zeros in on the important point. Once you have eliminated specific absorptions by rendering an object colorless, one needs only to eliminate the differences between the refractive indices of the object and the surrounding medium to also render it completely invisible (9):

And there is another fact you will know to be true. If a sheet of glass is smashed, Kemp, and beaten into a powder, it becomes much more visible while it is in the air; it becomes at last an opaque white powder. This is because the powdering multiplies the surfaces of the glass at which refraction and reflection occur. In the sheet of glass there are only two surfaces; in the powder the light is reflected or refracted by each grain it passes through and very little gets right through the powder. But if the white powdered glass is put into water, it forthwith vanishes. The powdered glass and water have much the same refractive index; that is, the light undergoes very little refraction or reflection in passing from one to the other. You make the glass invisible by putting it into a liquid of nearly the same refractive index; a transparent thing becomes invisible if it is put in any medium of almost the same refractive index. And if you will consider only a second, you will see also that the powder of glass might be made to vanish in air, if its refractive index could be made the same as that of air; for then there would be no refraction or reflection as the light passed from glass to air.

The invisible man's point about the visibility or invisibility of powdered glass can be nicely demonstrated using pyrex glass and a liquid composed of 590 mL of carbon tetrachloride and 410 mL of benzene. This forms the basis of a standard chemical magic trick known as the "Disappearing Beaker" (10).

Griffin completes his discourse by pointing out that most biological tissues are colorless and that, in any case, he has not only discovered a way of altering the refractive index of substances so as to render colorless materials invisible in air, he has also discovered a

method of bleaching colored biological tissues, such as the red blood cells, without altering their physiological properties. Though the bleaching process is presumably chemical in nature (and minimal in Griffin's case because he is an albino), the process for altering the refractive index is based on physics rather than chemistry (9):

... the essential phase was to place the transparent object whose refractive index was to lowered between two radiating centers of a sort of ethereal vibration, of which I will tell you more fully later. No, not these Röntgen vibrations – I don't know that these others of mine have been described. Yet they are obvious enough. I needed two little dynamos, and these I worked with a cheap gas engine. My first experiment was with a bit of white wool fabric. It was the strangest thing in the world to see it in the flicker of the flashes soft and white, and then to watch it fade like a wreath of smoke and vanish.

The passing reference to Röntgen vibrations or X-rays, which had been discovered less than two years before the appearance of Wells' novel, though not germane to Griffin's process, is an example of Wells' exploitation of current scientific advances in order to create the convincing "scientific patter" necessary to make the premise of his story plausible to the lay reader.

Since the hero of *The Invisible Man* is clearly a physicist and his process is based on a vague manipulation of ethereal vibrations, the reader might well ask what all of this has to do with chemistry. The answer has less to do with the original novel itself than with its transformation into a highly successful movie, staring Claude Rains, by Universal Studios in 1933 (figure 3). Griffin has now suddenly acquired the first name of "Jack" and he and Kemp are now no longer former medical students, but rather chemists working as assistants for a certain Dr. Cranley, and also rival suitors for Cranley's Harlow look-alike daughter, Flora. Their research for Cranley does not involve the mysteries of the fundamental equations of optics nor the selective alternation of molecular properties, but rather a straight-forward practical problem that the average American moviegoer could understand. As Kemp explains to the somewhat dim-witted Flora (11):

Your father is a scientist Flora. He's discovered more about preserving food than any man living and Jack and I were employed to help him. It's a plain, straight-forward job. It's not romantic, but it saves hundreds of deaths and thousands of stomach aches.

Kemp's discussion with Flora is prompted by the fact

Figure 3. Scene from the 1933 movie version of the *Invisible Man* in which the local police and townsfolk confront Claude Rains in his makeshift chemical laboratory.

that Jack has mysteriously disappeared – an event that doesn't surprise Kemp, since, as he again explains to Flora, Jack will "never care about anything but chemicals and test tubes."

Later, on exploring Griffin's empty laboratory, Cranley and Kemp discover that he has been carrying on unauthorized experiments with a dreaded drug called "monocaine." As Cranley explains (11):

Monocaine is a terrible drug ... It's a drug that's made from a flower that grows in India. It draws color from everything it touches. Years ago they tried it for bleaching cloth. They gave it up because it destroyed the material.

Cranley also reveals that the Germans (who else?) had tried it on rats and found that it caused insanity.

In short, what we have is a typical Hollywood vulgarization – gone are the distinctions between transparency and refraction, gone are the dynamos and ethereal vibrations. In their place we have mysterious drugs from the East which "draw color" and their equally mysterious manipulation by the magic of chemistry at the hands of the stereotypical mad chemist obsessed with "chemicals and test tubes." The culmination of this exercise in negative public relations comes in the final confrontation between Griffin and Flora in which he explains that he was tempted into his mad pursuit of the dream of transparency by the lure of fame, money, and power – not for themselves, mind you – but because of his desire to impress her, made necessary, as he laments, by the fact that "I had nothing to offer you Flora. I was just a poor struggling chemist" (11).

The First Men in the Moon

Wells' sixth major science fiction novel, *The First Men in the Moon*, was first published in 1901 and is narrated by a failed business investor named Bedford, who has retired to a rented bungalow in Lympne, Kent, in order to recover from his financial losses and to write plays (12). Here he makes the acquaintance of his eccentric neighbor, an inventor named Cavor, who soon tells Bedford of his latest project (13, 14):

The object of Mr. Cavor's search was a substance that should be "opaque" - he used some other word I have forgotten, but "opaque" conveys the idea – to all forms of radiant energy. "Radiant energy," he made me understand, was anything like light or heat or those Röntgen rays there was so much talk about a year or so ago, or the electric waves of Marconi, or gravitation. All these things, he said, radiate from centers and act on bodies at a distance, whence comes the term "radiant energy." Now almost all substances are opaque to some form or other of radiant energy. Glass, for example is transparent to light, but much less so to heat, so that it is useful as a fire-screen; and alum is transparent to light, but blocks heat completely. A solution of iodine in carbon bisulfide, on the other hand, completely blocks light but is quite transparent to heat. It will hide a fire from you but permit all its warmth to reach you. Metals are not only opaque to light and heat but also to electrical energy [i.e. radio or Marconi waves], which passes through both iodine solutions and glass almost as though they were not interposed. And so on. Now all known substances are "transparent" to gravitation. You can use screens of various sorts to cut off the light or heat or electrical influence of the sun, or the warmth of the earth from anything; you can screen things by sheets of metal from Marconi's rays, but nothing will cut off the gravitational attraction of the earth. Yet why there should be nothing is hard to say. Cavor did not see why such a substance should not exist and certainly I could not tell him.

Here again we see Wells making a passing reference to the latest scientific and technological developments in order to give plausibility to his scientific patter. Though Guglielmo Marconi had begun to experiment with radio waves as early as 1894, it was not until 1901, the same year that Wells' novel appeared, that he finally succeeded in sending the first transatlantic telegraphic radio transmission, and there is little doubt that popular press accounts about the properties of Marconi's radio waves – most notably their selective screening by metals – inspired Wells' idea of a possible gravity screen. We also see some rather dubious asso-

ciations in Wells' argument – most notably the assertion that gravity is a form of radiant energy, as well as a very loose use of the term electrical energy as a synonym for Marconi or radio waves.

The suspicion that Wells is becoming sloppy about the way in which he constructs his scientific patter is further confirmed by the rest of the chapter (13):

He [i.e., Cavor] showed me by calculations on paper which Lord Kelvin, no doubt, or Professor Lodge or Professor Karl Pearson, or any of those great scientific people might have understood, but which simply reduced me to a hopeless muddle, that not only was such a substance possible, but that it must satisfy certain conditions. It was an amazing piece of reasoning ... Suffice it for this story that he believed he might be able to manufacture this possible substance opaque to gravitation out of a complicated alloy of metals and something new – a new element I fancy called, I believe, helium, which was sent to him in sealed stone jars. Doubt has been thrown upon this detail, but I am almost certain it was helium he had sent him in sealed stone jars. It was certainly something very gaseous and thin.

Though the mention of Lord Kelvin and Sir Oliver Lodge has some relevance to Wells' topic, as both were physicists, and Lodge, in particular, was involved in the early development of radio, the inclusion of Karl Pearson in this passage is something of a mystery. Pearson was a well-known biostatistician and leader of the eugenics movement founded by Francis Galton. He certainly had nothing to do with the physics of either gravitation or electromagnetic radiation. Wells may have tossed in his name because the second edition of Pearson's well-known book on the philosophy of science, *The Grammar of Science*, had appeared the year before and had become something of an intellectual fad among the socialists with whom Wells associated, or it may simply be that to Wells, the traditional descriptive biologist, the kind of heavy duty application of mathematics to biological problems associated with Pearson's work made him appear as a paragon of mathematical wizardry.

The most dubious part of this passage, however, is Wells' explicit exploitation of the popular confusion between the effects of gravitation, on the one hand, and those of buoyancy, on the other, in order to lend added plausibility to Cavor's antigravity alloy. Helium had been discovered only six years earlier by Sir William Ramsay (figure 4) and its potential as a nonflammable substitute for hydrogen in lighter-than-air balloons would have been well known to Wells' readers. But rather than disabusing them of the fallacy that such a
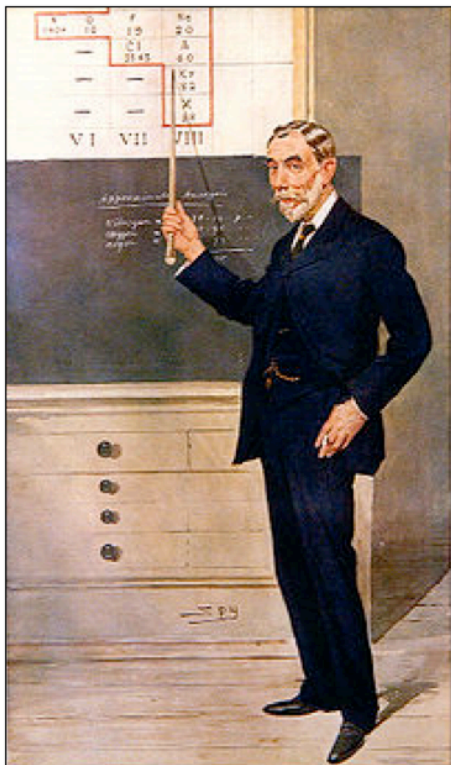
Figure 4. Caricature of Sir William Ramsay (1852-1916), the discoverer of the noble gases, by Spy for *Vanity Fair*.

balloon could operate in outer space, Wells uses this common misunderstanding for his own purposes and reinforces it with the quaint notion that helium has to be shipped in heavy sealed stone jars, apparently in order to prevent the jars from floating away (15).

It goes without saying that Cavor is successful in producing his antigravity alloy, which he rather immodestly names "Cavorite," though not without accidentally endangering the lives of himself and his assistants and nearly destroying his home and that of his neighbors when the first solidified sheet of Cavorite is propelled into space along with a substantial portion of the surrounding atmosphere. However, Cavor soon learns how to control his discovery and conceives the idea of using it to construct a spherical vehicle (figure 5) which will allow him to travel to the moon – a vehicle, as Bedford observes, not unlike "Jules Verne's apparatus in *A Trip to the Moon* [sic]" (13).

First published in 1865 and 1870, respectively, Verne's novels, *From the Earth to the Moon*, and its sequel, *All Around the Moon*, afford us with an opportunity to compare the way in which Wells and Verne use or misuse science in their fiction, and indeed we have already quoted Verne's own judgment on this matter (16). However, not unexpectedly, most of these

comparisons involve the facts of astronomy and physics, and we will have to content ourselves with a single chemical example – namely the question of how the two authors propose to maintain a viable atmosphere in their respective space vehicles.

After first outlining the chemical facts relating to respiration and the composition of the atmosphere, Verne, as usual, provides a detailed description of his scheme for air purification (16):

.. two things were clearly to be done: 1, to renew the absorbed oxygen; 2, destroy the exhaled carbonic acid [carbon dioxide]. Both these objects could readily be obtained by means of potassium chlorate and caustic potash [potassium hydroxide]. Potassium chlorate, the well-known salt from which oxygen is most readily obtained for experimental purposes, crystallizes in large six-sided plates, and, when heated to about 800° Fahrenheit, readily parts with its oxygen, chloride of potash being the residue. As eighteen pounds of this salt yield seven pounds of oxygen, two hundred pounds would evidently be more than even twice the quantity required before the travelers got to the Moon. Oxygen being thus supplied, carbonic acid could be readily destroyed by potassium hydrate, commonly called caustic potash. This white crystalline substance is well known for its powerful affinity for water and carbonic acid, both of which it immediately absorbs from the air, and uniting readily with them, becomes a moist carbonate of potash. By combining these two operations, the distinguished French chemists, Reiset and Regnault, had succeeded in purifying polluted air and restoring its life-sustaining properties.

This is almost a textbook description of the well-known reactions:

Figure 5. A modern artist's rendition of the "Cavor Sphere"

$$2K(ClO_3)(s) + heat \rightarrow 2KCl(s) + 3O_2(g) \qquad [1]$$

$$2K(OH)(s) + CO_2(g) \rightarrow K_2(CO_3)(s) + H_2O(l) \qquad [2]$$

and Verne would also consider using them five years later to renew the atmosphere aboard Captain Nemo's infamous submarine, "The Nautilus," in his novel *Twenty Thousand Leagues Under the Sea* (17). Though I have not tracked down Verne's reference to the experiments of the well-known French chemist, Henri Victor Regnault, nor the identity of his coauthor, Reiset, there is little doubt that both exist. Not only does Verne outline the necessary chemistry, he has his engineers conduct a preliminary test of the system with a man sealed in the space vehicle, and he also proposes to increase its efficiency by enclosing the necessary chemicals in a mechanical recirculating device, which he describes as "an apparatus, self acting and extremely ingenious, invented by a member of the Franklin Institute of Philadelphia ..." (16).

By way of contrast, Wells' description of Cavor's proposed system for air renewal is – to put it diplomatically – a good deal more concise (13):

And then we had to discuss and decide what provisions we were to take, compressed foods, concentrated essences, steel cylinders containing reserve oxygen, an arrangement for removing carbonic acid and waste from the air and restoring oxygen by means of sodium peroxide, water condensers, and so forth.

Here Wells not only conforms to the first rule of good engineering design – redundant backup systems – he also shows originality. Indeed, his choice of the chemical reaction:

$$2Na_2(O_2)(s) + 2CO_2(g) \rightarrow 2Na_2(CO_3)(s) + O_2(g) \quad [3]$$
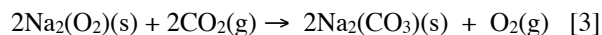
for his air purification system is actually based on known technology as, according to Partington, it was at one time (and may still be, for all I know) used for this purpose on submarines (18).

All of these details occur quite early in the novel, which is concerned not so much with how Cavor gets to the moon as with what he discovers after arriving.

The Food of the Gods

First published in 1904, Wells' seventh major science fiction novel, *The Food of the Gods, and How It Came to Earth*, records the consequences of a major biochemical breakthrough made by two British scientists named Redwood and Bensington. Redwood is described as a "Professor of Physiology at the Bond Street College of the University of London ... [who] had been grossly libeled by the anti-vivisectionists time after time" and Bensington as "a Fellow of the Royal Society and a former President of the Chemical Society ... who had won his spurs ... by his splendid researches upon the 'More Toxic Alkaloids'" (19).

The initial idea for the discovery comes about as a result of Bensington having read one of Redwood's papers in the *Philosophical Transactions* on the growth rates of living organisms (19):

Redwood, you know, had been measuring growing things of all sorts, kittens, puppies, sunflowers, mushrooms, bean plants and (until his wife put a stop to it) his baby, and he had showed that growth went on, not at a regular pace ... but with bursts and intermissions ... and that apparently nothing grew regularly and steadily ... it was as if every living thing had first to accumulate force to grow, grew with vigor only for a time and then had to wait for a space before it could go on growing again. And in the muffled and highly technical language of the really careful "scientist," Redwood suggested that the process of growth probably demanded the presence of a considerable quantity of some necessary substance in the blood that was only formed very slowly, and that when this substance was used up by growth, it was only very slowly replaced, and that meanwhile the organism had to mark time.

Bensington concludes that this "necessary" but mysterious substance in the blood "might probably be due to the presence of just the very substance he had recently been trying to isolate in his researches upon such alkaloids as are most stimulating to the nervous system." This proves to be the case, and he suggests that the newly isolated growth factor, which he and Redwood succeed in preparing on their fourth attempt, be called either *Titanophorbia* (food of the Titans) or *Herakleophorbia* (the food of Hercules). Though Bensington and Redwood decide on the latter name, the story's narrator prefers the more descriptive phrase "The Food of the Gods," while the public in general opts for the nickname "Boomfood."

Having first rejected the use of tadpoles as test subjects, Bensington hits on the rather improbable course of testing *Herakleophorbia* by raising a race of gigantic chickens. He establishes an experimental farm for this purpose but, through a combination of poor planning and blatant mismanagement, things soon get out of control when insects and rodents get into the treated grain supply (figure 6). Eventually the growth factor is also administered to human babies and results in a race of gigantic human children.

Though the last third of the novel degenerates into

Figure 6. A traveler's horse startled by a giant rat produced by eating chicken feed doused with *Herakleophorbia*

a preachy satire on society and politics, the first two parts contain some delightful caricatures of science and scientists. Thus, at one point, Wells says of Bensington (19):

I heard [him] also once – in the old days – at an educational conference in Bloomsbury. Like most eminent chemists and botanists, Mr. Bensington was very authoritative upon teaching – though I am certain he would have been scared out of his wits by the average Board School class in half-an-hour – and so far as I can remember now he was propounding an improvement of Professor Armstrong's Heuristic method, whereby at the cost of three or four hundred pounds' worth of apparatus, a total neglect of all other studies, and the undivided attention of a teacher of exceptional gifts, an average child might with a peculiar sort of thumby thoroughness acquire in the course of ten or twelve years almost as much chemistry as one could learn from one of those objectionable shilling textbooks that were then so common at that date ...

This is a brilliantly sarcastic commentary on the educational theories of the British chemist, Henry Edward

Armstrong (figure 7), who was a well-known and a very outspoken advocate of what we would today call the "laboratory self-discovery" approach to teaching chemistry (20-21). Best known for his work as a chemical educator, Armstrong had an almost unblemished record for backing the wrong horse when it came to matters of chemical theory and practice. A brilliant and sarcastic writer himself, he used his pen and considerable wit to oppose, in his time, such findings as the ionic theory of dissociation, the theory of radioactive transmutation, the electronic theory of valence, and the nonmolecular structure of sodium chloride as established by the Bragg's early use of X-ray diffraction (22). While his fellow chemists seemed to take all this in stride and even to relish his outbursts, some physicists, at least, were not equally amused, and it is reported that on one occasion an excessively irritated Ernest Rutherford curtly dismissed Armstrong as "a sort of literary chemical buffoon."

Though I am not certain whether Armstrong ever read Wells' novel, it is interesting to note that the few passing reference to Wells in Armstrong's own writings are not overly complimentary. Thus, in commenting on the short-comings of Wells' former teacher, Thomas Huxley, Armstrong quickly lapsed into a critique of Wells as an author (23):

Figure 7. Henry Armstrong (1848-1937).

Had he [i.e., Huxley] been otherwise, more consciously formative and persuasive as a teacher, his influence would have been far greater: he would have secured more than a select following of intimates. Men such as H. G. Wells would have been inspired to engage in higher work than mere literary froth-blowing: made closer students of the boundless beauty of Nature, they would not have projected the impossible as our human future and would have preached a higher morality, especially to women.

Even earlier in the novel, the narrator relates the experience of attending a session of the British Association for the Advancement of Science and of seeing Professor Redwood in action (19):
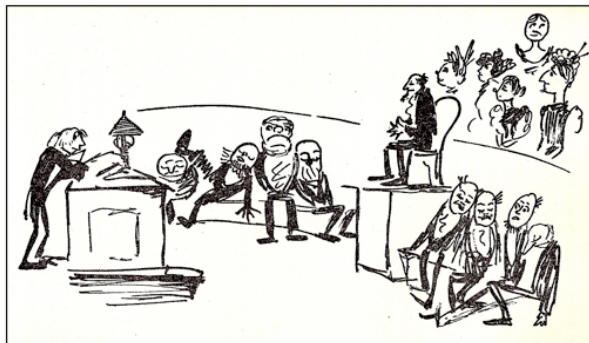

Figure 8. A doodle or "picshua" by Wells of a meeting of the Royal Institution, not unlike that of the British Association meeting described in *The Food of the Gods*.

I watched the lantern slides come and go, and listened to a voice (I forget what it was saying!) which I believe was the voice of Professor Redwood, and there was a sizzling from the lantern and another sound that kept me there, still out of curiosity, until the lights were unexpectedly turned up. And then I perceived that this sound was the munching of buns and sandwiches and things that the assembled British Association had come there to eat under cover of the magic-lantern darkness. And Redwood I remember went on talking all the time the lights were up and dabbing at the place where his diagram ought to have been visible on the screen – and so it was again so soon as the darkness was restored. I remember him then as a most ordinary, slightly nervous-looking man, with an air of being preoccupied with something else and doing what he was doing just then under an unaccountable sense of duty.

I defy anyone who has sat through a session at a National ACS meeting or through a departmental seminar to read this paragraph without being overwhelmed by a sense of déjà vu (figure 8).

But perhaps the most revealing passage in the novel is when the narrator gives his views on the nature of scientists in general and their impact on society – a passage which doubtlessly reflects Wells' own personal disillusionment at the inflexible dullness shown by several of his professors during his unhappy experience as science student at South Kensington (19, 24):

Quite ordinary persons you perceive, .. outside their science. Or if anything on the unpractical side of ordinary. And that you will find is the case with "scientists" as a class all the world over. What there is great about them is an annoyance to their fellow scientists and a mystery to the public, and what is not is evident.

There is no doubt about what is not great, no race of men have such obvious littleness. They live so far as

their human intercourse goes, in a narrow world; their researches involve infinite attention and an almost monastic seclusion; and what is left over is not very much. To witness some queer, shy, misshapen, grey-headed, self-important little discoverer of great discoveries, ridiculously adorned with the wide ribbon of an order of chivalry and holding a reception of his fellow men, or to read the anguish of Nature at the "neglect of science" when the angel of the birthday honors passes the Royal Society by, or to listen to one indefatigable lichenologist commenting on the work of another indefatigable lichenologist, such things force one to realize the unfaltering littleness of men.

And withal the reef of science that these little "scientists" built and are yet building is so wonderful, so portentous, so full of mysterious half-shapen promises for the mighty future of man! They do not seem to realize the things they are doing. No doubt long ago even Mr. Bensington, when he chose this calling, when he consecrated his life to the alkaloids and their kindred compounds had some inkling of the vision – more than an inkling. Without some great inspiration, for such glories and positions only as a "scientist" may expect, what young man would have given his life to this work, as young men do? No, they must have seen the glory, they must have had the vision, but so near that it has blinded them, mercifully, so that for the rest of their lives they can hold the light of knowledge in comfort – that we may see.

On the whole, however, given both the explicitly biological nature of the story and his own training as a biologist, Wells' use of science in this novel is rather disappointing, and we again see him resorting to popular misconceptions in order to lend plausibility to his scientific patter. Thus we find no reference to hormones or enzymes, but rather vague suggestions of exhausted blood and nerve stimulants – concepts more suitable to

Figure 9. Frederick Soddy (1877-1956).

latest about the atomic theory and sources of energy ... My idea is taken from Soddy. Men are supposed to find out how to set up atomic degeneration in the heavy elements just as they found out long ago how to set up burning in coal. Hence limitless energy.

Published the next year, the novel in question was entitled *The World Set Free: A Story of Mankind*, and was inspired, as Wells intimated in both his letter and in the novel's dedication, by his reading of the book *The Interpretation of Radium*, by the British radiochemist, Frederick Soddy (figures 9-10).

Soddy had begun his research career in collaboration with Ernest Rutherford at McGill University, where, between 1902 and 1903, they had jointly proposed the theory of radioactive disintegration for which Rutherford would receive the 1908 Nobel Prize in Chemistry (27). Though Soddy would eventually receive his own Nobel Prize in 1921 for his work on the radioactive displacement laws and the isotope concept, there is little doubt that the failure of both the Nobel Committee and Rutherford to publicly recognize the collaborative nature of the disintegration theory in 1908 upset him and, after parting ways in 1903, he and

a patent medicine man than to a trained biologist. Even more blatant is Wells' apparent ignorance of the laws of biomechanics and the major changes in the relative proportions of the various body parts of an organism that such radical size changes would necessitate in order for the organism to remain mechanically viable – though it must be confessed that this failing is shared by virtually all science fiction literature dealing with this theme, whether it be gigantic life forms gone amuck or incredible shrinking men (25).

The World Set Free

Starting with the publication of *Love and Mr. Lewisham* in 1900, which was based on his experiences as a student at South Kensington, the major thrust of Wells' work began to slowly shift from the science fiction fantasies that had dominated his first decade as an author towards the writing of semi-autobiographical main stream novels, mostly dealing with the mores of love and marriage. However, Wells never completely abandoned the science fantasy genre, and in 1913 he wrote to his friend A. T. Simmons (26):

I have suddenly broken out into one of the good old scientific romances again, and I want to know quite the
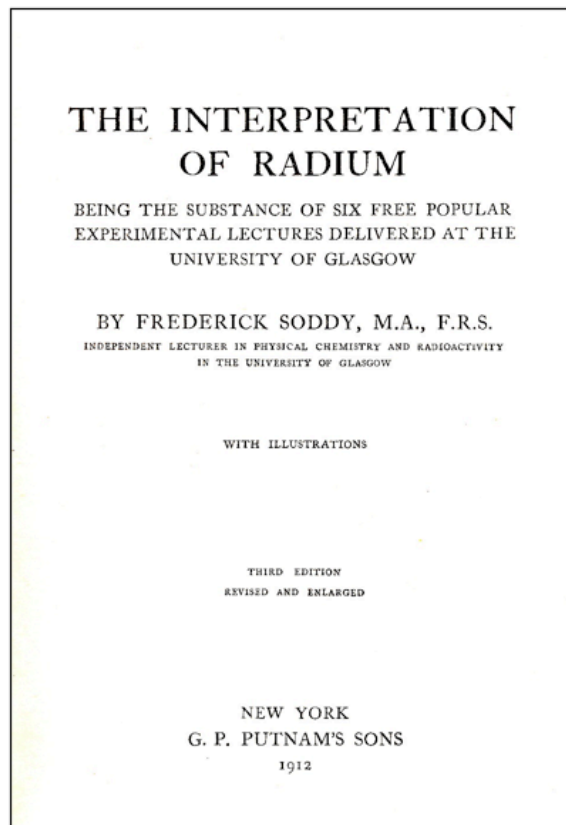

Figure 10. Title page of the 1912 edition of Soddy's *The Interpretation of Radium* which inspired Wells' novel.

Rutherford maintained a cold, but respectful, competition for the rest of their careers.

Between 1903 and 1913 – the year of Wells' letter to Simmons – Soddy and Rutherford would each write three books on the subject of radioactivity, but very different books. Whereas Rutherford's volumes were all straight-forward summaries of research techniques and results directed at his fellow physicists, at least two of Soddy's books were intended for the lay public and all of them bristled with brilliant passages speculating on the potential impact of radiochemistry on such concepts as the periodic law, the nature of the chemical elements, and the interrelation of matter and energy. The second of these books, *The Interpretation of Radium*, first appeared in 1909, and was based on a series of six free popular lectures on radioactivity which Soddy had delivered at the University of Glasgow during his tenure there as a Lecturer in Physical Chemistry and Radioactivity. This proved to be the most popular of Soddy's books and passed through numerous editions between 1909 and the late 1930s, when it was finally retitled *The Interpretation of the Atom* (28).

The novel itself opens with a scene in a lecture hall at the University of Edinburgh where a physicist named Rufus – who is obviously modeled on Soddy – is giving a course of public lectures on radium and radioactivity (29):

And we know now that the atom, that once we thought hard and impenetrable, and indivisible and final and ... lifeless, is really a reservoir of immense energy. That is the most wonderful thing about all this work. A little while ago we thought of the atoms as we thought of bricks, as solid building material, as substantial matter, as unit masses of lifeless stuff, and behold! these bricks are boxes, treasure boxes, boxes full of the intensest force. This little bottle contains about a pint of uranium oxide; that is to say about fourteen ounces of the element uranium. It is worth about a pound. And in this bottle, ladies and gentlemen, in the atoms in this bottle there slumbers at least as much energy as we could get by burning a hundred and sixty tons of coal. If at a word in one instant I could suddenly release that energy here and now, it would blow us and everything about us to fragments; if I could turn it into the machinery that lights this city, it could keep Edinburgh brightly lit for a week.

However, there is a problem with this delightful scenario since (29):

... at present no man knows, no man has an inkling of how this little lump of stuff can be made to hasten the release of its store. It does release it, as a burn trickles.

Slowly the uranium changes into radium, the radium changes into a gas called the radium emanation, and that again to what we call radium A, and so the process goes on, giving out energy at every stage, until at last we reach the last stage of all, which is, as far as we can tell at present, lead. But we cannot hasten it ... Why is the change gradual? ... Why does it dole itself out so slowly and so exactly? ... Why this decay by driblets; why not a decay en masse?

The answer that Rufus provides to his rhetorical questions is positively messianic (29):

Suppose presently we find it is possible to quicken that decay? ... It would mean a change in human conditions that I can only compare to the discovery of fire, that first discovery that lifted man above the brute. We stand today towards radioactivity exactly as our ancestor stood towards fire before he had learnt to make it. He knew it then only as a strange thing utterly beyond his control, a flare on the crest of the volcano, a red destruction that poured through the forest. So it is that we know radioactivity today. This ... is the dawn of a new day in human living. At the climax of that civilization which had its beginning in the hammered flint and the fire-stick of the savage, just when it is becoming apparent that our ever-increasing needs cannot be borne indefinitely by our present sources of energy, we discover suddenly the possibility of an entirely new civilization. The energy we need for our very existence, and with which Nature supplies us still so grudgingly, is in reality locked up in inconceivable quantities all about us. We cannot pick that lock at present, but ... we will.

Then that perpetual struggle for existence, that perpetual struggle to live on the bare surplus of Nature's energies will cease to be the lot of Man. Man will step from the pinnacle of this civilization to the beginning of the next. I have no eloquence, ladies and gentlemen, to express the vision of man's material destiny that opens out before me. I see the desert continents transformed, the poles no longer wildernesses of ice, the whole world once more Eden. I see the power of man reach out among the stars .....

Much of this speech is a paraphrase of Chapter 11 of Soddy's book and it is the consequences of Rufus' answer that Wells seeks to explore. What if man learns to control the energy of radioactivity? What social and economic upheavals will accompany the transition from the old chemical fuel-based civilization to the new nuclear-based civilization? Will the absence of the "struggle for existence" engendered by the limited energy resources of the past lead to a new morality? In short, what will happen if the world is set free?

The first stage in this process, the discovery of a way to induce radioactive decay in heavy elements and to control the rate of that decay is made in 1933 by a scientist named Holsten, whom Wells describes as a child prodigy and as "the greatest of European chemists" (29):

The problem which was already being mooted by such scientific men as Ramsay, Rutherford, and Soddy, in the very beginning of the twentieth century, the problem of inducing radioactivity in the heavier elements and so tapping the internal energy of atoms, was solved by a wonderful combination of induction, intuition and luck by Holsten so soon as the year 1933 ... He set up atomic disintegration in a minute particle of bismuth, it exploded with great violence into a heavy gas of extreme radioactivity, which disintegrated in its turn in the course of seven days, and it was only after another year's work that he was able to show practically that the last result of this rapid release of energy was gold.

The reason Wells couples the discovery of induced radioactive disintegration in bismuth with the discovery of a means of accelerating the release of atomic energy comes from yet another idea in Soddy's book – namely that all elements are slowing undergoing radioactive decay but, with the exception of those above bismuth, at rates which are too slow to detect. In other words, what Holsten has discovered is a way of accelerating the infinitely slow decay process already present in bismuth and in the lower elements. Note that there is no anticipation here of anything resembling a chain reaction. Indeed, the fact that Wells represents Holsten as a chemist rather than as a physicist strongly suggests that he pictures this acceleration process as something akin to chemical catalysis.

The second stage occurs in the 1950s with the invention of several engines capable of harnessing this energy release (29):

It was in 1953 that the first Holsten-Roberts engine brought induced radioactivity into the sphere of industrial production, and its first general use was to replace the steam engine in electrical generating stations. Hard upon the appearance of this came the Dass-Tata engine ... which was used chiefly for automobiles, aeroplanes, water-planes, and such-like mobile purposes. The American Kemp engine, differing widely in principle but equally practicable, and the Krupp-Erlanger came hard upon the heels of this, and by the autumn of 1954 a gigantic replacement of industrial methods and machinery was in progress all about the habitable globe.

These rapid economic changes lead, in turn, to massive unemployment, to social and political unrest, and eventually to war – a war which looks, as far as the combatants are concerned, suspiciously like the war that would break out in Europe the year Wells' novel was published. But there is also a significant difference. In Wells' futuristic war, the stalemate of conventional warfare is disrupted when the Germans drop an atomic bomb (Wells' actual term!) on the French headquarters in Paris (figure 11), an event which precipitates an all out atomic war between the Allies and the Central Powers.

Though all of this seems quite remarkable for a novel written in 1914, we should not overlook the significant differences between Wells' vision of nuclear war and what we now know to be the true reality. Wells' atomic bombs, for example, are not our own. His are made from a hypothetical artificial radioactive element called "Carolinum," discovered by a second world-famous radiochemist by the name of Hyslop, and are small enough for the bombardier of a typical biplane to carry three of them cradled between his legs. The bombs are dropped out of the plane by hand and are only powerful enough to destroy an entire building rather than an entire city (29):

Figure 11. An artist's interpretation of the "explosion" of one of H. G. Wells' imagined atomic bombs, circa 1914.

Those used by the Allies were lumps of pure Carolinum painted on the outside with unoxidized cydonator inducive enclosed hermetically in a case of Membranium. A little celluloid stud between the handles by which the bomb was lifted was arranged so as to be easily torn off and admit air to the inducive, which at once became active and set up radioactivity in the outer layer of the Carolinum sphere. This liberated fresh inducive, and so in a few minutes the whole bomb was a blazing continual explosion.

The main problem with the bombs is not so much their immediate explosive power as the persistence of their after-effects (29):

Always before in the development of warfare the shells and rockets fired had been but momentarily explosive, they had gone off in an instant once and for all, and if there was nothing living or valuable within reach of the concussion and the flying fragments, then they were spent and over. But Carolinum, which belonged to the β-Group of Hyslop's so-called "suspended degenerator" elements, once its degenerative process had been induced, continued a furious radiation of energy, and nothing could arrest it. Of all Hyslop's artificial elements, Carolinum was the most heavily stored with energy and the most dangerous to make and handle. To this day it remains the most potent degenerator known. What the earlier twentieth-century chemists called its half period was seventeen days; that is to say, it poured out half the huge store of energy in its great molecules in the space of seventeen days, the next seventeen days' emission was a half of that first period's outpouring, and so on. As with all radioactive substances, this Carolinum, though every seventeen day's its power is halved, though constantly it diminishes towards the imperceptible, is never entirely exhausted, and to this day the battle-fields of that frantic time in human history are sprinkled with radiant matter and so centers of inconvenient rays ...

What happened then when the celluloid stud was opened was that the inducive oxidized and became active. Then the surface of the Carolinum began to degenerate. This degeneration passed only slowly into the substance of the bomb. A moment or so after its explosion had begun it was still mainly an inert sphere exploding superficially, a big, inanimate nucleus wrapped in flame and thunder. Those that were thrown from aeroplanes fell in this state; they reached the ground still mainly solid and, melting the soil and rock in their progress, bored into the earth. There, as more and more of the Carolinum became active, the bomb spread itself out into a monstrous cavern of fiery energy at the base of what became very speedily a miniature active

volcano. The Carolinum, unable to disperse freely, drove into and mixed up with a boiling confusion of molten soil and superheated steam, and so remained, spinning furiously and maintaining an eruption that lasted for years or months or weeks according to the size of the bomb employed and the chances of its dispersal. Once launched, the bomb was absolutely unapproachable and uncontrollable until its forces were nearly exhausted, and from the crater that burst open above it, puffs of heavy incandescent vapor and fragments of viciously punitive rock and mud, saturated with Carolinum, and each a center of scorching and blistering energy, were flung high and far.

In this passage Wells has invented a new meaning for the word explosion, since quite obviously his bombs don't explode in any conventional sense of the word. It is also not apparent how far one should go in interpreting his "centers of inconvenient rays" as an anticipation of radioactive fallout. The novel contains no references to radiation sickness, which was not clearly recognized in 1914, nor to radioactive contamination via air currents, water supplies, or the food chain.

One of the interesting sociological sidelights of the novel (and the primary reason we are discussing it here) is the significant role which Wells assigns to fictional chemists, such as Holsten and Hyslop, in developing atomic energy. From the initial discovery of radioactivity in 1896 through the late 1920s, chemists, such as William Crookes, Marie Curie, Frederick Soddy, Otto Hahn, Kasimir Fajans, Fritz Paneth, Georg von Hevesy, and Bertram Boltwood, played an important role in its study and in the development of early electronic models of the atom. Indeed, so dominant was this role that Rutherford was given, much to his chagrin, the 1908 Nobel Prize in chemistry rather than physics. Unhappily, this role has been largely forgotten in introductory chemistry textbooks, which now give a totally ahistorical account of the development of radioactivity and modern atomic theory in which only physicists play a role. Even more tragically, in the few cases in which early radiochemists are mentioned, they are frequently misidentified as physicists. This is a result of imposing our current ideas of research specialities on a time when they did not exist, and Wells, writing in 1914 before the center of the field had clearly shifted from chemistry to physics, was still justified in assuming that chemists would continue to dominate the study of radioactivity (30).

The atomic war described by Wells is the final death rattle of the old civilization and the rest of the novel is devoted to a typical Wellsian description of its socialistic successor. Despite its intriguing anticipations of nuclear energy and atomic bombs, *The World*

Set Free is not a well-written book. It show signs of extremely hasty composition, and its rapidly shifting cast of characters and interdispersed third-person historical commentary make it hard to follow. Nevertheless, it remains, as David Dowling notes in his study, *Fictions of Nuclear Disaster*, the first known example of a nuclear disaster novel – a distinctive 20th-century literary genre which now includes literally thousands of novels, short stories and movies (26). But even more intriguing is the tribute paid to Wells by the Hungarian physicist, Leo Szilard, one of the few scientists to take the prospect of an atomic bomb seriously and one of the earliest to warn against the consequences of such a bomb being developed by Nazi Germany. In 1933, the same year as Wells' fictional chemist, Holsten, discovers how to accelerate the rate of nuclear decay, Szilard developed the idea of using a neutron-induced chain reaction for the same purpose and even applied for a patent on the process the next year. However, he kept much of this a secret because, as he later wrote, he knew "what this would mean," having read a German translation of the *World Set Free* the year before (31).

The New Machiavelli

Though not a "scientific romance," like the previous four books, Wells' 1911 novel, *The New Machiavelli*, does contain a brilliant critique of how chemistry was being taught in the typical British public school during the last decades of the 19th century and is thus well worth quoting.

The father of the novel's narrator teaches science in one of these schools and, as one of his father's students, the narrator is able to provide an entertaining description of how the rigidly proscribed curriculum and competitive standardized exam system used at the time had virtually ossified both the textbooks and the teaching methods used in the classroom (32):

A number of competing firms of publishers sprang into existence specializing in the Science and Art Department work; they set themselves to produce textbooks that should supply exactly the quantity and quality of knowledge necessary for every stage of each of five and twenty subjects into which desirable science was divided, and copies and models and instructions that should give precisely the method and gestures esteemed as proficiency in art. Every section of each book was written in the idiom found most satisfactory to the examiners, and test questions extracted from papers set in former years were appended to every chapter. By means of these last the teacher was able to train his class to the highest level of grant-earning efficiency, and very naturally he cast all other methods

of exposition aside. First he posed his pupils with questions and then dictated model answers ... That was my father's method of instruction.

The effects of this soul deadening routine on the teaching of an experimental science like chemistry was nothing short of tragic (32):

He did not do experiments if he could possibly help it, because in the first place they used up time and gas for the Bunsen burner and good material in a ruinous fashion, and in the second they were, in his rather careless and sketchy hands, apt to endanger the apparatus of the Institute and even the lives of his students. Then thirdly, real experiments involved washing up. And moreover they always turned out wrong, and sometimes misled the too observant learner very seriously and opened demoralizing controversies.

This latter observation apparently referred to the personal experiences of the narrator himself as is apparent from his further comments (32):

Quite early in life I acquired an almost ineradicable sense of the unscientific perversity of Nature and the impassable gulf that is fixed between systematic science and elusive fact. I knew, for example, that in science, whether it is subject XII, Organic Chemistry, or subject XVII, Animal Physiology, when you blow into a glass of lime water it instantly becomes cloudy, and if you continue to blow it clears again, whereas in truth you may blow into the stuff from the lime-water bottle until you are crimson in the face and painful under the ears, and it never becomes cloudy at all. And I knew too, that in science if you put potassium chlorate into a retort and heat it over a Bunsen burner, oxygen is disengaged and may be collected over water, whereas in real life if you do anything of the sort the vessel cracks with a loud report, the potassium chlorate descends sizzling upon the flame, the experimenter says "Oh Damn!" with astonishing heartiness and distinctness, and a lady student in the back seats gets up and leaves the room.

The solution to these difficulties adopted by the narrator's father is quite simple (32):

Science is the organized conquest of Nature, and I can quite understand that ancient libertine refusing to co-operate in her own undoing. And I can quite understand too my father's preference for what he called an illustrative experiment, which was simply an arrangement of the apparatus in front the the class with nothing whatever by way of material, and the Bunsen

burner clean and cool, and then a slow luminous description of just what you did put in when you were so ill-advised as to carry the affair beyond illustration, and just exactly what ought anyhow to happen when you did. He had considerable powers of vivid expression, so that in this way he could make us see all he described.

This "virtual" approach was particularly well adapted to training the students for their competitive exams by providing model answers to questions concerning laboratory experiments (32):

The class, freed from any unpleasant nervous tension, could draw this still life without flinching, and if any part was too difficult to draw, then my father would produce a simplified version on the blackboard to be copied instead. And he would also write on the board any exceptionally difficult, but grant-earning words, such as "empyreumatic" or "botryoidal."

Some words in constant use he rarely explained. I remember once sticking up my hand and asking him in the full flow of description, "Please sir, what is flocculent?"

"The precipitate is."

"Yes sir, but what does it mean?"

"Oh! flocculent!" said my father, "flocculent! Why ..." He extended his hand and arm and twiddled his fingers for a second in the air. "Like that," he said.

I thought the explanation sufficient, but he paused for a moment after giving it. "As in a flock bed, you know," he added and resumed his discourse.

I find these descriptions particularly relevant because, in the State of Ohio at least, the intervention of ignorant legislators in university affairs has resulted in the chemistry curriculum degenerating into the very state satirized by Wells so many years ago. We are now required to use a standard textbook and to evaluate student performance using a standardized exam, and at the University of Cincinnati we are no longer allowed to use demonstrations or experiments involving flames or explosions, however intentional and controlled. Indeed, neither of the experiments mentioned by Wells, be it the reaction of carbon dioxide with lime water:

$$CO_2(g) + Ca(OH)_2(aq)\ Ca(CO_3)(s) + H_2O(l) \qquad [4]$$
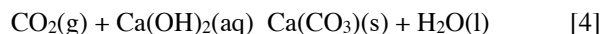
or the preparation of dioxygen gas from potassium chlorate:

$$2K(ClO_3)(s) + heat\ \rightarrow\ 2KCl(s) + 3O_2(g) \qquad [5]$$

are done by students today, and at Cincinnati we would no longer be able to perform the latter experiment even

if we wished to, since our laboratories no longer have Bunsen burners. Perhaps we should take a hint from the narrator's father and use only virtual or "illustrative experiments" instead.

The Late Mr. Wells

With the outbreak of the First World War, Wells' emphasis began to shift again. His works became increasingly political in nature, and he began to think of himself less and less as a novelist and more and more as a "publicist" for what he described as "the coming future world state." This transformation did not go unnoticed by his contemporaries and, as early as 1919, the curmudgeonly American critic, H. L. Mencken, who was no lover of "social reformers and uplifters," but was an admirer of Wells' middle period as a main-stream novelist, saw fit to write Wells' literary obituary, even though Wells would remain active for another 27 years. Appropriately entitled "The Late Mr. Wells," this masterpiece of Menckenian invective ended with a succinct summary of Wells' evolution as a writer (33):

What remains of Wells? There remains a little shelf of very excellent books, beginning with Tono-Bungay [1909] and ending with Marriage [1912]. It is a shelf flanked on one side by a long row of extravagant romances in the manner of Jules Verne, and on the other side by an even longer row of puerile tracts. But let us not underestimate it because it is in such uninviting company. There is on it some of the liveliest, most original, most amusing, and withal most respectable fiction that England has produced in our time. In that fiction there is a sufficient memorial to a man who, between two debauches of claptrap, had his day as an artist.

Alas, posterity has decreed otherwise, and the public, with its usual disregard of those who seek to dictate what it should or should not like, has continued to read and admire the wrong section of the shelf.

References and Notes

1.   First written in 1993 for inclusion in J. Stocker's collection, *Chemistry and Science Fiction*, and subsequently revised in 1995 for publication in the *Chemical Intelligencer*, it ultimately appeared in neither source for the reasons given in the preface to this book. A more detailed analysis of Wells' treatment of science and scientists, which I was unaware of when writing this essay, may be found in R. D. Haynes, *H. G. Wells Discoverer of the Future: The Influence of Science on His Thought*, New York University Press: New York, NY, 1980.

2.   H. G. Wells, *Experiment in Autobiography: Dis-*

coveries and Conclusions of a Very Ordinary Brain, Macmillan: New York, NY, 1934, p. 427.

3. See the bibliography given in P. Castello, *Jules Verne: Inventor of Science Fiction*, Scribner: New York, NY, 1978, pp. 223-225.

4. See the bibliography given in N. MacKenzie, J. MacKenzie, *H. G. Wells: A Biography*, Simon and Schuster: New York, NY, 1973, pp. 469-473.

5. A. B. Evans, *Jules Verne Rediscovered: Didacticism and the Scientific Novel*, Greenwood Press: Westport, CT, 1988.

6. Quoted in reference 3, p. 186.

7. H. G. Wells, *Seven Famous Novels*, Knopf: New York, NY, 1934, pp. vii, viii.

8. Reference 4, chapters 4-5.

9. H. G. Wells, *The Invisible Man: A Grotesque Romance*, Pearson: London, 1897; also reference 7, pp. 161-262. All quotes from reference 7, pp. 212, 219-220, 223.

10. L. A. Ford, *Chemical Magic*, Dension: Minneapolis, MN, 1958, pp. 38-39.

11. Transcribed from the original movie dialog.

12. In addition to the six popular novels listed earlier, Wells had published the lesser-known science fiction novel, *When the Sleeper Wakes*, in 1899.

13. H. G. Wells, *First Men in the Moon*, Newnes: London, 1901; also reference 7, pp. 391-528. All quotes from reference 7, pp. 398-399, 408, 410.

14. An interesting anticipation of Wells' antigravity metal can be found in an early 19th century American novel by George Tucker entitled *A Voyage to the Moon*. Published by E. Bliss of New York in 1827, the story involves a trip to the moon by two men in a copper box. This box, which is fitted with a telescope, a source of compressed air, and circular glass portholes cut in each side, is propelled by means of a special gravity metal called "Lunarium" held to the outside by a mechanical release mechanism. However, unlike Cavorite, which acts as a gravity screen, Lunarium works on the assumptIon that each object in the solar system has a gravitational attraction only for specific materials, and Taylor's vehicle is controlled by alternately releasing spheres of Lunarium, which is specifically attracted to the moon, and spheres of lead, which is specifically attracted to the earth. It is doubtful that Wells was aware of Taylor's novel, which had a totally different story line and is vastly inferior in terms of both plot and character development

15. For a clever attempt at rationalizing a balloon trip to the moon, the reader should consult Edgar Allan Poe's tale, "The Unparalleled Adventure of One Hans Pfaall."

16. J. Verne, T*he Space Novels of Jules Verne: From the Earth to the Moon and All Around the Moon*, Dover: New York, NY, 1960. This an unabridged reprint of the 1874 and 1876 translations by Edward Roth. Most English editions of these novels delete the technical details quoted here from pp. 176, 191.

17. W. B. Jensen, "Captain Nemo's Battery: Chemistry and the Science Fiction of Jules Verne," this volume.

18. J. R. Partington, *A Text-Book of Inorganic Chemistry*, Macmillan: London, 1927, p. 767.

19. H. G. Wells, *The Food of the Gods and How It Came to Earth*, Macmillan: London, 1904; also reference 7, pp. 531-688. All quotes from reference 7, pp. 531, 532-533, 535-536.

20. J. V. Eyre, *Henry Edward Armstrong, 1848-1937, The Doyen of British Chemists and Pioneer of Technical Education*, Butterworths: London, 1958.

21. A sample of Armstrong's writings on chemical education and science education in general can be found in H. E. Armstrong, *The Teaching of Scientific Method and Other Papers on Education*, Macmillan: London, 1903; and W. H. Brock, Ed., *H. E. Armstrong and the Teaching of Science, 1880-1930,* Cambridge University Press: Cambridge, 1973.

22. Some good examples of Armstrong's splendid but misdirected wit can be found in H. E. Armstrong, *Essays on the Art and Principles of Chemistr*y, Macmillan: New York, 1927.

23. Brock, reference 21, p. 59. See also pp. 136. 141.

24. Reference 2, Chapter 5.

25. For a recent popular treatment see T. A. McMahon, J. T. Bonner, *On Size and Life,* Scientific American Library: New York, NY, 1983. The classic in this field is, of course, W. D'Arcy Thompson, *On Growth and Form*, Cambridge University Press: Cambridge, 1917.

26. D. Dowling, *Fictions of Nuclear Disaster,* University of Iowa: Iowa City, IW, 1987. Quote p. 43.

27. G. Kauffman, Ed., *Frederick Soddy (1877-1956), Early Pioneer in Radiochemistry*, Reidel, Dordrecht, 1986.

28. F. Soddy, *The Interpretation of Radium*, 3rd ed., Putnam's Sons: New York, NY, 1912. I have selected this edition as the one most likely to have been read by Wells.

29. H. G. Wells, *The World Set Free, A Story of Mankind*, Dutton: New York, NY, 1914. Quotes on pp. 33-38, 40-41, 51-52, 109, 114-117.

30. L. Badash, "The Suicidal Success of Radiochemistry," in reference 28, pp. 27-41.

31. W. Lanouette, B. Szilard, *Genius in the Shadows: A Biography of Leo Szilard*, Scribners: New York, NY, 1992, pp. 134, 137, 140, 179. It is also of interest to note that Irene and Frederic Joliot-Curie discovered artificial radioactivity within a year (1934) of Wells' fictional chemist.

32. H. G. Wells, *The New Machiavelli*, Lane: London, 1911. All quotes are from the 2005 Penguin edition, pp. 25-27.

33. H. L. Mencken, "The Late Mr. Wells," *Prejudices: First Series*, Knopf: New York, NY, 1919, pp. 34-35.

VI

Tom Swift Among the Diamond Makers

Synthetic Diamonds in Fact and Fiction

The Forgotten Triumph

Though most historical accounts of the development of modern chemistry make much of the triumphs of synthetic organic chemistry with respect to the late 19th-century coal-tar dye and pharmaceutical industries, little is said of the equally impressive triumphs of inorganic chemistry with respect to the synthesis of artificial gems and minerals, even though a perusal of popular fiction during the final decades of the 19th century and early decades of the 20th century quickly reveals an ongoing fascination with this subject, and especially with attempts to synthesize that most precious of gems – the diamond (1, 2).

The Diamond Maker

One of the earliest fictional works to deal with the synthesis of diamonds is a short story by H. G. Wells entitled "The Diamond Maker" which appeared in his collection, *The Stolen Bacillus and Other Incidents*, first published in 1895. The story opens when the anonymous narrator, who has taken a late evening stroll along the Embankment in London, is approached by a beggar. To the narrator's surprise, instead of asking for a handout, the beggar offers instead to sell him an enormous diamond (3):

... suddenly unbuttoning his wretched coat he pulled out a little canvas bag that was hanging by a cord round his neck. From this he produced a brown pebble. "I wonder if you know enough to know what that is?" He handed it to me. Now a year or so ago, I had occupied my leisure in taking a London science degree, so that I have a smattering of physics and mineralogy. The thing was not unlike an uncut diamond of the darker sort, though far too large, being almost as big as the top of my thumb. I took it, and saw it had the form of a regular octahedron, with the carved facets peculiar to the most precious of minerals. I took out my penknife and tried to scratch it – vainly. Leaning forward toward the gas-lamp, I tried the thing on my watch-glass, and scored a white line across that with the greatest ease.

When the narrator asks the beggar the source of

Figure 1. Herbert George Wells (1866-1946).

the diamond, the beggar replies that he made it. The narrator, however, is skeptical as he had "heard something of Moissan, but ... knew his artificial diamonds were very small."

Goaded by this apparent lack of belief, the beggar reveals further details about himself and his method for producing synthetic diamonds (3):

Diamonds ... are to be made by throwing carbon out of combination in a suitable flux and under a suitable pressure; the carbon crystallizes out, not as black-lead or charcoal-powder, but as small diamonds. So much has been known to chemists for years, but no one yet has hit upon exactly the right flux in which to melt up the carbon, or exactly the right pressure for the best results. Consequently the diamonds made by chemists are small and dark, and worthless as jewels. Now I, you know, have given up my life to this problem ... I began to work at the conditions of diamond making when I was seventeen, and now I am thirty-two.

Not only has the beggar squandered his time, but

his inheritance as well (3):

I had ... about a thousand pounds when I was twenty-one, and this, I thought, eked out by a little teaching, would keep my researches going. A year or two was spent in study, at Berlin chiefly, and then I continued on my own account ... At first I had a little laboratory, but as my resources began to run out I had to conduct my experiments in a wretched unfurnished room in Kentish Town, where I slept at last on a straw mattress on the floor among all my apparatus. The money simply flowed away. I grudged myself everything except scientific appliances. I tried to keep things going by a little teaching, but I am not a very good teacher, and I have no university degree, nor very much education except in chemistry, and I found I had to give a lot of time and labor for precious little money. But I got nearer and nearer the thing.

Finally, the beggar provides some tantalizing details about his process (3):

Three years ago I settled the problem of the composition of the flux, and got near the pressure by putting this flux of mine and a certain carbon composition into a closed-up gun barrel, filling up with water, sealing tight, and heating ... It burst, and smashed all my windows and a lot of my apparatus; but I got a kind of diamond powder, nevertheless. Following out the problem of getting a big pressure upon the molten mixture from which the things were to crystallize, I hit upon the researches of Daubree at the Paris Laboratorie des Poudre et Salpetres. He exploded dynamite in a tightly screwed steel cylinder, too strong to burst, and I found he could crush rocks into a muck not unlike the South African bed in which diamonds are found. It was a tremendous strain on my resources, but I got a steel cylinder made for my purpose after his pattern. I put in all my stuff and my explosives, built up a fire in my furnace, put the whole concern in, and went out for a walk.

Indifferent to the possibility of his cylinder exploding and killing the other inhabitants of the tenement, the beggar returns from his walk to find that it is luckily still intact, though he is now faced by a further problem (3):

You know time is an important element in crystallization. If you hurry the process the crystals are small – it is only by prolonged standing that they grow to any size. I resolved to let this apparatus cool for two years, letting the temperature go down slowly during that time.

Figure 2. Ferdinand Frederik Henri Moissan (1852-1907) in his laboratory, c. 1895. Note the control board for his electric furnace and the anvil, presumably used in his diamond experiments.

The time in question had expired only three weeks ago and the beggar, on opening the cylinder and chiseling out the contents, had discovered three large diamonds and five small ones among the debris.

However, the beggar's odd behavior, his chemical equipment, and the repeated explosions had convinced the other inhabitants of the tenement that he was really an anarchist manufacturing bombs, and they turn him into the police. He is able to escape with his diamonds shortly before the police raid on his room and is now wandering the streets of London trying to get the funds to reestablish himself. Unhappily no one will believe his story of how he got the diamonds. The narrator also remains cautious and, rather than buying the diamond on the spot, he asks the beggar to come to his office the next day. However, the beggar has become suspicious to the point of paranoia and the two never quite succeed in making contact again, thus leaving the narrator to wonder whether he should have chanced the purchase after all.

The question of synthetic diamonds would have attracted public attention about the time of the publication of Wells' short story as a result of the researches of the French chemist, Ferdinand Frederic Henri Moissan (figure 2), who is mentioned in passing by the story's
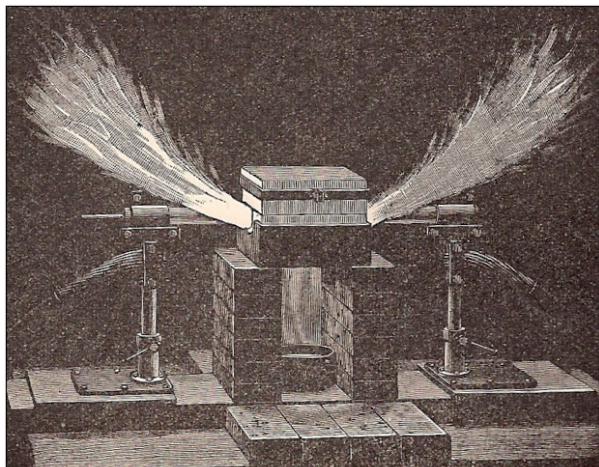
Figure 3. Moissan's electric furnace in action.

narrator. Most famous for his successful isolation of the element fluorine in 1886, Moissan had been pursuing the synthesis of diamonds since 1893 (4-5). Moissan's approach was a modification of a procedure developed by the English chemist, R. S. Marsden, and consisted of dissolving carbon in molten metal and rapidly cooling the melt. Since metallic solutions of carbon expand on cooling, the solidification of the still molten interior trapped within the solid shell initially produced by the rapid cooling is able to generate large pressures on the small pockets of carbon which are deposited as both the temperature of the liquid melt and the solubility of the carbon decrease (6). Marsden had dissolved sugar carbon in molten silver and in silver-platinum alloys. Moissan, who reported that he had "frequently" repeated Marsden's process using retort coke and a graphite crucible heated in a wind furnace, claimed "that it is possible to obtain, in such an operation, black diamond more or less crystalline"
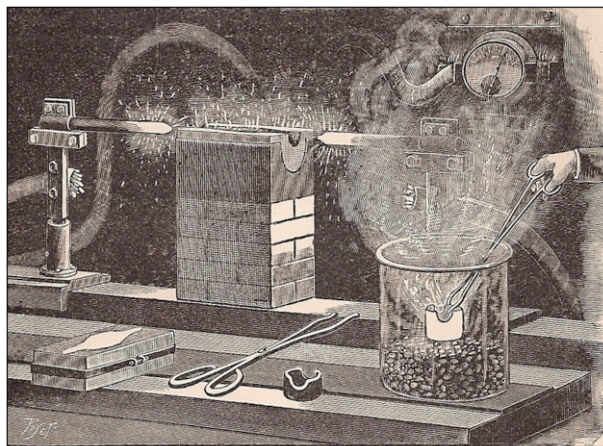
Figure 4. Cooling the carbon - iron melt in ice water.

(7). Moissan then further modified Marsden's approach by substituting molten iron for molten silver and the higher temperatures of his newly-developed electric carbon arc furnace for those of a conventional laboratory wind furnace (figures 3-4).

The curious thing about Wells' story, however, is that, despite his name dropping, the beggar does not use the Marsden-Moissan approach to diamond synthesis, but rather one which resembles the earlier work of the Scottish chemist, James Ballantyne Hannay (8). In 1880 Hannay reported that he had successfully made diamonds by heating mixtures of paraffin oil (i.e., kerosene), rectified bone oil (primarily pyridine), and lithium metal in 20" x 6" wrought iron tubes with half-inch bores. These were welded shut at the ends and
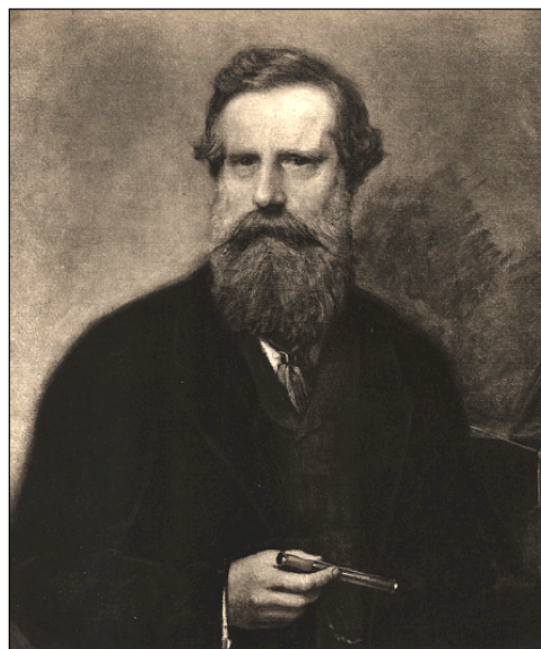

Figure 5. William Crookes (1832-1919).

maintained at red heat for fourteen hours, leading to decomposition of the organic materials and the production of high pressures. After cooling, the tubes were dissolved in acid to separate out any diamonds. Out of 80 trials, most of which exploded, three produced tiny crystals (about 0.25 mm in length) which Hannay claimed were diamonds.

Wells' preference for the Hannay approach was doubtlessly based, because of the ever-present danger of an explosion, on its greater dramatic impact – an impact which he intensifies by invoking the work of the French geologist, Gabriel-August Daubree, on the use of explosives to generate high pressures. Daubree was an expert on the origins of rocks and minerals and
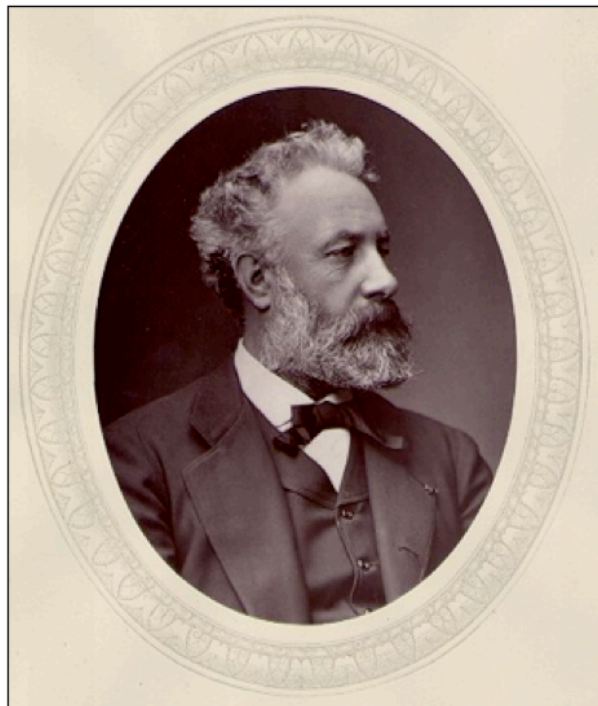
Figure 6. Jules Verne (1828-1905).

on their experimental reproduction in the laboratory, though I have found no reference to his work in standard historical accounts of the diamond synthesis (9). However, ten years after the publication of Wells' story, the English chemist, William Crookes (figure 5), claimed to have successfully synthesized diamonds by exploding cordite with carbon in a closed steel vessel (20), and in 1961 Paul S. DeCarli and John C. Jamieson successfully made diamond by subjecting graphite to a five-million pound per square inch shock wave generated by an explosive charge (11). This shock wave process is currently used on a commercial basis by DuPont.

The Star of the South

It is of some interest to compare Wells' short story with an even earlier work based on the synthesis of diamonds – in this case a full-length novel published by Jules Verne (figure 6) in 1884 (12). This provides us with a rare opportunity to directly experience the vast differences in scientific detail found in the writings of these two authors when dealing with a common theme. Entitled *The Star of the South* (figure 7), Verne's novel revolves around the exploits of a young French mining engineer named Cyprien Mere, who is visiting South Africa as part of a geological survey sponsored by the French Academy of Sciences, and who is trying to gather data for the completion of his doctoral thesis on

"the diamantiferous basin of the Vaal" (13). Mere rents a house for use as a laboratory from a British rancher named John Watkins. He eventually strikes up a friendship with the rancher's daughter, Alice, who frequently visits him at his laboratory (figure 8) to listen to him discourse on the geology and chemistry of diamonds (12):

The young engineer's laboratory with its weird-looking apparatus interested her greatly, and she was especially anxious to learn what she could about the nature of the diamond, that precious stone which loomed so large in the conversation and commerce of the region.

Eventually Alice broaches the question of why, if diamonds are merely crystalline carbon, as Mere claims, chemists have not attempted to make them artificially (12):

Why don't you chemists crystallize it as you did the sulfur in those pretty needles the other day? It would be so much more convenient surely, than having to dig among the rocks to find it.
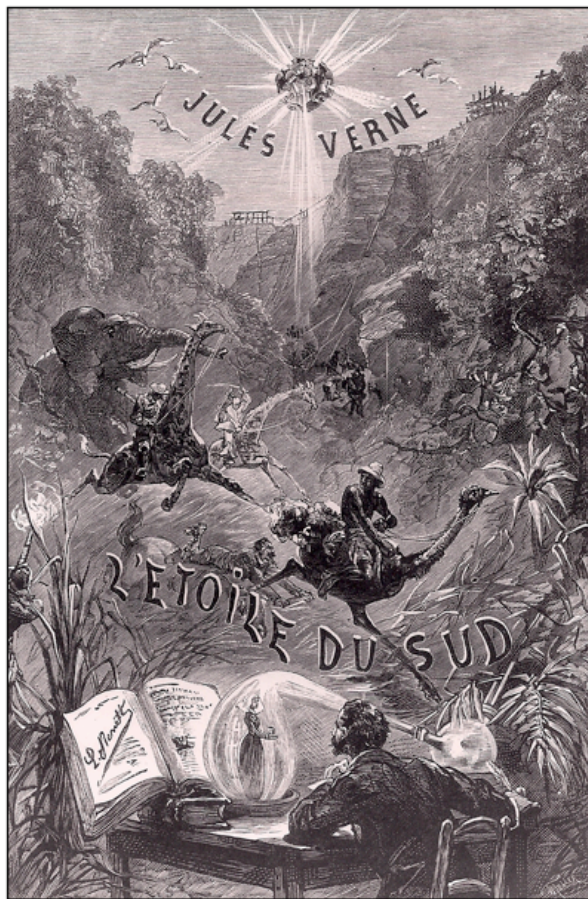

Figure 7. Title page of the original 1884 French edition of *The Star of the South*. Note the metaphor for a chemist in love at the bottom of the page!
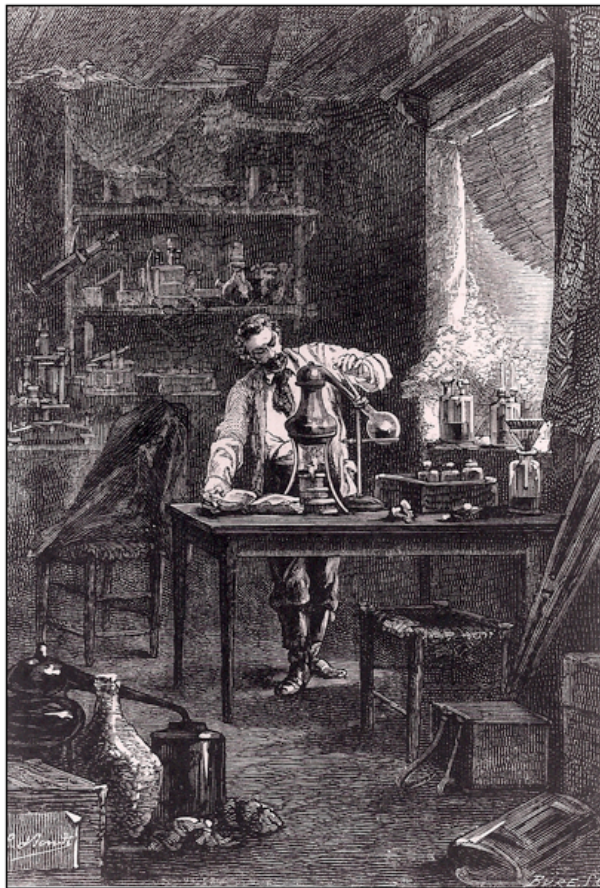
Figure 8. Cyprien Mere in his chemical laboratory.

to which Mere replies:

People have often tried to do so and to manufacture diamonds by crystallizing pure carbon. To a certain extent they have succeeded. Recently some experimenters have produced diamond dust by using a strong electric current in vacuo to act on carbon rods free from any mineral substances, and prepared from sugar-candy. But so far the problem has not met with any solution of commercial value. It may be only a question of time. Any day, perhaps at this very moment, some method of making diamonds may be discovered.

The experiments to which Mere refers were actually done by the French physicist Cezar Mansuete Despretz – not recently, as Verne claims, but between 1849 and 1853, and involved the deposition on platinum wires placed in a carbon arc of a crystalline dust capable of scratching glass (14).

The friendship with Alice predictably blossoms into romance, but when Mere approaches Watkins to ask for his daughter's hand in marriage, he is rebuffed because he owns neither land nor diamond mines.

Mere's initial response is to return to France in defeat, but Alice, on hearing the news, chides him for giving up so easily, while simultaneously making a sly reference to their tutorial sessions on elementary chemistry (12):

Going away! And you're going to run away from your scholar before she has finished her chemistry? You are going to leave me in the oxygen with the mysteries of nitrogen a closed book to me? It's too bad of you, sir!

Chastened, Mere decides instead to stay. In order to gain the wealth necessary to satisfy Watkins, he abandons his scientific work and buys a diamond claim, but it proves worthless, though the experience gains him the loyalty of three devoted servants, a Chinese named Li and two Kaffirs named Matakit and Bardik.

The solution to his dilemma is, as usual, suggested by Alice, who is unhappy with Mere wasting his time as a diamond prospector (12):

If you want to find diamonds so badly ... why don't you look where you are most likely to find them – in your crucible? ... You're a chemist, knowing more than anybody else about these wretched stones which people value so highly ... If I were in your place I'd not try to find diamonds. I'd make them!

Mere is enthusiastic about her suggestion (12):

And why not? ... To make artificial diamonds may have appeared Utopian a century ago but now it's as good as done. Some French savants have made rubies, emeralds and sapphires and, after all, these are only differently colored crystals of aluminum [sic]. Two Glasgow men actually made diamonds whose only fault was that they were so horribly dear – much dearer than the natural diamonds – and so their discovery wasn't of any commercial value, but when the scientific solution of a problem has been arrived at, the industrial solution can't be far away.

The two "French savants" referred to in this passage are probably the French chemist, Edmond Frémy (figure 9), and his assistant, Charles Feil, who succeeded in 1877 in making small synthetic rubies by reacting lead oxide and crude alumina (i.e. dialuminum trioxide) to make lead aluminate. This was then slowly reacted with silica to produce lead silicate and pure alumina or dialuminum trioxide (Al_2O_3) in the form of clear crystalline plates. Addition of 2-3% potassium dichromate to the melt resulted in ruby plates. Though true rubies, the plates were too thin and fragile to be of much commercial value, and it is to the 1902 process developed by Frémy's assistant, Auguste Victor-Louis

Figure 9. Edmond Frémy (1814-1894).

Verneuil (figure 10), that we owe the first commercially successful synthetic rubies (15). Note that Verne, or possibly his translator, has confused aluminum and alumina in this passage.

The two "Glasgow men" mentioned by Verne are, without a doubt, the Glasgow industrial chemists, James Mactear and James Ballantyne Hannay. Between December of 1879 and February of 1880, both claimed to have independently synthesized diamonds. Both submitted samples to Nevil Story-Maskelyne, the keeper of minerals at the British museum. Contrary to Verne's statement, Mactear's samples proved to be silica, but Story-Maskelyne certified that Hannay's samples were true diamonds (16).

If there is any question that Verne is referring to Hannay, it is dispelled in the next chapter when Mere describes his own process for making diamonds (12):

In the course of a year's brilliant researches into the solubility of solids in gas, Cyprien had not failed to notice that certain substances, silica and alumina for instance, though normally insoluble in water, are soluble by water vapor at a high temperature, and under great pressure. This gave him the idea of finding a gaseous solvent for carbon with a view to its subsequent crystallization ... Several analogies had lead the young engineer to think that diamond might be formed in the kopjes much as sulphur is in solfataras. For, as is well known, in these the sulfur results from a partial oxidation of sulphuretted hydrogen [hydrogen sulfide];

after part of it is changed into sulfurous acid [sulfur dioxide], the residue is deposited as crystals [of sulfur] on the sides of the solfatara. Perhaps ... these deposits in which the diamonds occur are really rich in carbon? If so much hydrogen and carbon is produced in streams and alluvial deposits as marsh gas, why shouldn't there have been an oxidation of the hydrogen with partial oxidation of carbon, leading to a crystallization of the excess. With this idea in mind, a chemist had little difficulty in selecting a compound to play the part of the oxygen in an analogous, but artificial reaction.

The first sentence of this quote is almost verbatim from the opening paragraph of Hannay's preliminary notice of his experiments on the synthesis of diamonds, which had, in turn, evolved out of his earlier interest in the use of supercritical fluids as solvents (17). Hannay's rationale was to generate "nascent" gaseous carbon via the dehydrogenation of paraffin oil with metallic lithium:

$$(2n + 2)Li(l) + C_nH_{2n+2}(g) \rightarrow (2n+2)LiH(s) + nC(g) \quad [1]$$
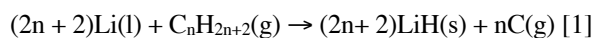
This nascent carbon was assumed to be soluble in the supercritical hydrocarbon-pyridine vapor, from which it slowly crystallized as the reaction vessel was cooled.
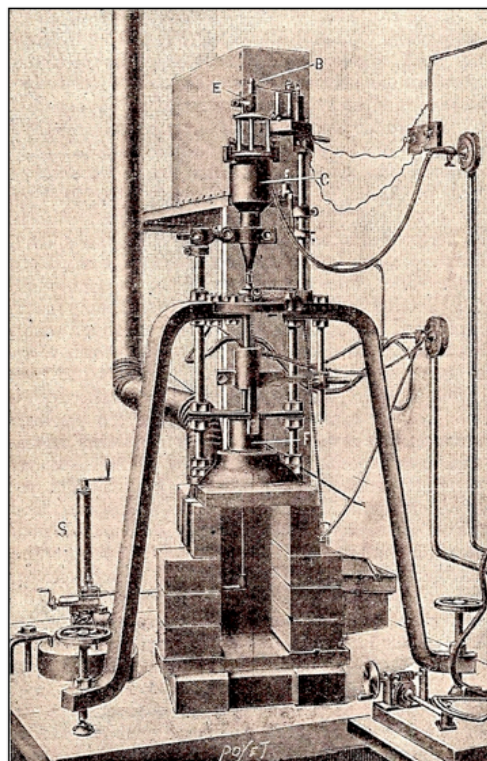

Figure 10. Verneuil's apparatus for the commercial synthesis of rubies.

The high pressures and temperatures were incidental to driving reaction 1 and to the creation of the supercritical gaseous solvent and were not a result of an understanding of the phase diagram for carbon and the role played by pressure in the interconversion of graphite and diamond. Indeed, almost all 19th-century attempts at synthesizing the diamond were based on the idea that the difference between diamond and the other forms of carbon was simply that of a crystalline versus an amorphous solid. What was needed was a proper solvent for the carbon which would allow its slow deposition in the form of large crystals. Thus, even Marsden looked upon his molten silver and silver-platinum melts as solvents for carbon and not as devices for generating high pressures. It is Moissan who appears to have been the first to appreciate the role of pressure in the graphite-diamond transition and even then his understanding came from an analysis of the probable geochemical origins of natural diamonds within igneous, high-pressure rocks, and not as a result of applying thermodynamics and Le Chatelier's principle (18).

What is curious, however, is that Verne mixes Hannay's experimental setup with an entirely different set of chemical reactions based on the assumption that the diamond is a sedimentary mineral slowly formed via "the transportation by water of the gem's constitu-

ents"– a theory which Mere propounds earlier in the novel (12). He compares this with the deposition of sulfur crystals in the vents or solfataras of volcanoes via the reaction of the hydrogen sulfide and sulfur dioxide in the volcanic gases (19):

$$2H_2S(g) \ + \ SO_2(g) \ \rightarrow \ 2H_2O(g) \ + \ 3S(s) \qquad [2]$$
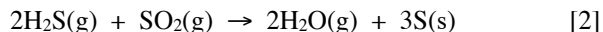
and proposes the high temperature – high pressure acceleration of a similar reaction for carbon in his Hannay-like reactor:

$$H_4C(g) \ + \ CO_2(g) \ \rightarrow \ 2H_2O(g) \ + \ 2C(s) \qquad [3]$$
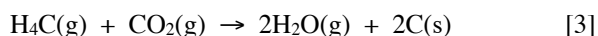
Despite the negative mass action effect of water on these reactions, Partington reports that reaction 2 can only take place in its presence (20), and Mellor describes a graphic example of its operation in a sulfur spring at Kriswoik, Iceland, from which the water (21):

... is said to be ejected to a height of five to eight feet and to be accompanied by steam impregnated with sulfur dioxide and hydrogen sulfide. The water subsequently deposits sulfur and in many places the surface of the ground has a crust of sulfur two to three feet thick.

For his purposes Mere selects a section of a steel cannon barrel "about half a yard long, two inches thick and three inches in bore." He coats the inside with a mortar made from mud taken from natural diamond deposits and adds "a few fragments of copper and about three pints of water" (12):

Then he filled it with marsh gas [methane], and after carefully luting it with his mortar, he stopped up each end with metal plugs strong enough to withstand any force. The apparatus constructed, the only thing to do was to submit it to an intense heat. For this purpose it was put into a large reverberating furnace kept going night and day for a fortnight so as to keep it at a constant white heat. Furnace and tube were then enveloped in a thick coating of refractory earth, first to retain the greatest possible amount of heat and then to cool down as slowly as possible at the proper time. The furnace looked like a huge beehive or an Eskimo hut.

Note that Mere never specifies the nature of his oxidizing agent or source of carbon dioxide.

When the reaction is complete, the furnace is slowly cooled for another two weeks and then opened, only to find that the "barrel had split like a glass test tube" (figure 11). However, inside Mere finds a large diamond. Since this event happens only about one third through the novel, many additional adventures follow

Figure 11. Mere examining his exploded reaction vessel.

in which both the unusual gastronomic habits of ostriches and the misplaced devotion of loyal servants play a key role.

The Silent Bullet

Yet a third fictional reference to the synthesis of diamonds occurs in the 1910 short-story collection, *The Silent Bullet*, by the American author Arthur B. Reeve. The stories in this collection detail the adventures of Craig Kennedy, a professor of chemistry and "scientific detective" in the mold of R. Austin Freeman's Dr. Thorndyke (figure 12). Entitled, like Wells' original tale, "The Diamond Maker," the adventure in question begins with the head of an insurance company's fraud division seeking Kennedy's assistance in solving the mystery of the death and robbery of one of their insured clients – a jeweler by the name of Morowitch.

Found wandering on the street late at night in a semi-delirious state, Morowitch is taken home by a passing cab driver, where, despite the efforts of the family doctor, he soon dies of apparent lung failure. The next morning his business partner discovers that their office has been ransacked and several thousand dollars worth of diamonds have been removed from their heavy steel safe by boring a hole through its top.

Kennedy first asks to see the safe, bringing with him several glass-stoppered bottles from his chemical laboratory at the university. After carefully examining the edges of the hole in the top of the safe (22):

... just a trace of a smile of satisfaction flitted over his face ... Without saying a word he took the glass stopper out of the larger bottle which he had brought and poured the contents on top of the safe near the hole. There it lay, a little mound of reddish powder. Kennedy took a little powder of another kind from the other bottle and lighted it with a match. "Stand back – close to the wall," he called as he dropped the burning mass on the red powder. In two or three leaps he joined us at the far end of the room.

Almost instantly a dazzling, intense flame broke out and sizzled and cracked. With bated breath we watched. It was incredible, but that glowing mass of powder seemed literally to be sinking, sinking right down into the cold steel. In tense silence we waited. On the ceiling we could still see the reflection of the molten mass in the cup which it had burned for itself in the top of the safe.

At last it fell through into the safe – fell as the burning roof of a frame building would fall into the building. No one spoke a word, but as we cautiously peered over the top of the safe we instinctively turned to Kennedy for an explanation.
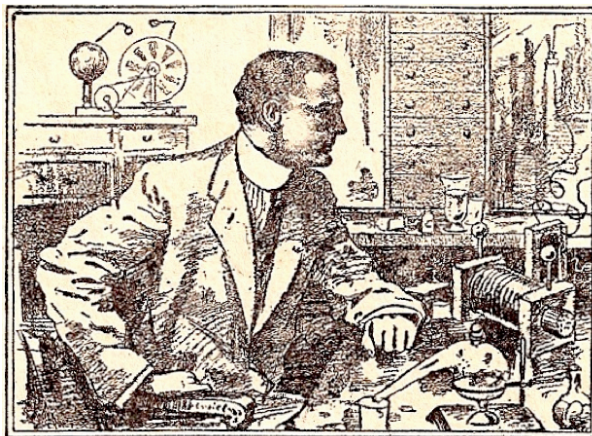

Figure 12. Craig Kennedy, chemist and "scientific detective," as pictured on the title page of the 1914 novel *Guy Garrick*.

The desired explanation is quick in coming (22):

"Thermite," was all Kennedy said .. "an invention of a chemist named Goldschmidt, of Essen, Germany. It is a compound of iron oxide, such as comes off a blacksmith's anvil or the rolls of a rolling mill, and powdered aluminum. You could thrust a red-hot bar into it without setting it off, but when you light a little magnesium powder and drop it on thermite, a combustion is started that quickly reaches fifty-four hundred degrees Fahrenheit. It has the peculiar property of concentrating its heat to the immediate spot on which it is placed. It is one of the most powerful oxidizing agents known, and it doesn't even melt the rest of the steel surface. You see how it ate its way through the steel. Either red or black thermite will do the trick equally well.

Though thermite is actually a physical mixture of iron oxide and aluminum rather than a compound of the two, and I am uncertain just how one would go about pouring burning magnesium powder (one actually places it on top of the thermite before lighting it or, even better, uses a strip of magnesium ribbon as a fuse), this is still a fairly decent description of the well-known thermite reaction:

$$Fe_2O_3(g) \ + \ 2Al(s) \ \rightarrow \ Al_2O_3(s) \ + \ 2Fe(l) \qquad [4]$$
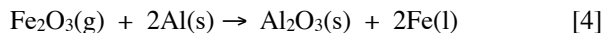
first commercially developed by the German industrial chemist, Hans Goldschmidt (figure 13), in 1895 (23). The phrase "red thermite" refers to the thermite mixture made with the red oxide of iron (Fe_2O_3) as described in the above equation. The phrase "black thermite" is more ambiguous and may refer either to a mixture made with the black oxide of iron (FeO) or with black manganese dioxide (MnO_2).

Figure 13. Hans Goldschmidt (1861-1923) of thermite fame.

This manner of entering a locked safe suggests someone with chemical training and this suspicion is further reenforced on interviewing the family doctor, who suspects that Morowitch was somehow poisoned, and by Morowitch's wife, who reveals that he had business dealings with a French chemist named Poissan , who was attempting to get Morowitch to invest in a process which he had developed for the synthesis of artificial diamonds. The further discovery that all of Morowitch's files under the letter P have been stolen and that Poisson's laboratory is located on the very street on which Morowitch was found semi-conscious, make it virtually certain that Poissan is the culprit.

The next day Kennedy visits Poissan's laboratory, where he arranges to return that same evening for a demonstration of Poissan's diamond synthesis with his roommate/narrator and Dr. Watson clone – Walter Jameson – in tow posing as the son of a rich banker named Spencer who is interested in possibly investing in the process. The insurance investigator and several detectives accompany them as well, but remain outside, where they await a prearranged signal from Kennedy to enter the building.

What happens next is described in some detail by Jameson and is almost straight out of Moissan's famous book on the electric furnace (indeed Poissan's very name appears to be a thinly disguised play on Moissan) (22):

We seated ourselves some distance from a table on which was a huge, oblong contrivance that reminded me the diagram of a parallelopiped which had caused so much trouble in my solid geometry class.

"That's the electric furnace, sir," said Craig to me with an assumed deference, becoming a college professor explaining things to the son of a great financier. "You see the electrodes at either end? When the current is turned on and led through them into the furnace you get the most amazing temperatures in the crucible. The most refractory chemical compounds can be broken up by that heat. What is the highest temperature you have attained, Professor?"

"Something over three thousand degrees Centigrade," replied Poissan, as he and his assistant busied themselves about the furnace.

At last Poissan announces he is ready to begin the demonstration and proceeds to explain the process to his perspective investor (22):

"You see, here is a lump of sugar carbon – pure amorphous carbon. Diamonds as you know are composed of pure carbon crystallized under enormous pressure. Now my theory is that if we combine an enormous pressure and an enormous heat we can make diamonds artificially. The problem of the pressure is the thing, for here in the furnace we have the necessary heat. It occurred to me that when molten iron cools it exerts a tremendous pressure. That pressure is what I use."

With this introduction Poissan begins the actual demonstration (22);

"I take this sugar and place it in this soft iron cup. Then I screw on this cap over the cup, so. Now I place this mass of iron scraps in the crucible of the furnace and start the furnace."

He turned the switch, and long yellowish-blue flames spurted out from the electrodes on either side. It was weird, gruesome. One could feel the heat of the tremendous electric discharge. As I looked at the bluish-yellow flames they gradually changed to a beautiful purple, and a sickish sweet odor filled the room. The furnace roared at first, but as the vapors increased, it became a better conductor of electricity, and the roaring ceased.

In almost no time the mass of iron scraps became molten. Suddenly Poissan plunged the iron cup into the seething mass. The cup floated and quickly began to melt. As it did so he waited attentively until the proper moment. Then with a deft motion he seized the whole thing with a long pair of tongs and plunged it into a vat of running water. A hugh cloud of steam filled the room.

I felt a drowsy sensation stealing over me as the sickish sweet smell from the furnace increased. Gripping the chair, I roused myself and watched Poissan attentively. He was working rapidly. As the mass cooled and solidified he took it out of the water and laid it on an anvil. Then his assistant began to hammer it with careful, sharp blows, chipping off the outside.

"You seem we have to get down to the core of carbon gently," he said, as he picked up the little pieces of iron and threw them in the scrap box. "First rather brittle cast iron, then hard iron, then iron and carbon, then some black diamonds, and in the very center the diamonds."

However, at this juncture Kennedy intervenes and requests to stand over the assistant in order to observe the actual diamond extraction. Poissan refuses, claiming that Kennedy is unqualified to identify the rough diamonds. Kennedy then demands to see the palms of Poissan's hands to make sure that he is not palming diamonds which he intends to secretly insert into the reaction mixture. This request causes Poissan to fly into a homicidal rage (22):

The Frenchman faced us, his face livid with rage. "You call me a prestidigitator, a fraud – you shall suffer for that! Sacreblue! Ventre du Saint Gris! No man ever insults the honor of Poissan. François, water on the electrodes!" The assistant dashed a few drops of water on the electrodes. The sickish odor increased tremendously. I felt myself almost going, but with an effort I again roused myself. I wondered how Craig stood the fumes, for I suffered an intense headache and nausea.

Kennedy is fully aware that the cornered Poisson is attempting to kill both him and Jameson in the same manner as he had earlier killed Morowitch (22):

"Stop!" Craig thundered. "There is enough cyanogen in this room already. I know your game – the water forms acetylene with the carbon, and that uniting with the nitrogen of the air under the terrific heat of the electric arc forms hydrocyanic acid. Would you poison us, too? Do you think you can put me unconscious out on the street and have a society doctor diagnose my case as pneumonia?"

Here Kennedy is assuming that the following reactions are taking place in the carbon arc:

$$H_2O(g) + 3C(g) \rightarrow C_2H_2(g) + CO(g) \qquad [5]$$

$$C_2H_2(g) + N_2(g) \rightarrow 2HCN(g) \qquad [6]$$
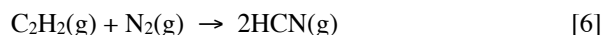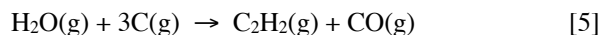
though the latter reaction seems improbable even at high temperatures and both the C_2H_2 and HCN are most likely the competitive products formed from the reactions of HC radicals in the arc:

$$2CH(g) + N_2 \rightarrow 2HCN(g) \qquad [7]$$
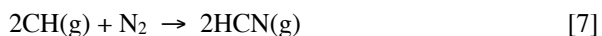
Also one cannot help but wonder how many of the symptoms reported by Jameson were actually due to carbon monoxide (CO) rather than hydrocyanic acid or hydrogen cyanide (HCN).

In any case, before Poisson can complete his attack, Kennedy succeeds in signaling the waiting detectives, who burst into the laboratory and save Kennedy and Jameson from almost certain death – though not before Poisson manages to plunge the diamonds stolen from Morowitch into the carbon arc, where they are instantly reduced to "a shapeless piece of valueless black graphite."

Tom Swift Among the Diamond Makers

Though there has been debate as to whether the adventure novels of Jules Verne were intended solely for juveniles or were also written with adult readers in mind, there is no doubt whatsoever that our fourth and final example of a fictional story based on the theme of
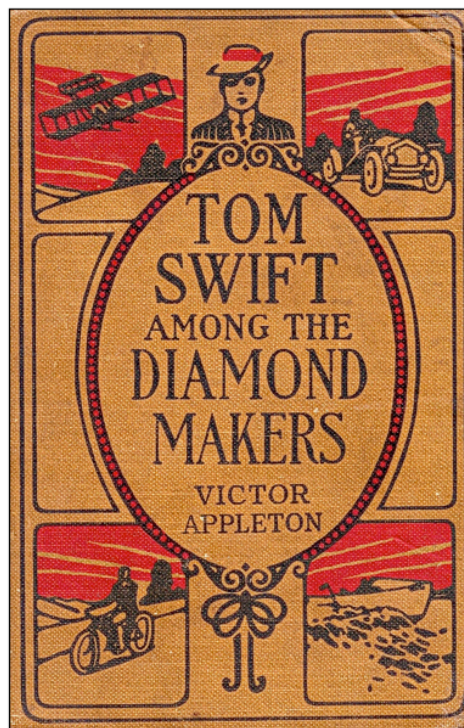

Figure 14. Cover of the 1911 thriller *Tom Swift Among the Diamond Makers of the Secret of Phantom Mountain*.

Figure 15. The diamond makers of Phantom Mountain inspecting their product.

synthetic diamonds was intended exclusively for young boys – the plot is improbable, the character development nonexistent, the dialog insipid, and the use of racial stereotypes rampant. The novel, entitled *Tom Swift Among the Diamond Makers or the Secret of Phantom Mountain* (figure 14), is one of more than 100 Tom Swift novels published between 1910 and 2007 detailing the doings of the teenage inventor and adventurer, Tom Swift, and his assorted friends and family. Conceived by Edward Sratemeyer, who had also originated such juvenile successes as the *Old Glory* war hero series, *Bomba the Jungle Boy*, *The Ted Scott Flying Stories*, *The Rover Boys*, and *The Bobbsey Twins*, the Tom Swift books was written by a series of ghost writers under the pseudonym of Victor Appleton using plot outlines provided by Sratemeyer and his assistant Howard Garis, and was by far the most successful and popular of Stratemeyer's various publishing ventures (24).

Tom Swift Among the Diamond Makers was published in 1911 and was the seventh book in the original series (25). It begins with Tom Swift encountering a character from an earlier adventure named Barcoe Jenks, who claims to know of a process for producing synthetic diamonds. Jenks came to possess this knowledge as a result of helping a poor beggar. A few days later the beggar reappears at Jenks' apartment to thank him and to offer him a business proposition. He reveals that he is a member of a cartel of diamond makers who

have discovered a process – "partly in a scientific manner, and partly by the forces of Nature" – for making synthetic diamonds, and who have established a laboratory for that purpose in a cavern inside a place known as Phantom Mountain located somewhere among the Rocky Mountains. However, because of a lack of funds, the cartel has had to temporarily disperse until they can collect sufficient financial backing to resume their work, which explains the beggar's down and out appearance. To prove his story, he then offers Jenks several artificial diamonds to be tested by an expert jeweler.

The diamonds prove real and Jenks agrees to invest, provided that he is allowed to see the process in operation and to share in any future profits. The deal is accepted and Jenks is taken blindfolded to Phantom Mountain to participate in a demonstration. This is successful, whereupon Jenks gives the diamond makers a substantial sum of money, only to find himself awakening from a drug-induced sleep in a hotel room several days later with the newly made synthetic diamonds in his pocket but no idea of where Phantom Mountain or the diamond makers are to be found.

Though the synthetic diamonds are worth as much as the money he gave the diamond makers, Jenks feels that he has been defrauded, since part of the agreement was that he was also to share in their future profits as well and he is determined to find them and demand his rightful share. With this in mind, he has sought out Tom Swift and his various air ships and other inventions to aid him in his quest. Tom agrees, but the diamond makers are aware that Jenks is in pursuit. As a result, many adventures befall the search team before they finally locate Phantom Mountain and observe the diamond makers in action (figure 15), beginning with the mixing of the necessary ingredients (25):

"The diamond makers!" whispered Tom hoarsely, pointing to several men grouped about a number of strange machines ... The men were unaware of the presence of our friends, and were busily engaged. Some attended to the grinding machine, the roar and clatter of which made it possible for Tom and the others to talk and move about without being overheard. Into this machine certain ingredients were put, and they were then pulverized, and taken out in powdery form.

These powders are then mixed, fashioned into small balls, and placed in an annealing oven (25):

As the powder was taken out [from a gasoline driven mixing machine], other men fashioned it into small balls, which were put on a pan, and into a sort of oven,

that was heated ... "That is evidently the first step," said Mr. Jenks. "Those balls of powdered chemicals are partly baked, and then put into the steel box. In some way terrific heat and pressure are applied, and the diamonds are made. But how the heat and pressure are obtained is what we have yet to learn.

But the answer is quick in coming, when one of the diamond makers announces that an electrical storm is brewing outside. This provides the clue for Mr. Parker, a scientist who is also part of Tom Swift's search team (25):

"I know the secret of making diamonds," said the scientist ... "It is by the awful power of lightning bolts!" ... "Everything is explained now – the reason why they make diamonds in this lonely place, near the top of a mountain. They need a place where the lightening is powerful. I can understand it now – I suspected it before. They make diamonds by lightning!"

Parker's guess is soon confirmed as the lightning storm reaches its zenith (25):

The men opened the small oven in which the balls of white chemicals and carbon mixed had been baked, and a pile of things that looked like irregularly-shaped marbles were placed in the steel box. This box, which was about the size of a trunk, was of massive metal. It was placed in a recess in the solid rock, and all about were layers of asbestos and other substances that were nonconductors of heat ...

There was a terrific crash outside. The rocky floor of the cave trembled. "Here she comes!" cried Folwall [the diamond maker first encountered by Jenks]. "Get back everybody! I am going to pull the switch now!" ... Watching with eager eyes, the adventurers saw sparks flash from the steel box. Instantly it became red hot, and then glowed white and incandescent. It was almost at the melting point ...

The diamond makers then open the electrical switch and prepare to harvest their creations (25):

There was a period of waiting until the box was cool enough to open. Then the heavy door was swung back. With a long iron rod Folwell drew something from the retort. It was the tray which had held the white balls. but they were white no longer, for they had turned into diamonds. From their hiding-place Tom and the others could see the flashing gems for, in spite of the fact that the diamonds were uncut, some of them sparkled most brilliantly due to the peculiar manner in which they were made. "We have the secret of the diamonds!" whis-

pered Mr. Jenks. "There must be a quart of gems there!"

At one point the members of Tom's search party speculate on how this process supposedly works (25):

"But bless my watch-charm!" exclaimed Mr. Damon, "I didn't know that lightning made diamonds."
"It does not – always," went on the scientist. "But great heat and pressure are necessary to create the gems. In nature this was probably obtained by prehistoric volcanic fires and by the terrific pressure of immense rocks. It is possible to make diamonds in the laboratory of the chemist, but they are so minute as to be practically valueless.

This is, of course, no explanation at all. The whole scenario seems to be an exercise in the myth of "scaling up" – if Moissan got small diamonds using an electric furnace, then it must follow that a lightning bolt will produce large diamonds. It also exploits the mystery, attendant superstitions, and power of lightning which Hollywood would later use when it attempted to jazz up Mary Shelley's rather tepid description of how Frankenstein animated his monster. In reality, the proper answer to Mr. Damon's outburst:

"But bless my watch-charm! I didn't know that lightning made diamonds"

is that neither did anyone else.

Synthetic Diamonds Today

Before leaving the theme of synthetic diamonds, it is perhaps worth saying something about their current status. Conventional wisdom now has it that all of the 19th-century claims to have successfully synthesized the diamond are invalid and that this feat was first accomplished in late 1954 by Howard Tracy Hall of the General Electric Company (26). Based on our current knowledge of the phase diagram for carbon (figure 16), one line of argument maintains that, since estimations of the pressures and temperatures obtained by Hannay, Marsden, Moissan, Crookes, and others are insufficient to convert graphite into diamond, no diamond could have been formed in their experiments. The problem with this argument is that Hannay, Marsden, and Moissan, at least, did not simply subject bulk graphite to high pressures and temperatures. In all cases they generated "nascent" gaseous carbon *in situ* via a chemical reaction and, as Mellor pointed out in 1947, there is nothing to prevent these reactions from forming diamond as a kinetically metastable reaction intermediate under thermodynamically unstable conditions (26).
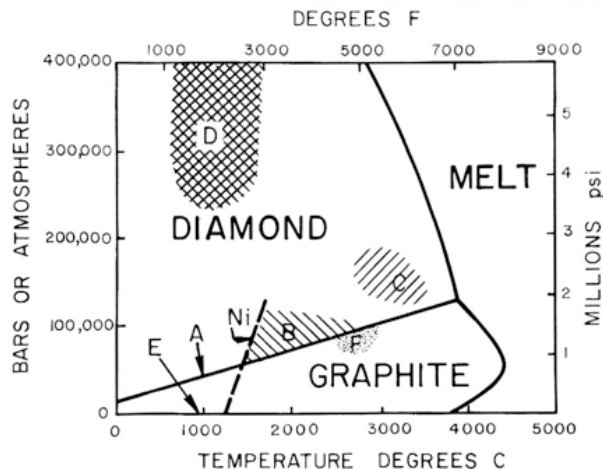
Figure 16. A simplified phase diagram for carbon showing the thermodynamic stability regions for diamond, graphite, and liquid carbon.

Indeed, chemists routinely prepare thermodynamically unstable species in the laboratory in this fashion, the best known examples in the case of elemental allotropes being those of ozone and yellow phosphorus.

A second line of argument is based on a supposed lack of experimental reproducibility. Thus, in 1928 the British inventor, Sir Charles Algernon Parsons, after many attempts at reproducing Moissan's experiments, concluded that Moissan had mistaken small crystals of spinel for diamond (27). Moissan had used the triple test of hardness, density, and carbon dioxide produced per gram of sample on combustion to characterize his samples, but Parsons and his assistant claimed that the latter results were actually due to the combustion of fine carbon dust on his crystals and apparatus. Further ambiguities revolve around the fact that apparently none of Moissan's diamond samples were preserved after his death and that Moissan's widow supposedly confided to Parsons that Moissan's assistant had faked several results by introducing small diamond fragments into the products in order to avoid having to repeat the laborious acid digestions required to isolate the diamonds from the other reaction by-products (28). However, despite this, Gmelin reports that papers claiming to have reproduced Moissan's results were being published as late as 1937 (9).

The case of Hannay is even more intriguing. In 1943 the twelve samples which Hannay had sent to Story-Maskelyne in 1880 were rediscovered in the British Museum and eleven of them were shown to be true diamonds by Kathleen Lonsdale and F. A. Bannister using X-ray diffraction techniques (29). Indeed, several proved to be rare "Type II" diamonds, which account for about only one percent of naturally occur-

ring diamonds, a circumstance which the authors felt enhanced the probability of their being synthetic in origin. This announcement touched off an extensive discussion of Hannay's claims in the pages of *Nature* (30). However, in 1965 Lonsdale apparently revised her original conclusions and decided, based on a detailed comparison of the properties of synthetic versus natural diamonds, that Hannay's diamonds were natural rather than synthetic in origin, though one might question the validity of such a comparison given that Hannay's process is entirely different from that used to manufacture the synthetic diamonds used in the study (31). Likewise, though Nassau claims that many other researchers have tried to duplicate Hannay's process and failed, Gmelin reports no such published attempts, either pro or con (9).

References and Notes

1. First written in 1993 for inclusion in J. Stocker's collection, *Chemistry and Science Fiction*, and subsequently revised in 1995 for publication in the *Chemical Intelligencer*, it ultimately appeared in neither source for the reasons given in the preface to this book.

2. Period summaries of this little-known field of chemical activity include C. W. C. Fuchs, *Die künstlich dargestellten Mineralien*, Haarlem, 1872; and F. Fouqué, M. Lévy, *Synthèse des minéraux et des roches*, Masson: Paris, 1882.

3. H. G. Wells, "The Diamond Maker" in *The Famous Short Stories of H. G. Wells*, Garden City Publishing, Garden City, NY, 1938, pp. 246-253.

4. H. Moissan, "Sur la preparation du carbone sous une forte pressure," *Compt. rend.*, **1893**, *116*, 218-224; "Nouvelles experiences sur la reproduction du diamant," *ibid.*, **1894**, *118*, 320-326; "Sur quelques experiences nouvelles relatives a la preparation du diamant," *ibid.*, 1**896**, *123*, 206-210; "Researches sur les differentes varietes de carbonne 3: reproduction du diamant," *Ann. chim. phys.*, **1896**, *8*, 466-558; "Sur quelques experiences nouvelles relatives a la preparation du diamant," *Compt. rend.*, **1905**, *140*, 277-283; "Nouvelles reserches sur la production du diamant," *Ann. chim. phys.*, **1905**, *5*, 174-208. Most of this work is summarized in reference 5.

5. H. Moissan, *Le flour electrique*, Steinheil: Paris. 1897; translated as H. Moissan, *The Electric Furnace*. 2nd ed., Chemlcal Publishing, New York, NY, 1903.

6. This is exactly opposite the behavior of pure metals, which usually contract upon solidification, see reference 5 (1903), p. 136, footnote.

7. Reference 5 (1903), p. 86.

8. J. B. Hannay, "On the Artificial Formation of the Diamond," *Proc. Roy. Soc.*, **1879-1880**, *30*, 188-189 and *Chem. News,* **1880**, *41*, 106; "Artificial Diamonds," *Proc.*

Roy. Soc., **1879-1880**, *30*, 450-461; and *Nature*, **1880**, *22*, 255-257; also *Proc. Roy. Soc.*, 1**881**, *32*, 407-498 and *Moniteur Sci.*, **1881**, *11*, 222-227.

9.   For historical accounts of the diamond synthesis, see J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 5, Longmans, Green, & Co: London, 1924, pp. 730-738; *Gmelin's Handbuch der Anorganische Chemie*, 8th ed., C, Teil B. Lfg. 1, Verlag Chemie: Weinheim, 1967, pp. 240-241; K. Nassau, *Gems Made by Man*, Chilton: Radnor, PA, 1980, Chapters 14-16; R. M. Hazen, *The New Alchemists: Breaking Through the Barriers of High Pressures*, Times Books: New York, NY, 1993, and R. M. Hazen, *The Diamond Makers*, Cambridge University Press: New York, NY, 1999.

10. W. Crookes, *Diamonds,* Harper: New York, NY, 1909 and *Proc. Roy. Soc.*, **1905**, *76A*, 458.

11. See Nassau, reference 9, pp. 196-197 and Hazen, ibid., pp. 179-180.

12. J. Verne, *The Southern Star Mystery*, Associated Booksellers, Westport, CT, 1966, pp. 26, 28, 30-32, 34-35, 61-62, 63, 64, 69-70. As may be seen from figure 7, a more accurate translation of the French title would be *The Star of the South*. This novel also formed the basis of the 1968 film, *The Southern Star*, which was produced by Columbia Pictures and starred George Segal, Ursula Andress, Orson Welles and Harry Andrews.

13. It is interesting to note how often the heroes of Verne's novels are engineers, even when the novel revolves around chemistry, physics or astronomy, rather than engineering. The best example of this is the engineer Cyrus Harding in Verne's "chemical romance" *The Mysterious Island*.

14. For details see references 5 and 9.

15. For details on the history of the ruby synthesis see Nassau, reference 19, Chapters 3-6.

16. See Anon., "Crystallization of Carbon," *Chem. News*, **1879**, *40*, 306; W. Crookes, "The Crystallization of Carbon," *ibid.*, **1880**, *41*, 13; A. H. Allen, "On the Artificial Production of Precious Stones," *ibid.*, **1880**, *41,* 68-69; N. Story-Maskelyne, "Artificial Production of the Diamond," *ibid.*, **1880**, *41*, 97-98.

17   Reference 8, also J. B. Hannay, J. Hogarth, "On the Solubility of Solids in Gases," *Chem. News*, **1880**, *41*, 103-106.

18. Reference 5 (1903), pp. 118-120.

19. K. Rallkama, Th. G. Sahama, *Geochemistry*, University of Chicago,: Chicago, IL, 1950, pp. 754-755.

20. J. R. Partington, *A Text-Book of Inorganic Chemistry*, 5th ed., Macmillan: London, 1939, pp. 484-485.

21. J. W. Mellor, *Modern Inorganic Chemistry*, Longmans, Green and Co: London, 1927, p. 472.

22. A. B. Reeve, *The Silent Bullet: The Adventures of Craig Kennedy, Scientific Detective*, Grosset & Dunlap: New York, NY, 1910, pp. 157-187.

23. H. Goldschmidt, *Verfahren zur Herstellung von Metallen oder Metalloiden oder Legierungen derselben*, Deutsche Reichs Patent No. 96317 (13 March 1895).

24. A. Prager, "Bless My Collar Button! If it isn't Tom Swift, the World's Greatest Inventor!" *American Heritage* **1976**, *27 (December)*, 65-75.

25. V. Appleton, *Tom Swift Among the Diamond Makers,* Grosset & Dunlap: New York, NY, 1911.

26. Nassau, reference 9, Chapters 14-16. For possible exceptions to this claim see, however, Hazen, *ibid.*

27. D. P. Mellor, "On the Possibility of a Chemical Synthesis of Diamond," *J. Chem. Phys.,* **1947**, *7*, 525-526. For a more recent review of this question, see D. V. Fedoseev, V. P. Varnin, B. V. Deryagin, "Synthesis of Diamond in Its Thermodynamic Metastability Region," *Russ. Chem. Rev.*, **1984**, *53(5)*, 435-444. I am assuming that carbon doesn't simply dissolve in molten metal, but rather reacts to form carbides.

28. Parsons' conclusions were presented with his permission in C. H. Desch, "The Problem of Artificial Production of Diamonds," *Nature*, **1928**, *121*, 799-800.

29. Reported in Nassau, reference 9, p. 168.

30. F. A. Bannister, K. Lonsdale, "Laboratory Synthesis of Diamond," *Nature*, **1943,** *151*, 334-335.

31. R. J. S. Rayleigh, "Laboratory Synthesis of Diamond." *Nature,* **1943**, *151*, 394; C. H. Desch, "Artifical Production of Diamonds," *ibid.*, **1943**, *152*, 148-149; R. J. S. Rayleigh, "J. B. Hannay and the Artifical Production of Diamonds," *ibid.*, 597; M. W. Travers, "J. B. Hannay and the Artificial Production of Diamonds," *ibid.*, 726; and K. Lonsdale, "Diamonds, Natural and Artificial," *ibid.*, **1944**, *153*, 669-672.

32. Reported in Nassau, reference 9, p. 164.

VII

Sir Humphry Davy and the Hollow Earth

The Geochemistry of Verne's Journey to the Center of the Earth

Bibliographic Preliminaries

In earlier essays I have discussed the electrochemistry of Jules Verne's famous novel *Twenty Thousand Leagues Under the Sea* (1870), as well as the industrial chemistry found in its sequel, *The Mysterious Island* (1874), and the chemistry of synthetic diamonds referred to in his later novel *The Southern Star Mystery* (1884) (1). In this essay I hope to focus on the geochemistry found in one of his earliest works, *Voyage au centre de la terre* or *Journey to the Center of the Earth*, first published in 1864 (figure 1).

As mentioned in these earlier essays, the major problem in working with English translations of Verne is the large number of defective 19th-century transla-

Figure 2. Professor Lidenbrock.

tions that were made and which continued to be reprinted throughout most of the 20th century (2). These often changed the names of the various characters, removed entire paragraphs dealing with scientific background, and even added material not found in the French originals. Luckily, in the case of *Journey to the Center of the Earth*, Frederic Paul Walter has recently published a new and accurate translation and this will be used as the basis for what follows (3).

Professor Lidenbrock Makes a Discovery

The novel opens in 1863 in the city of Hamburg in the home of a professor of mineralogy at the local gymnasium by the name of Otto Lidenbrock (figure 2) and is narrated by his young nephew and student, Axel, who

Figure 1. Title page to an early combined French edition of *Journey to the Center of the Earth* and *Five Weeks in a Balloon*.

soon provides the reader with an evaluation of his uncle's character (3):

He was a professor at the Johanneum, Hamburg's renowned prep school, and he taught a course in mineralogy during which he lost his temper once or twice like clockwork. It wasn't that he was concerned with having diligent students in his classes, or how closely they paid attention to him, or how successful they were in later life; these details didn't bother him in the least. To use an expression from German philosophy, he taught "subjectively," for his own benefit rather than for the benefit of others. He was a self-centered scholar, a well of scientific knowledge whose pulley groaned when you tried to draw something out of it. In short, he was stingy with his learning.

Axel attributes his uncle's short temper and constant swearing to his difficulty in pronouncing complex words, a serious problem for a teacher of mineralogy, since the subject is resplendent with (3):

... many half-Greek, half Latin terms that are difficult to pronounce, scientific terms so harsh sounding that they would scald a poet's lips. I don't want to be critical of this science, far from it. But when one is faced with expressions like rhombohedral crystallization, retinasphalt resin, ghelenite, fangsite, lead molybdate, manganese tungstate, and zircon titanate, the most agile tongue can be excused for stumbling.

Despite these apparent flaws, Axel is also anxious to assure the reader of Lidenbrock's competence as both a geologist and mineralogist (3):

... I can't say too often that my uncle was a true scientist. Though he sometimes broke his specimens due to the overly rough way he tested them, he had both a geologist's soul and a mineralogist's eye. Wielding his hammer, his steel pry bar, his magnetic needle, his blowtorch, and his flask of nitric acid, he was a man to reckon with. By the way that it fractured, its appearance, its hardness, its melting point, its sound, smell, and taste, he could classify any mineral without hesitation, putting it in its right place among the 600 varieties science has tallied to date.

In this passage there is some room for improvement, as far as Walter's translation goes, since rendering "blowtorch" as "blowpipe" and "flask" as "bottle" would result in a far more realistic description of actual mineralogical practice (figure 3).

It is characteristic of Verne's fiction that he always attempts to give both his characters and plots an aura
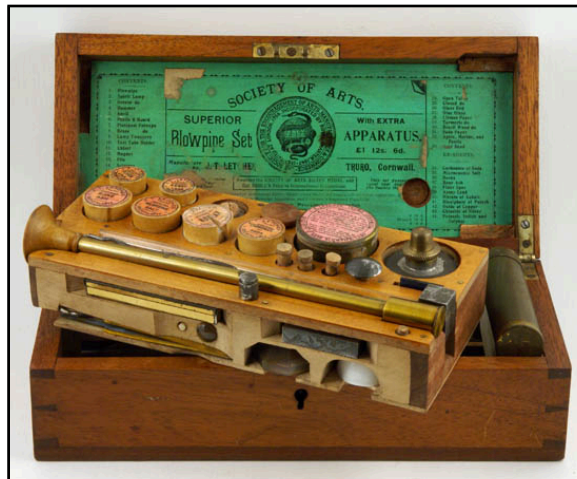

Figure 3. A typical 19th-century blowpipe kit for the identification of minerals.

of scientific verisimilitude by making reference to actual scientists and discoveries of the period in question, and Axel is quick to do the same for his uncle, revealing in the process that Lidenbrock is not only a competent mineralogist and geologist but also a competent chemist (3):

Accordingly the name Lidenbrock was resoundingly honored in the schools and national societies. Famous scientists such as Messrs. Humboldt and Humphry Davy or Captains Franklin and Sabine never neglected to pay him a visit when they passed through Hamburg. Messrs. Ebelmen, Becquerel, Brewster, Jean-Baptiste Dumas, Milne-Edwards, and Henri Sainte-Claire Deville consulted him enthusiastically on the most enthralling matters of chemistry. This science was indebted to him for some pretty splendid discoveries, and in 1853 there appeared in Leipzig a "Treatise on Transcendental Crystallography" by Professor Otto Lidenbrock, a huge folio volume with plates, which, however, didn't sell enough to break even.

This is quite an eclectic list of fellow scientists, though there are some puzzling inclusions. Thus, while both Sir Humphry Davy (1778-1829) and Jacques-Joseph Ebelmen (1814-1852) were chemists who, at least in part, concerned themselves with questions of geochemical interest, Jean-Baptiste Dumas (1800-1884) was an organic chemist and Henri Milne-Edwards (1800-1885) a famous zoologist, and it is difficult to conceive of how their interests would have overlapped with those of Lidenbrock. Likewise, though both Alexander Humboldt (1769-1859) and Sir Edward Sabine (1788-1883) were famous explorers and naturalists, one would most likely classify their work as geo-

graphical rather than geological in nature, and Sir John Franklin (1786-1847) was a British naval officer and arctic explorer sans any scientific training or interests whatsoever. Antoine César Becquerel (1788-1878) and Sir David Brewster (1781-1868) were both physicists who had done some work on the piezoelectric and optical properties of crystals, but who had no interest in purely geochemical questions. Lastly, though the famous French chemist, Henri Sainte-Claire Deville (1818-1881), did do some important work on the synthesis of minerals, one cannot help but wonder whether Verne has confused him with his older brother, Charles Sainte-Claire Deville (1814-1876), who was a famous geologist. This is even more surprising given that most biographers of Verne claim that he was friends with Charles and had gotten some of his ideas for the novel from discussions with him (4, 5). Also puzzling is why a German mineralogist would, with the exception of Humboldt, have only British and French colleagues.

It should also be noted that the birth and death dates for these scientists allow us to approximate Lidenbrock's own age. If he was to have had any significant interaction with Davy, who died in 1829, he must have been born between 1799 and 1800, which would make him between the ages of 64 and 63 when the novel first opens in May of 1863.

Just as Axel finishes his musings over his uncle's

Figure 4. Discovering Sakmussemm's route.

merits and eccentricities, Lidenbrock makes a sudden appearance bearing an ancient volume he has just purchased from a local used book dealer. This turns out to be a bound manuscript, written in runic characters, of the *Heimskringla,* an early account of the Norwegian kings of Iceland by the 12th-century historian and poet Snorre Sturluson (1179-1241). However, while perusing this volume, Axel and his uncle discover a piece of parchment, also written in runes, tucked among its pages. This is apparently in the form of a code of some sort, and only after successfully deciphering it do they discover that it is the work of a (fictional) 16th-century icelandic alchemist named Arne Sakmussemm and that it makes the extraordinary claim that Sakmussemm was able to successfully travel to the center of the earth via an opening in the crater of a dormant Icelandic volcano known as Snaefells.

Given Lidenbrock's impetuous nature and his passion for geology, it is hardly surprising that he immediately decides to test Sakmussemm's claim by repeating his journey and, with this in mind, he and Axel travel to Iceland where they engage the services of a local guide by the name of Hans Bjelke and the three of them begin their descent into the crater of the volcano to discover the opening described by Sakmussemm (figure 4).

Lighting Their Way

There are three lava tubes or chutes at the bottom of the crater and Sakmussemm's instructions require that the explorers descend down the one in the middle. Once they pass beyond the light provided by the opening of the tube, they must use an artificial light source for the rest of their journey. This is provided by an electric miner's lamp or "Rumkorff device," as Verne calls it (3):

With that my uncle reached up and clutched the Ruhmkorff device hanging from his neck; with his other hand he put the electric current in contact with the glass spiral inside the lantern, and a tolerably bright light dispelled the shadows ... Hans carried our second Ruhmkorff device, which he activated as well. This inventive use of electricity let us travel a good while by creating an artificial daytime even in the midst of the most inflammable gases.

Heinrich Daniell Rumkorff (1803-1877) was a German-born instrument maker who operated a shop in Paris and who, in 1851, patented a highly-successful version of the induction coil (figure 5) for the conversion of low voltage, high amperage DC currents into high voltage, low amperage AC currents. In the electric
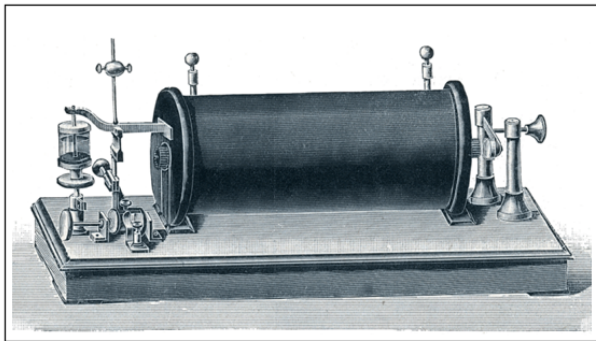
Figure 5. A typical 19th-century induction or Rumkorff coil.

miner's lamp, invented by Alphonse Dumas and Camille Benoit in 1862 (6), this high voltage source was used to electrically excite a sealed and coiled glass tube containing dilute carbon dioxide gas, thereby causing it to give off a white light (figure 6). Indeed this same device would later be used by Verne to supply light for his underwater explorers in *Twenty Thousand Leagues Under the Sea* (7).

More problematic is the claim that this light could be used in the presence of inflammable gases since, when an induction coil is in operation, it is not uncommon to observe sparking between its interruptor plate and the core, and such sparks would be ideal ignition sources for a gas explosion. Presumably, the inventors of the light had some means of dealing with this problem as it was explicitly designed for the use of miners and had been awarded a prize by the French Academy of Sciences in 1864.

Users of the light also had to carry a shoulder bag containing the induction coil and a DC battery. Since dry cells were not invented until 1888 (8), this battery would have contained corrosive liquid electrolytes. The
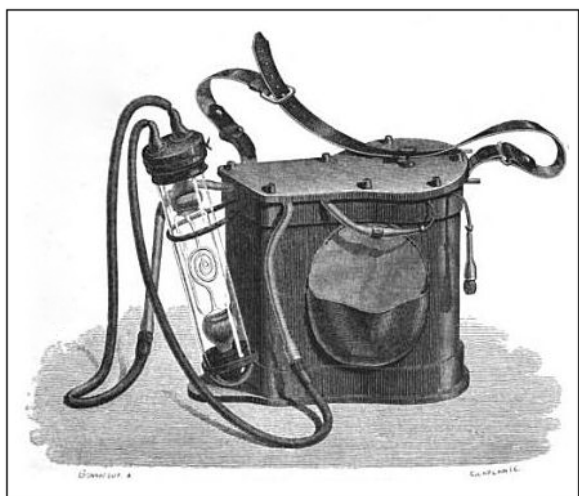
most likely choice, the Bunsen carbon cell, used corrosive nitric acid and emitted obnoxious nitrogen dioxide fumes during operation (9), whereas the most likely alternative, the Daniell gravity cell, was unable to withstand violent shaking and subsequent mixing of its copper and zinc sulfate electrolytes (10). In short, none of the available DC battery sources were good candidates for the rugged climbing (and falling!) conditions encountered by our three explorers.

Given these potential problems, it is surprising that Verne did not consider using a standard coal miner's safety lamp (figure 7), first introduced in 1815 by the British chemist, Sir Humphry Davy, of Professor
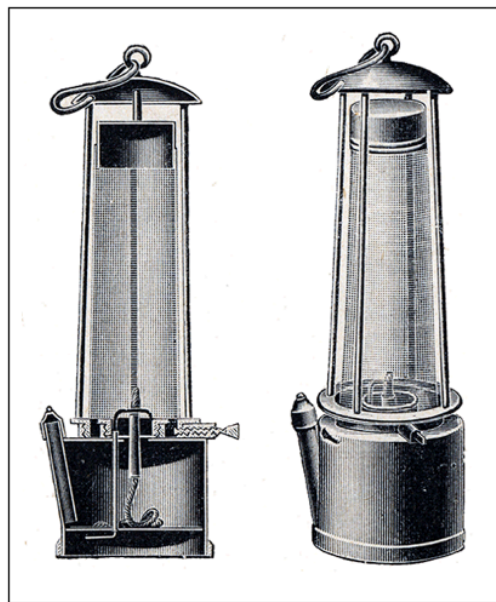

Figure 7. The Davy safety lamp.

Lidenbrock's presumed acquaintance. A simple oil lamp surrounded by a fine wire screen to prevent flame propagation, it was far more portable and durable than the electric lamp, though much less of a technological novelty and of much lower candle power.

But it is precisely the increased illumination presumably provided by the electric light that Verne wishes to exploit as it provides the explorers with spectacular views of the geological and mineralogical wonders they encounter in their underground journey once they leave the lava tube and make their way through a system of natural underground passageways and caverns. As Axel explains later in the novel (3):

... no mineralogists had ever before met up with such wondrous conditions for studying nature on the spot. Our own two hands, our own two eyes, were going to touch and study aspects of the earth's inner texture that

Figure 6. A Dumas-Benoit electric miner's lamp.

no borings by crude, mindless machinery could bring to the surface.

Not only do they encounter typical geological deposits and rock formations but also vast collections of minerals and metals, of which the following two descriptions, each emphasizing the role of the electric lights, are typical (3):

Our electric light made the shale, limestone, and old red sandstone in the walls sparkle marvelously. You would have sworn you were on a dig out in the middle of Devonshire, which this type of terrain is named after. Magnificent specimens of marble covered the walls, some an agate gray whimsically accented with white veins, others a crimson color or a yellow mottled with patches of red; farther off were samples of dark-colored griotte marble in which some brighter shades of limestone stood out.

The shale system was tinted with lovely shades of green, and winding through it were iridescent veins of copper and manganese with a few traces of platinum and gold. I thought about this fortune that lay stashed in the bowels of the globe, this wealth that greedy humanity would never enjoy! The upheavals of the first days had buried this treasure so deep, no mattock or pick could wrest it from its grave.

After the shale came the gneiss, whose formations were laid out in sheets notable for the orderliness and parallel lines of each layer, then the mica schist, organized into big plates made pleasing to the eye by the glimmer of white mica. Reflecting off the tiny facets in the mass of rock, the light from our Ruhmkorff devices sent fiery jets crisscrossing from every direction, and I fancied I was traveling inside a hollow diamond whose rays had shattered into a thousand dazzling sparks [figure 8].

As may be inferred from the reference to shale, limestone and sandstone, these encounters include buried sedimentary deposits as well as igneous rocks, and at one point buried coals seams and fossils. It is with respect to this latter encounter that Verne makes one of his rare chemical errors (3):

The temperature hadn't changed noticeably from what it was when we'd crossed through the lava and shale. except that my nostrils were bothered by a very marked odor of methane. In this passageway I immediately recognized the presence of a significant amount of that hazardous elastic fluid that miners call firedamp, whose explosions have caused so many frightful catastrophes. Fortunately Rumkorff's clever devices lit our
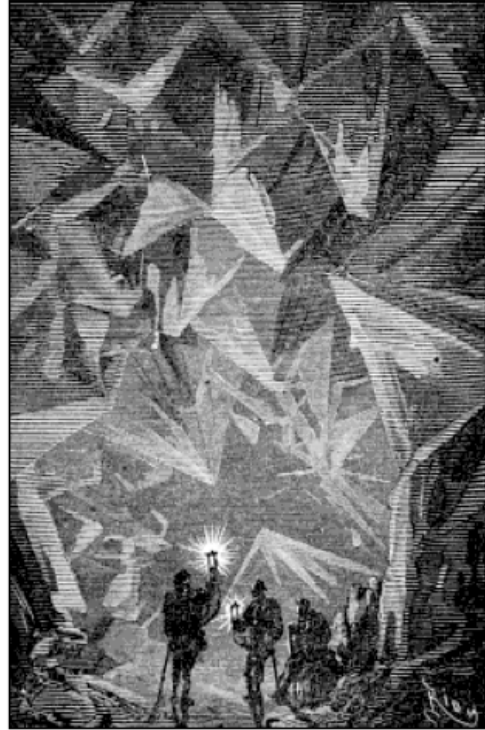

Figure 8. Viewing gigantic formations of mica schist using the electric miner's light.

way. If we had the bad luck and carelessness to explore this passage with torches in hand, a dreadful explosion would have concluded these travels by wiping out the travelers.

The problem is, of course, that methane is both colorless and odorless, which is why coal miners once used methane-sensitive canaries to detect its presence and why we now add methyl mercaptan (CH_3SH) to our urban natural gas supplies to warn us of any leaks.

The Origins of Volcanoes

The reference to the temperature in the latter quote is also of significance and is part of a running debate between Axel and his uncle on this subject as they begin their descent into the earth. Thus, after two hours, Axel notes (3):

... it wasn't getting noticeably warmer. This bore out Davy's suppositions, and more than once I was astonished when I checked our thermometer. Two hours after we'd started off, it still read 50° Fahrenheit, in other words, an increase of 7°. I felt justified in thinking that our descent was more sideways than straight down.

Convinced that the moderate increase in temperature

Figure 9. Nicolas Lémery (1645-1715).

meant that they had been traveling horizontally rather than vertically, Axel later confronts his uncle with this opinion (3):

"It seems to me we still haven't covered much of a distance vertically."

"What makes you assume that?"

"Because if we had gone a lot further inside the earth's crust, the heat would be more intense."

"According to your way of thinking," my uncle replied, "What does your thermometer show?"

"Barely 59° Fahrenheit, meaning an increase of only 16° since we started off."

"Alright, and your conclusion is?"

Axel's conclusion is, of course, that they are not that far inside the earth, but after a series of counterarguments and calculations, the professor finally succeeds in convincing Axel that they have in fact been moving downwards the entire time (3):

The professor's calculations were the correct ones. We'd already gone 6000 feet below the greatest depths reached by man, the coal mines of Kitzbühel in Tirol and Wuttemberg in Bohemia. The temperature should have been nearly 178° Fahrenheit in this locality, but it was barely 59°, which was significant food for thought.

All of this has to do with two competing theories of the origins of volcanoes and with arriving at the choice which will make the possibility of traveling deep within the earth plausible. The first of these theories, supported by such luminaries as Kant and Laplace in the 18th century, postulated that the earth was originally formed as a molten mass and was still in the process of cooling down (11). Though its crust was now cool enough to support life, its interior was still molten and volcanoes were merely surface vents for this intense interior heat. This theory meant that, though volcanoes might become dormant, due to a blockage of some sort, they never truly became extinct. It also required that the temperature rapidly increase as one descended deeper into the earth and thus both falsified Sakmussemm's claim and doomed Lidenbrock's expedition to failure.

The second theory postulated that volcanoes were the result of exothermic chemical reactions within the crust of the earth (11). Since it was possible to consume the available chemical fuel, this theory predicted that individual volcanoes could eventually burn themselves out and become truly extinct. Furthermore, a descent into such an extinct volcano would not necessarily lead to an encounter with ever-increasing temperatures. The interchanges between Axel and his uncle regarding the temperature, as well as the uncle's repeated hints concerning "conclusions" and "food for thought" are obviously attempts to bring Axel around to the chemical point of view and so enhance the plausibility of the novel's plot.

Early proponents of the chemical theory vaguely assumed that the necessary fuel corresponded to buried deposits of such flammable materials as coal, bitumen, and especially sulfur, since deposits of the latter were frequently found near volcano vents (which may also account for the traditional association of fire and brimstone with the nether regions). Eruptions occurred when these burning materials and the resulting molten rock came into contact with subterranean water sources.

Yet another fuel source was first proposed by the 17th-century French chemist, Nicolas Lémery (figure 9) in the 1686 edition of his famous textbook, *Cours de chimie*, based on the exothermic reaction:

$$Fe(s) + S(s) \rightarrow FeS(s) + 102 \text{ kJ/mol} \qquad [1]$$
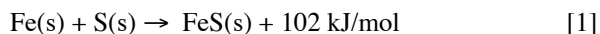
When the powdered iron and sulfur were made into a paste with water and allowed to sit, the resulting reaction was similar to the eruption of a miniature volcano, with the water serving both as a catalyst to initiate the reaction and as a source of steam.

As originally described by Lémery (12):

Take equal parts of the filings of Steel and Sulphur powdered. Mix them together and make them into a Paste with water. Put this Paste into an earthen Pan, and leave it a fermenting four or five hours ... The matter does grow so hot of itself, that a man can hardly endure his hand upon it. It is the same thing whether you make a smaller quantity or make five and twenty or thirty pounds of the Preparation at a time ... This Operation may very well help us to explicate after what manner the Sulphurs do ferment in the earth when it happens to tremble, and fires to burst forth, as does too often happen in many Countries and, among others, at Mount Vesuvius and Mount Aetna; for these Sulphurs mixing in Iron Mines may penetrate the Metal, produce a heat, and at last take flame after the same manner as they do in the present Operation.

Interestingly, Lémery's chemical volcano was still being described 200 years later in a popular chemistry book for children by the famous French entomologist and science popularizer, Jean Fabre, where it was made even more realistic by burying the iron-sulfur mixture in moist soil (13):

A generous allowance of mingled iron filings and sulphur was placed at the bottom of a large hole in the ground, water sprinkled over the mass, and a mound of damp earth was then heaped upon it. Soon this little mound would begin to behave exactly like a volcano in eruption: the ground would tremble all about the base of the mound, the heaped up mass would crack open here and there, and through the cracks would spurt jets of steam accompanied by hissing sounds, explosions and even tongues of flame. This was called an artificial volcano; but I must not omit to add that real volcanoes are set in action by something quite different from what is going on in that buried mixture of iron filings and sulphur, though this is not the time or the place to explain the difference.

As indicated by Fabre's concluding remark, Lémery's iron/sulfur theory of volcanism was no longer a serious contender by the 19th century. Rather Lidenbrock is fixated on yet a second chemical theory, first proposed by the British chemist, Sir Humphry Davy (figure 10), in 1808 (3):
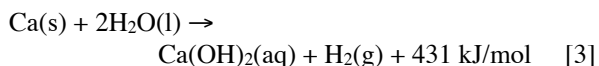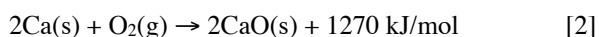
The further down I go, the more confident I feel. The organization of these volcanic rocks bears out Davy's thinking completely. We're deep in primeval terrain, a terrain that witnessed the chemical process of metals igniting after contact with air and water. I completely reject the concept of a central source. Anyway we'll soon see.

Figure 10. Sir Humphry Davy (1778-1829). Note the miner's safety lamp to his immediate left.

This explains why Davy is obliquely referred to in the earlier quotes concerning the temperature issue and why he is also listed among Lidenbrock's many scientific acquaintances.

Davy had long been interested in geology as well as chemistry (14) and the theory in question was prompted by his electrochemical isolation in the years 1807-1808 of the metals Na, K, Mg, Ca, Sr, and Ba. Impressed by the spontaneous and highly exothermic reactions that many of these metals undergo upon interacting with either water or air, such as:

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s) + 1270 \text{ kJ/mol} \qquad [2]$$

$$Ca(s) + 2H_2O(l) \rightarrow$$
$$Ca(OH)_2(aq) + H_2(g) + 431 \text{ kJ/mol} \qquad [3]$$

Davy suggested that contact between air and/or water and large, previously unoxidized, subterranean deposits of these metals might be the source of volcanic activity (15):

The metals of the earths cannot exist at the surface of the globe, but it is very possible that they may form a part of the interior, and such an assumption would offer a theory for the phenomena of volcanoes, the formation of lavas, and the excitement and effects of subterranean heat, and would probably lead to a general hypothesis in geology ... Let it be assumed that the

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metals of the earths [i.e., Mg, Ca, Sr, Ba] *and alkalies* [i.e., Na, K], *in alloy with common metals, exist in large quantities beneath the surface, then their accidental exposure to the action of air and water must produce the effects of subterranean fire, and a product of earthy and stoney matter analogous to lavas.*

Particularly striking is the description provided by Davy's biographer, John Paris, of a demonstration of this theory given by Davy in a lecture before an audience at the Royal Institution (16):

I remember with delight the beautiful illustration of his theory exhibited in an artificial volcano constructed in the theater of the Royal Institution. A mountain had been modeled in clay, and a quantity of the metallic bases introduced into its interior. On water being poured upon it, the metals were soon thrown into violent action – successive explosions followed – red hot lava was seen flowing down its sides from a crater in miniature – mimic lightnings played around, and in the instant of dramatic illusion, the tumultuous applause and continued cheering of the audience might almost have been regarded as the shouts of alarmed fugitives of Herculaneum and Pompeii.

Though Davy, near the end of his life, began to have severe doubts concerning his chemical theory of volcanism, it continued to have scattered supporters well into the 20th century (11).

A Paleontological Climax

Eventually the three explorers, via a series of accidents, make their way into a vast underground cavern. From this point on, the emphasis of the novel becomes more paleontological than geological. This underground world has its own mysterious light source and is populated by surviving prehistoric animals, plants, and even humans. It also contains a vast ocean, and while on a raft on this ocean, the explorers unintentionally cause part of it to drain into a deep lying shaft of an active volcano. This induces an eruption, causing both them and their raft to be ejected back to the surface of the earth through the vent of the famous volcano on the island of Stromboli, off the coast of Italy, more than 3000 miles from the beginning of their underground journey in Iceland.

All of this reveals that Verne was anything but a biblical literalist and that he not only accepted the modern concept of geological time, but the results of modern paleontology and the evolution of man as well. Placing a popular novel endorsing these concepts before the reading public, and especially one targeting young readers, was an exceptional act in 1864. As one Verne biographer later summarized the situation (5):

The novel was planned as a geological epic. From our point of view this seems a strange interest for Verne. For many religious people at the time, Catholic as well as Protestant, the findings of modern geology, which questioned the account of the creation of the world in Genesis, were anathema. Verne seems to have had few qualms about this. A scientific work, such as Sir Charles Lyell's "Principles of Geology," which Darwin had taken with him on his momentous voyage around the world in the Beagle, had shaken many beliefs. Darwin's "Origin of Species" had appeared in London in 1859. In 1863, while Verne was working on his novel, a French edition appeared in Paris. The great debate on the antiquity of the world and of man had entered its final stage. As Bishop Wilberforce had expressed it a few years before, one was either on the side of the apes or the angels. Verne, it seems, was on the side of the apes.

Symmes and the Hollow Earth

If Verne was able to exploit Davy's chemical theory of volcanism to make travel within the earth plausible to his readers, where did he get the central idea of the novel in the first place – namely that the earth itself was hollow and might contain living organisms? As it turns out, there was a long history of speculation on this subject extending back at least to the 17th century (17). However, in the 19th century these ideas were almost exclusively associated with the activities of an American crank by the name of John Cleves Symmes (figure 11).

A former captain in the United States Army, Symmes first announced his version of the hollow earth concept in 1818 in the form of a short flyer or circular which he mailed to 500 newspapers, scientific societies, and prominent scientists throughout the United States and Europe. He seems to have been convinced that Nature preferred to construct everything from planets to molecules using the principle of concentric spheres in order to conserve on material. In the case of the earth itself, he postulated five such concentric spheres, of which the outer surface was the fifth and largest (figure 12). Like the outer surface, each of the four internal spheres was inhabited by living organisms and each exposed to the atmosphere and to the heat and light of the sun by means of large openings located near the poles of the spheres immediately above them. In the case of the outer surface these holes were several thousand miles in diameter and were located near the north and south poles respectively.

Figure 11. Captain John Cleves Symmes (1780-1829), not to be confused with his uncle of the same name, Judge John Cleves Symmes (1742-1814). A charcoal sketch made by James Audubon for the Western Museum of Cincinnati, probably in the summer of 1820.

When critics pointed out that Symmes's plantary model violated the known laws of mechanics, optics and magnetism, he predictably responded, as most cranks are wont to do, with his own personal set of *ad hoc* alternative physical laws designed to fit his theory perfectly.

Symmes never published a book on his theory, though a follower named McBride published one in Cincinnati in 1826 (18). Rather he preferred to periodically issue circulars summarizing his latest discoveries and mailed, like the initial flyer, to various newspapers, scientific organizations, and scientists. He also disseminated his ideas by undertaking lecture tours throughout the United States and Canada, using Cincinnati as his base of operations, and employing specially altered globes, with openings cut in the right places, as teaching props. Yet further publicity was obtained when a follower by the name of Reynolds undertook to lobby President John Quincy Adams and Congress for support of a government-funded expedition to the poles in order to locate the openings postulated by Symmes.

There is little doubt the Verne was well aware of Symmes and his theories. Thus, when Axel first views the large central cavern with its vast ocean, he remarks (3):

Then I remembered the ideas of that English sea captain who had liken the earth to a huge hollow sphere. Inside the air pressure lit up the sky while two

heavenly bodies, Pluto and Prosperine, went along their secret orbits. Could he have been right?

Admittedly, this is very oblique, not to mention inaccurate. Symmes was American, rather than English, and was an army captain rather than a sea captain. But if there are still any doubts, one need only consult the novel, *The Voyages and Adventures of Captain Hatteras,* which Verne was writing about the same time as *Journey to the Center of the Earth,* but which was not published until 1866. This traces the adventures of an expedition to the north pole. As the expedition nears its destination, two of its American members have the following conversation (19):

"There is no point in the world which has given rise to more chimeras and hypotheses. The ancients, in their ignorance, placed the garden of the Hesperides there. In the Middle Ages it was supposed that the earth was upheld on axes placed at the poles, on which it revolved; but when comets were seen moving freely, that idea had to be given up. Later, there was a French astronomer, Bailly, who said that the lost people mentioned by Plato, the Atlantides, lived there. Finally, it has been asserted in our own time that there was an immense opening at the poles from which came the Northern Lights, and through which one could reach the inside of the earth; since in the hollow sphere two planets, Pluto and Proserpine, were said to move, and the air was luminous in consequence of the strong pressure it felt."

"That has been maintained?," asked Altamont.
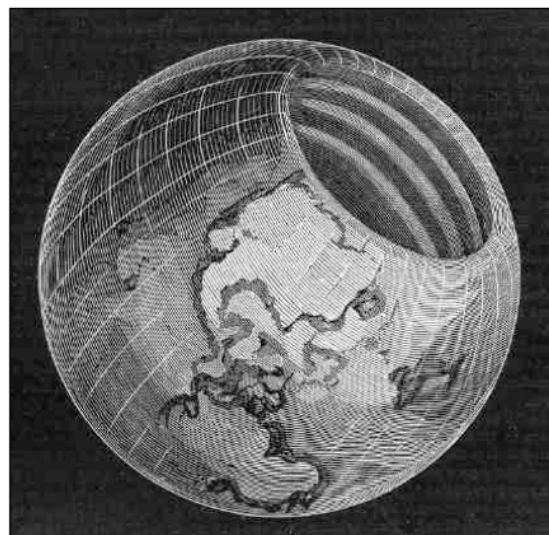
"Yes it has been written about seriously. Captain

Figure 12. Symmes' model of the hollow earth as viewed from the north pole.

Figure 13. The Symmes monument in Hamilton, Ohio, as it appears today.

The illuminating power of this light source, its vibrant coverage, its crisp white clarity, the fact that it wasn't much warmer than the air, and the reality that it shone more brightly than lunar light all clearly implied that it had an electrical origin. It was like an aurora borealis, an ongoing cosmic phenomenon, and it filled up a cavern that was spacious enough to hold an ocean.

The only puzzle in the above quotes are the references to the two inner planets of Pluto and Prosperine, as I have never come across mention of either in any of the secondary literature on Symmes that I have consulted.

Verne is often credited with being the founding father of modern science fiction. However, as pointed out in Essay III, Verne never wrote science fiction – or at least not science fiction as the term is now understood. There are no alien monsters, no mysterious superforces, no time travel, no magic materials, and no heroines in skimpy futuristic attire in his novels. Rather his works are a part of a tradition of French didactic writing known as the so-called "scientific novel" and were intended as a way of painlessly popularizing science for the lay public. They used an adventure story, combined with novel, but not improbable, applications of existing technology, as a framework into which were inserted sizable digressions on the facts of zoology, botany, geography, geology, astronomy, physics, and chemistry. Yet, as several biographers of Verne have noted, *Journey to the Center of the Earth* – which

Symmes, a countryman of ours, proposed to Sir Humphry Davy, Humboldt, and Arago to undertake the voyage! But they declined."

"And well they did."

"I think so, Whatever it may be, you see, my friend, that the imagination has busied itself about the Pole, and that sooner or later we must come to the reality."

In keeping with this quote, Symmes did indeed explicitly solicit the support of both Humphry Davy and Alexander Humboldt in his initial flyer, the same two scientists who top Verne's imaginary list of Professor Lidenbrock's scientific colleagues. It is also true that Symmes believed that the northern lights or *aurora borealis* were due to light escaping from the inner spheres via the polar openings on the earth's surface. This is of some interest given the rationale that Axel provides for the source of the mysterious light encountered in the large central cavern (3):

Figure 14. Close up of the globe on the top of the Symmes monument.

was one of Verne's earliest attempts at this genre – is, because of its use of the scientifically disreputable theme of the hollow earth, one of his few novels to truly qualify as science fiction (4, 5), though admittedly, by dispensing with all of Symmes' nonsense involving concentric spheres, polar openings, and non-Newtonian physics, Verne manages to give his version of the hollow earth, with its natural passageways, caverns and system of interconnected volcanoes, an aura of believability totally missing from Symmes.

Symmes died in 1829 and, as time passed, others began to proffer their own versions of the hollow earth idea. In order to prevent his father's ideas from being appropriated by others and to preserve his memory, Symmes' son, Americus Symmes, published a book-length summary of his father's theory in 1887 (20) and also erected a stone memorial to him in the town of Hamilton, Ohio, about 30 miles northwest of Cincinnati, which may still be seen today (figures 13-14).

Verne was neither the first nor the last writer of fiction to make use of the hollow earth idea. As early as 1820 Symmes' theory was made the basis of a novel entitled *Symzonia: Voyage of Discovery* written by an anonymous author under the pseudonym of Captain Adam Seaborn (21), and in 1838 Edgar Allen Poe made use of some of Symmes' ideas in his novelette, *The Narrative of Arthur Gordon Pym* (22). Often overlooked is the use of these ideas by the Cincinnati pharmacist, John Uri Lloyd, in his 1895 novel *Etidorhpa or the End of the Earth* (23). Indeed Lloyd appears to have taken more of his ideas from Verne than from Symmes, despite their common Cincinnati link. Thus Lloyd's traveler enters the earth through the cave system in Northern Kentucky and, while underground, encounters, like the travelers in *Journey to the Center of the Earth*, a forest of gigantic mushrooms, a vast underground sea, and a mysterious source of underground illumination called "earth light."

Lloyd was actually a manufacturing rather than a retail pharmacist and was Professor of Chemistry at the Eclectic Medical College of Cincinnati. Eclecticism was opposed to both mainstream medicine and pharmacy and was based almost exclusively on the use botanical extracts. Lloyd had no formal university training and had learned his trade through apprenticeship. This is reflected in the comments of his traveler on the geology and other natural phenomena he encounters in his underground adventures, which tend to emphasize the shortcomings of modern science and to suggest alternative nonmainstream explanations, rather than eulogizing modern technology and science like Verne. In addition, the entire novel is permeated by what can only be politely described as a kind of "Masonic Lodge mysticism."

References and Notes

1. See Essays III and VI in this volume.

2. Thus the 19th-century translation published by Sampson, Low, Marston & Co. of London in 1872 and reproduced in the anthology, A. K. Russell, Ed., *The Best of Jules Verne*, Castle Books: Secaucus. NJ, 1978, changes the professor's name from Lidenbrock to von Hardwigg, his nephew's name from Axel to Harry, his god-daughter's name from Grauben to Gretchen, and Snorre Sturluson's name to Snorre Tarleson, to name but a few. In addition, entire paragraphs, usually dealing with scientific references, have been omitted and/or replaced by others not found in the original.

3. F. P. Walter, Ed., *Jules Verne: Amazing Journeys, Five Visionary Classics*, State University of New York, Albany, NY, 2000.

4. J. Jules-Verne, *Jules Verne, A Biography*, Taplinger, New York, NY, 1976, pp. 63, 69, 73.

5. P. Costello, *Jules Verne, Inventor of Science Fiction*, Scribner: New York, NY, 1978. pp. 81-83.

6. A. Dumas, C. Benoit, "Note sur un appareil propre à éclairer les ouvriers mineurs dans leurs travaux souterrains au moyen de la lumière d'induction." *Comptes rendus*, **1862**, *55*, 439-440.

7. See Essay III

8. W. B. Jensen, "The Leclanché Cell," *Museum Notes*, January/February, 2014. Jensen website.

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14. See, for example, R. Siegfried, R. H. Dott Jr., Eds, *Humphry Davy on Geology: The 1805 Lectures for the General Audience*, University of Wisconsin Press; Madison, WI, 1980.

15. J. Davy, Ed., *The Collected Works of Sir Humphry Davy*, Vol. 5, Smith & Elder: London, 1840, pp. 138-139.

16. J. A. Paris, *The Life of Sir Humphry Davy*, Vol. 1, Colburn & Bentley: London, 1831, p. 306.

17. D. A. Griffin, "Hollow and Habitable Within: Symmes's Theory of Earth's Internal Structure and Polar Geography," *Phys. Geogr.*, **2004**, *5*, 382-397.

18. J. McBride, *Symmes's Theory of Concentric*

Spheres; Demonstrating that the Earth is Hollow, Habitable Within, and Widely Open about the Poles, Morgan, Lodge & Fisher: Cincinnati, OH, 1826.

19. J. Verne, *The Voyages and Adventures of Captain Hatteras*, Osgood: Boston, MA, 1875, pp. 419-420.

20. A. Symmes, *The Symmes Theory of Concentric Spheres; Demonstrating that the Earth is Hollow, Habitable Within, and Widely Open about the Poles. Compiled by Americus Symmes from the Writings of His Father, Capt. John Cleves Symmes*, Bradley & Gilbert: Louisville, KY, 1887.

21. A. Seaborn, *Symzonia: Voyage of Discovery*, Seymore: New York, NY. 1820.

22. E. A. Poe, *The Narrative of Arthur Gordon Pym*, Harper: New York, NY, 1838.

23. J. U. Lloyd, *Etidorhpa or the End of the Earth*, Clarke: Cincinnati, OH, 1895.

Did Vonnegut Read Bridgman?

Some Speculations on the Origins of Ice-Nine

Vonnegut and Cat's Cradle

The 1963 novel, *Cat's Cradle*, by the American author, Kurt Vonnegut Jr. (figure 1), has always been a favorite of scientists interested in clever applications of scientific concepts in fiction (1) and has even been employed by some to generate student interest when teaching the basic thermodynamics of phase changes (2).

The novel (figure 2) centers around the discovery of a hitherto unknown polymorph of ice known as "ice-nine," which melts at 114.4 °F (i.e., 45.78 °C) – in other words, a new form of ice which is a solid at ambient temperatures and pressures. This means that liquid water, under normal conditions, is actually kinetically metastable and exists only because of the absence of a suitable seed crystal needed to catalyze its conversion into the far more stable form of ice-nine. As it turns out, such a crystal has in fact been synthesized by a highly eccentric, and socially oblivious, scientist and Nobel Prize winner named Felix Hoenikker while in the employ of the industrial giant General Forge and Foundry Company of Ilium, New York, as part of a
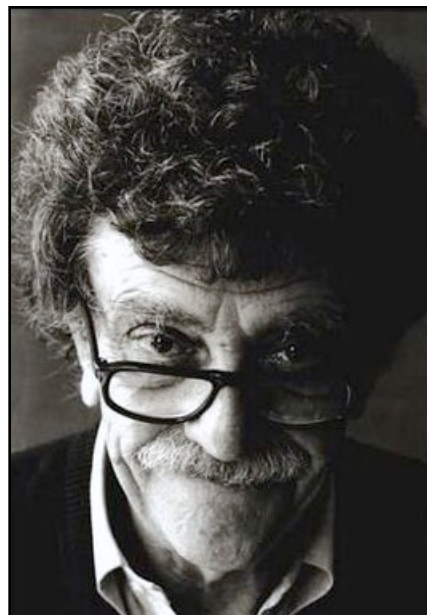
Figure 1. Kurt Vonnegut Jr. (1922-2007).
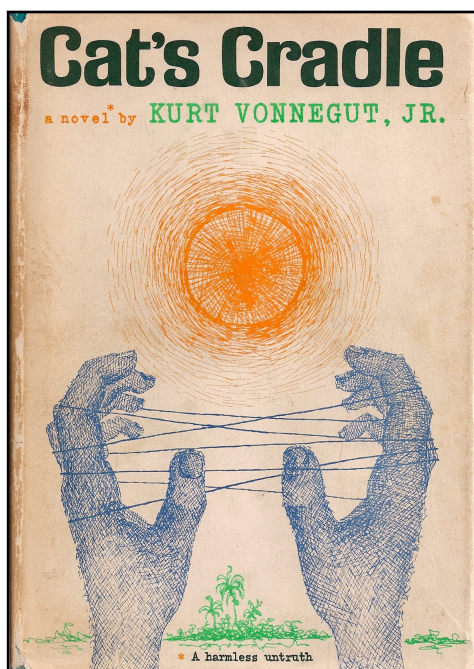
Figure 2. Dust jacket for the first edition (1963) of Vonnegut's novel *Cat's Cradle*.

request from the Marine Corp for a technical solution as to how to deal with the ubiquitous problem of mud in hampering military transport and other operations. Unknown to both his employer and fellow scientists, Hoenikker succeeds in making a seed crystal of "blue-white" ice-nine which will instantly freeze mud, and which he takes home for Xmas to show to his three highly disfunctional adult children. However, he suddenly dies before explaining its nature and purpose and the children, finding the bottle containing the crystal in his pocket, divide it among themselves. They, in turn, through a series of bad life choices and flawed judgment calls – involving many a pithy comment on religion, the unintended consequences of science, politics, sex, and fate – eventually, albeit accidently, allow its release into the environment, where it instantly causes all water to freeze solid and results in the destruction of all life on earth.

The Real Felix Hoenekker

In 1969 Vonnegut was invited to address the American Physical Society in New York City and in his talk,

Figure 3. Irving Langmuir (1881-1957), Vonnegut's proto-type for Dr. Felix Hoenekker.

which was finally published in 1974 (3), he gave an account of the origins of the concept of ice-nine. From 1947-1950 Vonnegut worked in the Public Relations Department of the General Electric Company of Schenectady, New York, where his older brother, Bernard Vonnegut (1914-1997) – a trained physicist – worked in the research laboratory with Irving Langmuir (figure 3) and Vincent Schaefer on the seeding of clouds with either dry ice or silver iodide in order to induce rain or snow formation (4). As Vonnegut related (3):

I got this lovely idea while I was working as a public-relations man at General Electric. I used to write Publicity releases about the research laboratory, where my brother worked. While there, I heard a story about a visit that H. G. Wells had made to the laboratory in the early Thirties.

General Electric was alarmed by the news of his coming, because they did not know how to entertain him. The company told Irving Langmuir, who was the most important man in Schenectady, the only Nobel Prize winner in private industry, that he was going to have to entertain Wells. Langmuir didn't want to do it, but he dutifully tried to imagine diversions that would delight Mr. Wells. He made up a science fiction story he hoped Mr. Wells would want to write. It was about a form of ice which was stable at room temperature. Mr. Wells was not stimulated by the story. He later died, and so did Langmuir. After Langmuir died, I thought to myself, well I think maybe I'll write a story.

This account strongly implies that the General Forge and Foundry Company of Ilium, New York, was a thinly disguised version of the General Electric Company of Schenectady, New York, and that Dr. Felix Hoenekker, industrial chemist and Nobel Prize winner, was a thinly disguised version of Irving Langmuir, industrial chemist and Nobel Prize Winner. Indeed this latter identification seems highly probable, since a reading of Albert Rosenfeld's 1961 biography, *The Quintessence of Irving Langmuir*, reveals that Langmuir had the same apparent child-like self-absorption in his work that Vonnegut would later attribute to Hoenekker (5).

This biography also reveals several other parallels. Thus, in the novel, the Vice-President of Research at General Forge and Foundry – one Dr. Asa Breed – under the false impression that Hoenekker had died before successfully synthesizing his magic seed crystal, expresses his relief that Hoenekker had failed because he is now fully aware that it would have had horrific environmental consequences beyond the mere freezing of mud for military convenience and thus dire legal repercussions for his company. Indeed, he becomes upset when he suspects that the narrator might be a yellow journalist intent on publicly exposing the entire project and so generating potentially negative publicity for the company.

A somewhat similar situation occurred in real life when the legal department at General Electric got wind of Langmuir's successful cloud-seeding experiments and realized that the possible side-effects could not be successfully controlled (5):

As a possible force for good, rainmaking and snow-making had tremendous potential, and the owner of those patents ought to have a large, steady income from the royalties. Yes – but suppose you made rain for a rancher, and the rain soaked a crop of hay drying in a nearby field; couldn't the farmer sue you for the loss of his hay? Or suppose you made rain in order to fill New York City's reservoirs during a dry summer; couldn't the owners of mountain and seaside resorts whose weather and business you ruined hold you accountable? ... GE decided to divorce itself from cloud-seeding in every possible legal manner. The company threw the patents open for public use and waived all royalty rights, and there was much relief when the government took over the work of Langmuir, Schaefer, and Vonnegut under project Cirrus, in March of 1947.

One of the more impressive scenes in *Cat's Cradle* is the description of what happened once a sliver of ice-nine is released into the environment and it initiates a chain-reaction as the ice-nine which it nucleates, nu-

cleates, in turn, yet more ice-nine, and so *ad infinitum* (1):

There was a sound like that of the gentle closing of a portal as big as the sky, the great door of heaven being closed softly. It was a grand AH-WHOOM. I opened my eyes – and all the sea was ice-nine. The moist green earth was blue-white pearl. The sky darkened. Bora-sisi, the sun, became a sickly yellow ball, tiny and cruel. The sky was filled with worms. The worms were tornadoes.

Once more we find a suggestive parallel with Langmuir's work on cloud-seeding. Impressed by the ability of a single silver iodide crystal to stimulate the formation of billions of small ice crystals, Langmuir, according to Rosenfeld, also began worrying that his seeding experiments might accidently generate a runaway effect (5):

"If the particles [i.e. seed crystals] retain the activity they had in laboratory tests, a wide distribution of them in the atmosphere might perhaps have a profound effect upon the climate"… Langmuir had become fascinated with the idea of causing a chain-reaction in the atmosphere. Just as a chain-reaction of atom-splitting can be caused by the impingement of a single slow neutron on a critical mass of uranium, so, Langmuir thought, could a single ice crystal or water droplet impinging on a critical cloud mass, under the right conditions, set off the entire cloud. "The chain reaction," he explained, "is one where you start out with one snow flake and by some mechanism it becomes two. Then those two become four, and those four, eight, and so on, and the thing propagates rapidly, in exactly the same way as a haystack when you light it with a match. It starts burning. It does not make a difference where it is ignited, in three places or one, it spreads through the whole haystack. The heat produced by burning one particle of hay has to be enough to heat the next particle.

On the other hand, though Rosenfeld explicitly describes Langmuir's tastes in music, art, fiction, religion, and politics, no mention is made of his ever having read any science fiction or of having ever met H. G. Wells. Likewise, official biographies of Wells fail to mention both the visit to General Electric and the meeting with Langmuir, though this most likely took place in May of 1934 when Wells visited the United States for the explicit purpose of evaluating the progress of Roosevelt's "New Deal" which he hoped to compare with Joseph Stalin's various economic reforms in the Soviet Union (6). That Wells had no interest in Langmuir's story proposal is hardly surprising.

Figure 4. Percy W. Bridgman (1882-1961).

All of Wells' science fiction had been written prior to the First World War and by the 1930s he had become obsessed with the subject of futuristic social and economic planning instead.

The Possible Role of Percy Bridgman

As suggestive as Vonnegut's account is, it still leaves some unanswered questions? As he admitted in his talk to the American Physical Society, neither Langmuir nor Wells had left an account of the plot to Langmuir's proposed story, and though, as we have just seen, there are some very suggestive parallels with the work of Langmuir and Bernard Vonnegut on cloud seeding, the heterogenous nucleation of saturated water vapor to form the normal liquid and/or solid and the homogeneous nucleation of a liquid to induce crystallization of a hitherto unknown solid polymorph differ sufficiently so as to require some further knowledge of the scientific literature on polymorphism.

The most probable scenario is that Vonnegut's older brother provided him with appropriate literature references and that Vonnegut was able to read and understand them because of his background in chemistry and mechanical engineering, both of which he had studied (albeit, by his own account, not very successfully) prior to the Second World War. But what was the nature of the scientific literature that he would have consulted?

Prior to World War II, the single most important authority on polymorphism and polymorphic transitions was, without a doubt, the Harvard physicist,
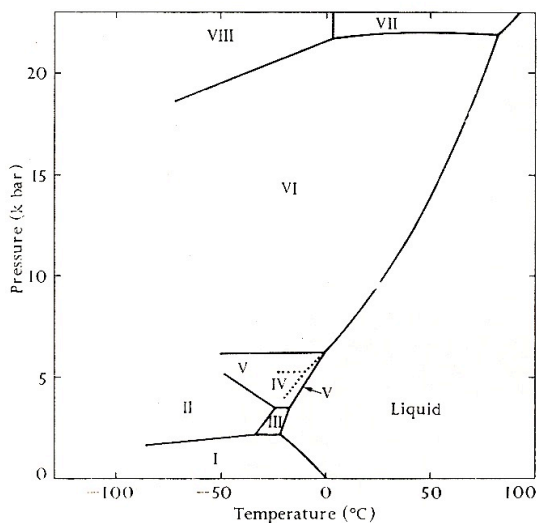
Figure 5. A phase diagram for the eight known polymorphs of ice as envisioned by Eisenberg and Kauzmann in 1969. Note that the type of transition envisioned by Vonnegut would be potentially possible for ice VI and liquid water around 50° C but only at pressures of 15 kbar rather than at room pressure.

Percy W. Bridgman (figure 4), who would receive the Nobel Prize in physics in 1946 "for his invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics." Much of Bridgman's work on high pressure polymorphs, including those of ice, was summarized in his 1931 monograph, *The Physics of High Pressures* (7). At the time six polymorphic varieties of ice were known to Bridgman, which he labeled as ice I - ice VI, where ice I refers to the common form. Ice II and ice III had been discovered by the German phase scientist, Gustav Tammann in 1900, and ice IV, ice V, and ice VI by Bridgman himself in 1912. In 1937 Bridgman discovered a seventh polymorph – ice VII – and an eighth form – ice VIII – was found by Kamb and Davis in 1965 (figure 5), two years after the publication of *Cat's Cradle* (8). Thus Vonnegut's numbering of his fictitious ice polymorph was in the right ball park, and certainly suggests that he was well aware of the existing state of research in this area. Currently more than 15 polymorphs of ice have been reported.

But the ice-nine concept requires more than an understanding of how many polymorphs of ice were known in the 1960s. It also requires a knowledge of the difference between true thermodynamic stability, on the one hand, and kinetic metastability, on the other, and the possibility of not only high-pressure polymorphs, but hitherto unknown polymorphs stable at ambient temperatures and pressures. As it turns out, these missing prerequisites may also be found in the

writings of Bridgman, and most particularly in what is perhaps his best known book – the 1941 monograph, *The Nature of Thermodynamics* (figure 6), in which, during a discussion of the role of kinetic hinderances to thermodynamically spontaneous phase transformations, we find the following remarkable statement (9):

In many cases it is easy enough to see when these hinderances to a complete and final smoothing out are operative, but in other cases it is impossible to be sure that the lowest potentialities have been realized, as in that of a test tube of supercooled water that suddenly changes to ice after ten day's quiescence, or the glycerin in the chemical laboratory at Berkeley that froze solid after the importation of a nucleus of the solid from Oregon. There is no way whatever of being sure that any of the ordinary objects of daily life do not have other polymorphic forms into which they may sometime change spontaneously before our eyes [emphasis added].

All of the necessary ingredients for the physics of ice-nine are present in this quote – the metastability of a liquid finally overcome by an imported seed crystal, the possibility that everyday materials might be only metastable rather than thermodynamically stable, etc.

Yet other suggestive hints are to be found in Bridgman's books. Thus with respect to the explosive
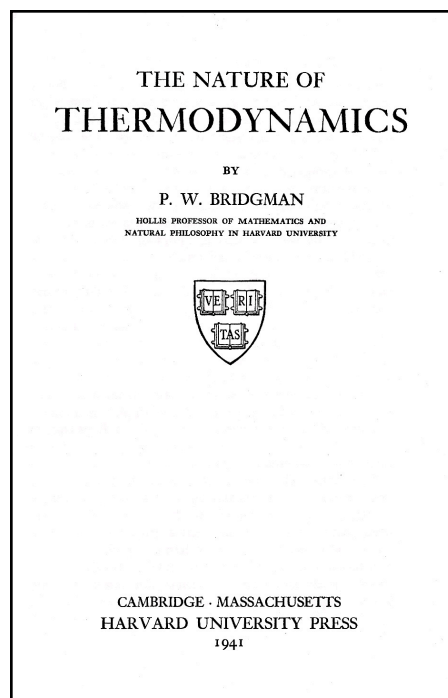

Figure 6. The title page of Bridgman's classic monograph, *The Nature of Thermodynamics* (1941).

transformation of normal water into ice-nine already mentioned above, we read the following comment by Bridgman on the rate of conversion of ice I onto ice III in his high pressure apparatus (7):

A particular striking example is that of ice I-III. Near the upper limit of this transition line, which is terminated by the triple point with the liquid, the transition runs with almost explosive rapidity; in fact pressure so rapidly follows the change of volume produced by the moving piston that the pressure gauge will show no change of pressure.

Of course, we will probably never know for certain whether Vonnegut – either at his brother's prompting or on his own – ever read Bridgman, but the parallels found in Bridgman's books with the underlying imaginative scientific speculations found in *Cat's Cradle* are far too suggestive to simply ignore.

The Case of EDT

In closing, it should be pointed out that Vonnegut left us with one more hint concerning his knowledge of the scientific literature dealing with crystallization and polymorphism. In attempting to explain the theory behind ice-nine to the novel's narrator, the Vice-President of Research at General Forge and Foundry, Asa Breed, makes reference to the compound ethylenediamine tartrate, $[C_2H_4(NH_3)_2][C_4H_4O_6]$, also known as EDT or 1,2-ethylenediammonium tartrate (1):

He told me about a factory that had been growing big crystals of ethylenediamine tartrate. The crystals were useful in certain manufacturing operations, he said. But one day the factory discovered that the crystals it was growing no longer had the properties desired. The atoms had begun to stack and lock – to freeze – in a different fashion. The liquid that was crystallizing hadn't changed, but the crystals it was forming were, as far as industrial application went, pure junk.

How this had come about was a mystery. The theoretical villain, however, was what Dr. Breed called "a seed." He meant by that a tiny grain of the undesired crystal pattern. The seed, which had come from God-only-knows-where, taught the atoms the novel way in which to stack and lock, to crystallize, to freeze.

In the late 1940s and 1950s, when Vonnegut was working for the Public Relations Department of GE, large crystals of this compound were attracting considerable attention for their potential use as a replacement for quartz in piezoelectric devices and Western Electric had constructed a large plant in Allentown, Pennsylva-

nia, for their manufacture (10). However, the subsequent development of techniques for growing synthetic quartz crystals eventually caused the plant to close.

The phenomenon referred to by Breed involves the initial synthesis of a useful, but metastable, polymorph which eventually becomes impossible to replicate once seed crystals of a less useful, but thermodynamically more stable, polymorph become prevalent in the environment. Dubbed "disappearing polymorphs" by Dunitz and Bernstein in 1995, numerous examples of this phenomena have been documented in the literature, most of them referring to compounds of pharmacological importance (11). The commercially useful crystals of EDT, referred to by Breed, were anhydrous and, after four years of operation, the chemical plant became infected with seed crystals of the more stable, and commercially worthless, monohydrate. Since this has a different composition than the anhydrous form, Breed's example was, strictly speaking, not a true case of competing polymorphs. In any case, the problem was soon identified and rectified by altering the temperature so as favor the formation of the anhydrous product rather than the monohydrate (12-13).

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IX
By the Light of the Silvery Moon
Tom Swift and his Photo Telephone

The Discovery of Selenium

The element selenium was first discovered in 1817 by the great Swedish chemist, Jöns Jacob Berzelius (figure 1), in the sludge of a sulfuric acid plant in Gripsholm, Sweden, which he owned in partnership with his older contemporary, Johan Gottlieb Gahn (figure 2), as recounted in his autobiography (1):

In 1816 I was persuaded by Gahn to buy, in company with himself and mine-master [Hans Peter] Eggertz, a factory at Gripsholm built to manufacture sulfuric acid, white lead, vinegar, and other chemical articles. This establishment was sold at auction in settlement of a bankrupt estate, and thus was obtainable at a price below its intrinsic value ... At this factory sulfuric acid was manufactured out of crude sulfur from Falun. The concentrated sulfuric acid deposited a golden brown powder. This I gathered in order to investigate it and was thus led to the discovery of selenium.

Figure 1. Jöns Jacob Berzelius (1779-1848)

The plant in question employed the well-known lead chamber process to manufacture its sulfuric acid. This, in turn, was based on the use of nitrogen dioxide gas to oxidize sulfur dioxide to sulfur trioxide and nitrogen oxide (2):

$$NO_2(g) + SO_2(g) \rightarrow SO_3(g) + NO(g) \qquad [1]$$
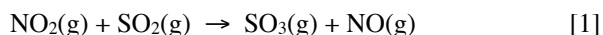
and the reaction of the resulting sulfur trioxide with water to produce dihydrogen sulfate or sulfuric acid:

$$SO_3(g) + H_2O(l) \rightarrow H_2(SO_4)(aq) \qquad [2]$$
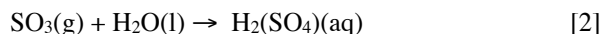
The nitrogen oxide by-product in reaction 1 was then reoxidized back to nitrogen dioxide via reaction with the dioxygen gas of the atmosphere:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad [3]$$
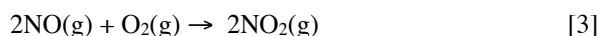
Doubling reactions 1-2 and adding them to reaction 3 gives the net reaction for the overall process:

$$2SO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 2H_2(SO_4)(aq) \qquad [4]$$

Figure 2. Johan Gottlieb Gahn (1745-1818). Note the alchemical symbol for iron on his lapel.
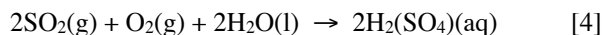
and thus reveals that the nitrogen oxides are functioning catalytically as oxygen carriers.

As stated by Berzelius, the sulfur dioxide in reaction 1 was produced by burning octasulfur manufactured at the famous copper mine in Falun Sweden:

$$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g) \qquad [5]$$
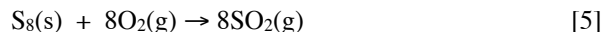
This, in turn, had been obtained from the roasting of a double sulfide of copper and iron known as copper pyrite or chalcopyrite (figure 3) – the principle copper ore found at Falun – under oxygen-poor conditions designed to selectively oxidize the iron and copper but not the majority of the sulfur, which was instead collected as a sublimate:

$$heat + 4CuFeS_2(s) + 5O_2(g) \rightarrow$$
$$2Fe_2O_3(s) + 4CuO(s) + S_8(g) \quad [6]$$
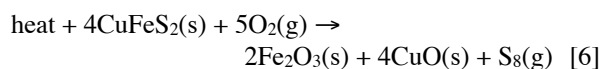
The metallic oxides were then reduced to the corresponding metals or, in the case of Fe_2O_3, also used for production of a popular Swedish red paint pigment known as Falun red.

Likewise, at the Gripsholm plant the requisite nitrogen dioxide was obtained by reaction of the sulfur dioxide with nitric acid placed in glass pans at the bottom of the lead chamber:

$$2SO_2(g) + 2H(NO_3)(aq) \rightarrow 2NO_2(g) + H_2(SO_4)(aq) \quad [7]$$
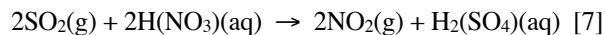
and this is also where the final product of sulfuric acid eventually collected.

With slight modifications – such as the generation of $NO_2(g)$ by adding nitre or potassium nitrate to the burning sulfur – small quantities of sulfuric acid had been industrially manufactured by this method ever since the work of Glauber in the 17th century, though output was limited by the size of available acid-resistant glass reaction chambers. However, in the 1740s the British industrial chemist, John Roebuck, succeeded in substantially "scaling up" production by substituting large wooden towers lined with sheet lead in place of the traditional glass reaction chambers – whence the name "lead chamber" process. Though the reactions of metallic lead with sulfuric acid and the various oxides of sulfur are thermodynamically favorable, they are kinetically inhibited by the formation of surface deposits of the resulting reaction products, thus allowing the lead sheets to act as a fairly inert liner for the reaction chamber.

The brown sludge in which Berzelius discovered selenium was found in the bottom of the nitric acid pans and its selenium content in all probability originally came from the copper pyrites used to manufac-
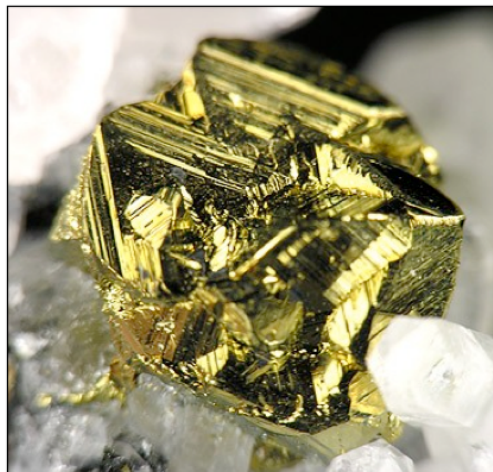

Figure 3. A typical crystal of chalcopyrite indicating why it was also called copper pyrite and often confused with iron pyrite or fool's gold. In fact, iron pyrite [Fe(S₂)] contains polydisulfide anions (S_2^{2-}) and has a 6/6 sodium chloride structure, whereas copper pyrite [CuFeS₂] contains simple sulfide anions (S^{2-}) and has a 4/4 sphalerite structure.

ture the sulfur used at Gripsholm. Selenium can substitute for sulfur in the anionic lattices of various sulfide minerals, such as chalcopyrite, $CuFe(S_{2-x},Se_x)$, and galena or lead sulfide, $Pb(S_{1-x},Se_x)$, which Berzelius claimed was also used in the sulfur production and, since the enthalpy of sublimation of octaselenium is virtually identical to that of octasulfur, any selenium released in the roasting process should have sublimed along with the unoxidized sulfur.

As for the composition of the brown sludge, $SeO_2(s)$ and $SeO_3(s)$ are both ruled out since both form colorless or white solids. Berzelius also stated that the sludge contained traces of red and yellow, and later implied that it was a mixture of elemental selenium and sulfur since he noticed that, on burning the sulfur from Falun to generate sulfur dioxide, the resulting heat caused a certain amount of the sulfur to sublime unoxidized, and since selenium dioxide has almost half the free energy of formation per mole of sulfur dioxide, one would suspect that this would have been the fate of much of the elemental selenium present as well.

That matters were probably not that simple is, however, suggested by Berzelius' initial examination of the sludge using a mineralogist's blowpipe (3):

In conjunction with J. G. Gahn, I was examining the method formally in use at Gripsholm for preparing sulfuric acid. We found in that acid a sediment, partly red and partly light brown, which, when heated before the blowpipe flame, gave an odor like that of rotten radishes, and left a grain of lead.

Figure 4. The great copper mine at Falun as it appeared in 1907. The building in the center with the tower is now a mining museum.

This strongly suggests that the lead walls of the reaction chamber and reactions, such as the following (which is thermodynamically favorable), may also have been involved in the formation of the reddish-brown sediment:

$$SeO_2(g) + 3Pb(s) \rightarrow PbSe(s) + 2PbO(s) \qquad [8]$$
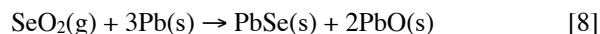
This would not only account for the formation of the lead bead in the blowpipe flame but for the color of the deposit, since the red lead oxide and gray lead selenide would give brown if combined in the proper ratio.

As for the odor of rotten radishes, this was at the time thought to be characteristic of the element tellurium, which had been discovered by Müller von Reichenstein in 1782, and it initially misled Berzelius into believing it was also present in the sludge. However, he could detect none of the other properties of tellurium and eventually showed that the association of the odor with that element was due to contamination with selenium. Since the famous German analytical chemist, Martin Heinrich Klaproth, had named Müller von Reichenstein's new metal "tellurium" in 1798 after the Latin word *tellus* for "earth," Berzelius, in recognition of its close resemblance to tellurium, chose to name his new element "selenium," after the Greek word *selene* for "moon."

As a passing note, when I briefly worked with selenium compounds as a graduate student at the University of Wisconsin, I was advised to immediately tell my advisor if my wife complained that my breath smelled of garlic or rotten radishes, as that was a strong indication that I had selenium poisoning.

The Mines of Falun

In 1770 the College of Mines had assigned Berzelius' future partner, Gahn, the task of improving the

manufacture of copper at Falun, which he did with great success, while simultaneously diversifying its operations by also introducing, as we have seen, the manufacture of sulfur, sulfuric acid and red orchre. As superintendent of the mine, Gahn also maintained a home and private laboratory at Falun, where he was visited by the British chemist, Thomas Thomson, in 1812 (4):

Johann Gottlieb Gahn, the intimate friend of Bergman and Scheele, was one of the best-informed men, and one whose manners were the most simple, unaffected, and pleasing, of all the men of science with whom I ever came in contact. I spent a few days with him at Falun in 1812 and they were some of the most delightful days I ever passed in my life. His fund of information was inexhaustible, and was only excelled by the charming simplicity of his manners, and by the benevolence and goodness of heart which beamed in his countenance.

Located in the famed *Stora Kopparberget* or great copper mountain, the mine at Falun (figure 4) had been in almost continuous operation since the 10th century (5). Indeed, until 19th-century advances in international shipping allowed for import of significant quantities of copper from Asia and the Americas, copper from Falun maintained a virtual European monopoly and served as a major source of income for the government of Sweden. The mine today lies at the bottom of an enormous pit. This was not created by strip mining but is rather the result of a massive cave-in of the original maze of random tunnels which occurred in the summer of 1687.

The productivity of the mine began to steadily decline throughout the 19th- and early 20th-centuries and it was finally closed in 1992. Today it is a tourist destination and houses a mining museum in several of its surviving 18th- and early 19th-century buildings. In 2001 it was also designated as a Unesco World Heritage Site.

This mine was the subject of a famous short story by the well-known early 19th-century German author of imaginative and supernatural tales, E. T. A. Hoffman (figure 5). Popular throughout Europe, many of Hoffman's short stories eventually became the subjects of musical compositions by famous composers of the day, including Offenbach's opera, *Tales of Hoffman*; Delibes' ballet, *Coppélia;* and – perhaps most famous of all – Tchaikovsky's ballet, *The Nut Cracker*.

First published in 1819, two years after Berzelius' discovery of selenium and a year after the death of Gahn, Hoffman's short story, "The Mines of Falun," opens with the return of a young sailor named Elis Fröbom to the Swedish port of Göteborg Sweden.

Finding that the last of his family has died during his absence, Fröbom falls into a depression during which he is approached by an elderly miner who listens sympathetically to his doubts about returning to the sea and his uncertainty over his future. The miner then begins to describe for him the lure of the miner's life deep within the bowels of the earth among nature's precious metals and gems, where in the darkness and silence one can stay attune with one's innermost thoughts, safe from the turmoil and unhappiness of life on the surface. The elderly miner than assures Fröbom that he was born to be a miner rather than a sailor.

Upset by his conversation with the miner, Fröbom wanders the city for the next few days in confusion. Then, convinced that he sees the miner leaving town by one of the roads, follows him, only to find himself, a few days later, standing in the rising mists of nearby lakes before the gaping pit which served as the *Pinge* or main entrance to the famous copper mine of Falun (6):

As is well known, the great entrance to the mine of Falun is about twelve hundred feet long, six hundred feet wide, and one hundred eighty feet deep. The blackish-brown side walls at first extend downwards more or less vertically. About halfway down, however. they are less steep because of the tremendous piles of rubble. Here and there in the banks and walls can be seen timbers of old shafts that were constructed of strong trunks laid closely together and joined at the ends in the way block houses are usually constructed. Not a tree, not a blade of grass was living in that barren, crumbled, rocky abyss. The jagged rock masses loomed up in curious shapes, sometimes like gigantic petrified animals, sometimes like human colossi. In the abyss there were stones – slag, or burned out ores – lying around in a wild jumble, and sulfurous gases rose steadily from the depths as if a hellish brew were boiling, the vapors of which were poisoning all of nature's green delights. One could believe that Dante had descended from here and had seen the Inferno with all its wretched misery and horror.

Fröbom soon makes the acquaintance of a "tall, slender, middle-aged man" with "a gentle smile, easy manners, and dark blue, sparkling eyes" named Pehrson Dahlsjö, who, not unlike Gahn in real life, is the chief official of the district and one of the mine owners. Impressed by Fröbom's apparent knowledge of mines (which he had in fact acquired from the elderly miner), Dahlsjö agrees to take him on as an apprentice miner. Predictably Dahlsjö also has a beautiful daughter named Ulla with whom Fröbom immediately falls in love.

One day while working alone in one of the deepest

Figure 5. E. T. A. Hoffman (1776-1822).

shafts, Fröbom once again encounters the elderly miner who begins chiding him for betraying his calling as a miner. Fröbom, he claims, is working the mine not out of love of his craft but because he wants to impress Dahlsjö and marry his daughter. As a result the *Metallfürst* of the mine will refuse to show him where the best veins and ores are because he really wants a life on the surface with Ulla.

After the elderly miner suddenly disappears again, Fröbom is found standing in the deep shaft in utter confusion by the chief foreman who asks what has happened. Telling him of the sudden appearance and disappearance of the elderly miner, the foreman reveals that it is the ghost of old Torbern, who had supervised the mine in the 17th century. Famous for his intimate knowledge of mining and ores, Torbern remained unmarried and scorned life on the surface. Upset by the thoughtless and greedy practices of his fellow miners, Torbern also predicted the famous mine collapse of 1687 in which he was apparently killed. The present-day miners, however, still report seeing him in the deeper shafts and claim that on occasion he has led them to a rich outcropping of fresh ore.

Eventually Fröbom and Ulla are to be married, but on the day of the wedding, he tells Ulla that it has been revealed to him in a dream that (6):

Down in the shaft a cherry red sparkling almadine lies enclosed in chlorite and mica, on which is inscribed the chart of our life. You must receive it from me as a wedding present.

Fröbom leaves his bride to retrieve the gem from the mine, but the shaft collapses and his body is never recovered – or rather not until fifty years after the event when all of the other participants are apparently dead and no one living has any memory of Fröbom, Dahlsjö or Ulla (6):

Then one day miners who were investigating an opening between two shafts found the corpse of a young miner lying in sulfuric acid in a bore nine hundred feet deep. When they brought the body to the surface, it appeared to be petrified.

Just why Hoffman imagined that sulfuric acid could act as a preservative for organic matter is a total mystery – apparently he never studied chemistry.

The Photoelectric Properties of Selenium

Following Berzelius' discovery, chemists quite naturally continued to study the chemical properties of both elemental selenium and its compounds. However, the next truly exciting discovery concerning this element did not come until 1873 and was made by an electrical engineer, rather than a chemist, and dealt with the physical, rather than the chemical, properties of selenium. The engineer in question was an Englishman by the name of Willoughby Smith (figure 6), who at the time was working for the Transatlantic Cable Company at its receiving station on Valentia Island off the coast of Ireland (7).

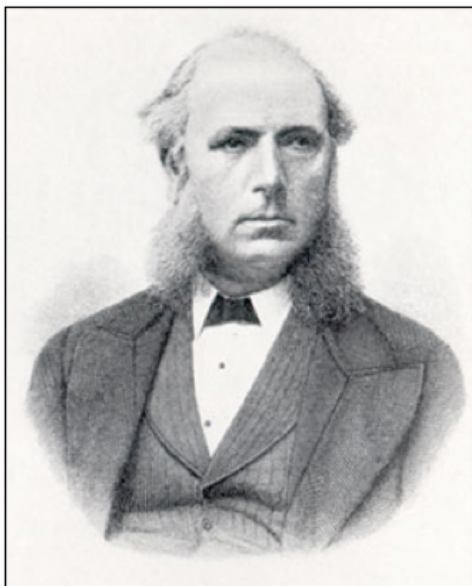As described in a brief letter to the weekly journal
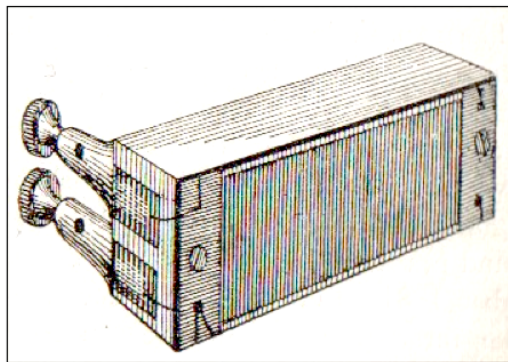

Figure 6. Willoughby Smith (1828-1891).

Figure 7. An early selenium cell.

Nature, Smith was attempting to increase the electrical resistance of the telegraphic system he was testing and decided to use for this purpose bars of metallic selenium, 5-10 cm in length, that were hermetically sealed in glass tubes with platinum contacts (8). However, attempts to quantitatively measure the resistance of these tubes gave highly erratic results until Smith discovered that their resistance was light sensitive. Placing his selenium resistors in a wooden box with a sliding lid, he found that the measured conductivity of the bars varied with the intensity of the light exposure and, in some cases, was more than double the value observed for bars kept in the dark.

Three years later the German-British engineer, Sir Carl William Siemens, constructed the first selenium photocell (figure 7). This basically consisted of two interpenetrating but nontouching grids of wire wound about an insulator with the spaces between them filled with metallic selenium. Only one end of each grid was available for connection to an external electrical circuit. In the dark the nonconducting selenium insulated the two systems of wires from one another and prevented completion of the circuit whereas in the light, the photoconducting selenium now allowed the two grids to make electrical contact and so completed the circuit.

The Silent Bullet

An early, but rather mundane, literary use of the selenium cell occurs in the short story, "The Diamond Maker," which appeared in the 1910 short-story collection, *The Silent Bullet*, by the American author, Arthur B. Reeve, detailing the adventures of his fictional detective, Craig Kennedy, and his companion, Walter Jameson. The basic plot of this story has already been described in some detail in an earlier essay in this volume entitled "Tom Swift Among the Diamond Makers" and need not be repeated here.

As will be recalled, having visited the laboratory of the fraudulent diamond maker, Poissan, during the day, Kennedy and his companion, disguised as a would-be investor, have arranged to return that evening for a demonstration of the so-called diamond synthesis. They are also accompanied by several detectives, who are, however, ordered to wait on the ground floor until they receive a signal from Kennedy – a signal which Kennedy transmits using a selenium cell which he has constructed in his laboratory earlier that day (9):

He was in his laboratory winding two strands of platinum wire carefully about a piece of porcelain and smearing on it some peculiar black, glassy, granular substance that came in some sort of pencil, like a stick of sealing wax. I noticed that he was very careful to keep the two wires exactly the same distance from each other throughout the entire length of the piece of porcelain, but I said nothing to distract his attention ...

Kennedy then anneals the entire device in a burner flame (9):

The black glassy substance was now a dull grey. "What is the stuff you were putting on the wire?" I asked. "Oh just a by-product made in the manufacture of sulfuric acid," answered Kennedy airily ...

Poissan's laboratory is located on the top floor of a tall office building, which is essentially unoccupied after hours, with the hallways unlit and only one of the elevators in operation. Handing the detectives an open circuit composed of a battery and electric bell, Kennedy tells them to wait for five minutes and then connect it to the wires which they will find dangling in the shaft of the unused elevator.

Proceeding to the top floor, Kennedy and Jameson open the door to the shaft of the nonworking elevator and drop down the wires in question. These are connected to Kennedy's photocell, and he then proceeds to string the remaining wire along the hallway until they come to Poissan's laboratory. From his earlier visit, Kennedy knows that the walls of the various offices adjacent to the hallways have large frosted windows in them designed to aid in lighting the interior hallways using daylight from the exterior rooms and Kennedy places his photocell on the ledge of one of these windows before entering Poissan's well-lit laboratory. Once inside, he places his coat and hat on the interior window ledge so as to block access of the light to the photocell.

Meanwhile, the waiting detectives have connected the battery and bell to the selenium cell circuit and, when Poissan threatens Kennedy and his companion,

Kennedy picks up his hat and coat as though attempting to leave (9):

"Put down your coat, Mistair Kennedy," he hissed. "The door has been locked ever since you have been here. Those windows are barred, the telephone wire is cut, and it is three hundred feet to the street.

However, unknown to Poissan, this simple act exposes the cell to the light from the laboratory, completes the circuit, and rings the bell summoning the detectives, who arrive just in time to save Kennedy and Jameson from almost certain death.

Not mentioned by Reeve is the fact that the battery-bell arrangement given to the detectives also had to contain a sensitive electrical relay. Even at its maximum conductivity, a selenium cell would not pass sufficient current to operate a conventional electric bell. Instead, the weak current from the photo-activated cell is used to trip a relay which, in turn, completes a secondary circuit which causes the bell to ring.

Tom Swift and His Photo Telephone

Far more inventive uses of selenium cells were not long in coming. One of the most famous of these was proposed in 1880 by none other than Alexander Graham Bell (figure 8) of telephone fame and was known as the "photophone" (10). Designed to transmit human speech by means of light rather than electrical wires, the transmitter replaced the usual diaphragm of the conventional telephone with a flexible mirror unto
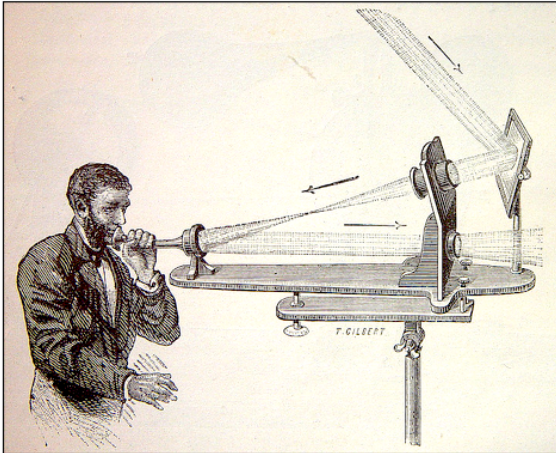

Figure 8. Alexander Graham Bell (1847-1922).

Figure 9. The transmitter for Bell's 1880 photophone.

which a strong light source was focused (figure 9). The variations in pressure produced by the speaker talking into the mouth piece caused the mirror to change back and forth between concave and convex and thus alternately concentrated and dispersed the reflected light beam. This modulated reflected light beam was, in turn, received by a parabolic mirror with a selenium cell at its focus (figure 10), and the resulting modulated electrical current used to recreate the sound using a conventional telephone receiver.

Though the photophone worked as planned and
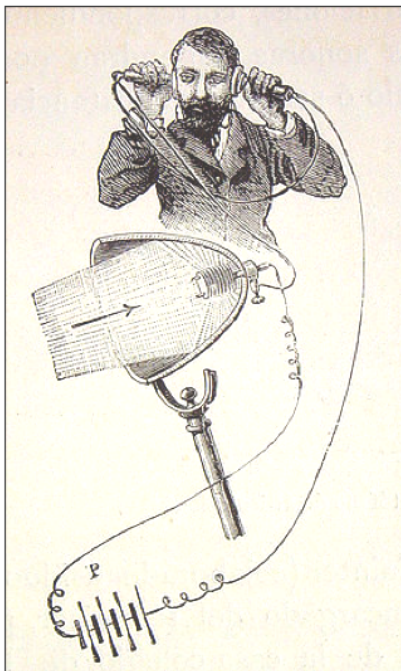
Figure 10. The receiver for Bell's 1880 photophone. Note the selenium cell at the focus of the parabolic collector.

caused something of a sensation in its day, it ultimately proved impractical as there was no way of producing light beams that remained coherent over long distances nor any way of dealing with the interfering effects of snow, rain, fog or man-made obstructions. Though telephone signals would ultimately be sent by means of light, rather than electrical currents in wires, these would require the use of fiber optic cables rather than relying on open light beams.

Attempts were also made to use selenium cells to transmit images rather than speech. Though some of these go back to the last quarter of the 19th century, the first practical system of selenium based "phototelegra-
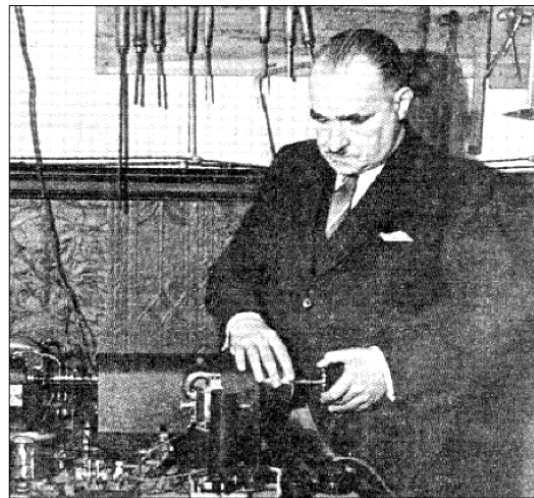

Figure 11. Arthur Korn (1870-1945).

phy," as it came to be called, is usually credited to the German-American physicist, Arthur Korn, (figure 11), who first demonstrated his version in 1902 (11) and who successfully transmitted an image of King Edward VII from Paris to London in 1907.

Korn placed a film of the image to be transmitted on a glass drum, which was scanned vertically, line by line, by a concentrated light beam. A mirror inside the drum reflected the transmitted variations in light intensity to a selenium photocell whose output controlled the shutter on a similar light source at the receiving end which also contained a drum with photographic paper mounted on it. Both the drum and the light source at the receiving end were synchronized with those at the transmitter end. Variations in the output of the selenium cell produced corresponding variations in the light exposure of the photographic paper, thereby reproducing the scanned image.

However, both Bell's photophone and Korn's phototelegraph pale in comparison with the uses of selenium envisioned by the fictional boy-inventor, Tom

Swift, in his 1914 adventure, *Tom Swift and his Photo Telephone or the Picture that Saved a Fortune* (figure 12). As with the Reeve story discussed in the previous section, the origins of the Tom Swift novels and their creator have already been discussed in the earlier essay in this volume entitled "Tom Swift Among the Diamond Makers" and need not be repeated here.

The 17th installment in the initial Tom Swift series, the novel opens with Tom explaining to his father his idea for a photo telephone which will transmit not only speech but also an image of the two speakers. In order to lend plausibility to his idea, he first describes a real invention which had recently been used to transmit photographs of the famous car races at Monte Carlo over five hundred miles of telegraph wire to a newspaper office in Paris (12):

... they took a photograph, and made a copper plate of it, as they would for a half-tone illustration. This gave them a picture with ridges and depressions in copper, little hills and valleys. so to speak, according to whether there were light or dark tints in the picture. The dark places meant that the copper lines stood higher there than where there were light colors.

Now, by putting this plate on a wooden drum, and revolving this drum, with an electric needle pressing lightly on the ridges of copper, they got a varying degree of electrical current. Where the needle touched a high place in the copper plate the contact was good, and there was a strong current. When the needle got to a light place in the copper – a depression, so to speak – the contact was not so good, and there was only a weak current.

At the receiving end of the apparatus there was a sensitized film placed on a similar wooden drum. This was to receive the image that came over the five hundred miles of wire. Now then, as the electrical needle, moving across the copper plate, made contacts of different degrees of strength, it worked a delicate galvanometer on the receiving end. The galvanometer caused a beam of light to vary – to grow brighter or dimmer, according as the electrical current was stronger or weaker. And this light, falling on the sensitive plate in Paris, made a picture, just like the one on the copper plate in Monte Carlo.

In other words, where the copper plate was black, showing that considerable printing ink was needed, the negative on the other end was made light. Then when that negative was printed it would come out black, because more light comes through the light places on a photograph negative than through the dark places. And so, with the galvanometer making the light flashes on the sensitive plate, the galvanometer being governed by the electrical contacts five hundred miles away,
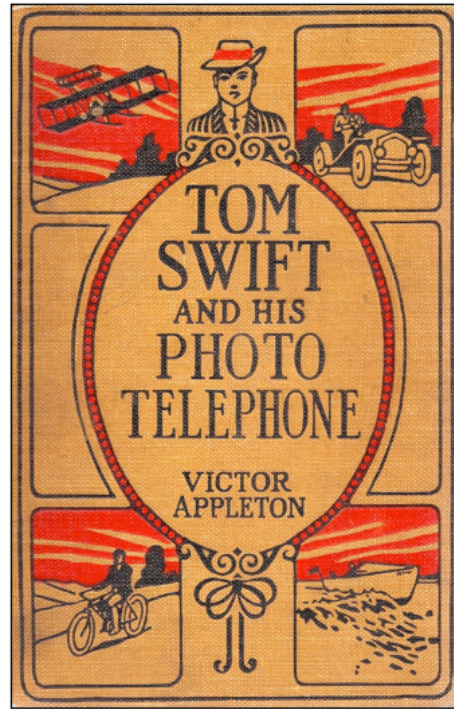

Figure 12. Cover of the 1914 thriller, *Tom Swift and His Photo Telephone or the Picture that Saved a Fortune*.

they transmitted a photograph by wire.

This is obviously a version of Korn's phototelegraph sans the selenium photocell – an oversight which Tom apparently intends to correct (12):

I shall probably use selenium, which is very sensitive to light, and which makes a good or a poor electrical conductor according as more or less light falls on it. After all, a photograph is only lights and shadows, fixed on a sensitive paper or films.

A little later in the novel Tom further explains to his boyhood friend, Ned, his reasons for choosing selenium and also elaborates on the origins and properties of the element (12):

"I think it is the only thing to use in this photo telephone experiment, though I might try the plate method, as they did between Monte Carlo and Paris. but I am not trying to make newspaper pictures."

"What is selenium anyhow?" asked Ned. "Remember, Tom, I'm not up on this scientific stuff as you are."

"Selenium," went on Tom, "was discovered in 1817 by J. J. Berzelius, and he gave it that name from the Greek word for moon, on account of selenium being so similar, in some ways, to tellurium. That last is named after the Latin word, tellus, the earth."

"So they dig it? Ned wanted to know.

"Well sometimes selenium is found in combination with metals, in the form of selenides, the more important minerals of that kind being eucharite, crooksite, clausthalite, naumannite and zorgit –"

"Good night!" interrupted Ned, with a laugh, holding up his hands. "Stop it, Tom!" he pleaded. "You'll give me a headache with all those big words."

"Oh, they are easy, once you get used to them," said the young inventor, with a smile. "Perhaps, it will be easier if I say that sometimes selenium is found in native sulfur. Selenium is usually obtained from the flue-dust or chamber deposits of some factory where sulfuric acid is made. They take this dust and treat it with acids until they get the pure selenium. Sometimes selenium comes in crystal forms, and again it is combined with various metals for different uses."

Though this is a fairly accurate historical and chemical summary, it is regrettably the last semblance of either science or plausibility to be found in the novel. Tom forms his selenium into light sensitive metal plates which are placed above the conventional telephone receiver and transmitter (figure 13). These plates can register an image only once and then must be replaced with freshly sensitized plates. Later he places a hidden plate in a phone booth which is used to
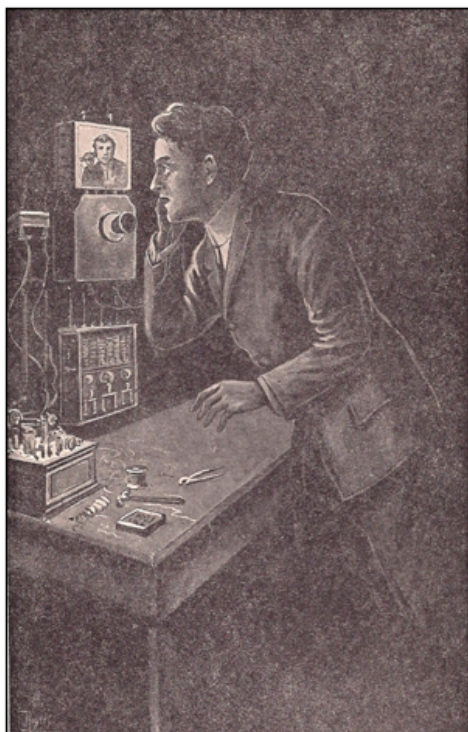

Figure 13. "Tom uttered a cry of joy, for there, staring at him from the plate, was the face of Ned."

trap the villain of the story, though this plate must be removed and chemically developed! Despite high voltages being invoked at one point, it is apparent that the ghost writer of this particular adventure had no idea how a selenium cell actually worked and has confused the entire process with conventional photography. As with the earlier novel on the diamond makers, the entire thing is based on the scaling up of superficial word analogies. If Moissan used an electric furnace to make diamonds, then an electrical lightning bolt should work even better. If the phototelegraphic device described at the beginning of the novel used a copper plate and photographic paper, than a photosensitive selenium plate should work even better, etc. etc.

Ironically, Tom Swift himself gave the best critical evaluation of the entire venture at the beginning of the novel when answering his father's objection that the photo telephone idea violated the basic laws of science (12):

"But stop and consider for a moment. This thing of sending a picture over a telephone wire is totally out of the question, and entirely opposed to the principles of science."

"What do I care for the principles of science?" cried Tom.

Never were truer words uttered.

The Moon Element and the Art of Prediction

Just how vividly the photoelectric properties of selenium had captured the imaginations of real-life inventors may be seen from a popular account of the element and its electrical properties published by the British physicist and inventor, Edmund Edward Fournier d'Albe, in 1924 – a decade after the appearance of Tom Swift's great adventure. Entitled *The Moon-Element: An Introduction to the Wonders of Selenium*, its intent was succinctly summarized by the author in his brief preface (13):

In this book the reader will find the first connected account of the properties and applications of a chemical element which has raised – and disappointed – more hopes than any other element known.

After briefly surveying the discovery of selenium by Berzelius, the discovery of its photoconductivity by Smith, the invention of the selenium cell by Siemens, the photophone of Bell and the phototelegraph of Korn, as well as several other inventions based on selenium cells, such as automatic buoy lights, light guided torpedo boats, etc., the vast majority of the

electrostatic (i.e., xerox) copying machine – was totally unforeseen by either Fournier d'Albe in fact or by Tom Swift in fiction.

References and Notes

1. J. J. Berzelius, *Autobiographical Notes*, Williams & Wilkins: Baltimore, MD, 1934, pp. 93-94. More detailed accounts may be found in M. E. Weeks, *Discovery of the Elements*, 6th ed., Journal of Chemical Education: Easton, PA, 1960, pp. 306-319; and J. W. Mellor, *A Comprehensive Treatise of Inorganic Chemistry*, Vol. X, Longmans, Green & Co: London, 1922, pp. 693-695.

2. The actual mechanism is more complicated than suggested here and may involve liquid-phase reactions and such intermediates as nitrous acid $[H(NO_2)]$ and nitrosylsulfuric acid $[(NO)H(SO_4)]$.

3. J. J. Berzelius, "Undersökning af en ny mineralkropp funnen i de orenare sorterna af det vid Falun tillverkade svaflet," *Afhand. Fysik. Kemi Min.*, **1818,** *6*, 42-144. German, English and French accounts also appeared of which the most accessible is J. J. Berzelius, "Recherches sur un nouveau corps minéral trouvé dans le soufre fabriqué à Falun," *Ann. chim. phys.*, **1818,** *9*, 160-180, 225-267, 337-365.

4. T. Thomson, *The History of Chemistry*, Vol. 2, Colburn and Bentley: London, 1831, pp. 242-243.

5. Weeks (reference 1) states that the mine was in use since the 13th century. This is indeed the date of the oldest documents referring to the mine, but more recent chemical analyses of copper artifacts extending back to the 10th century indicate that the copper used in their production came from Falun, thus pushing mining activities there back another 300 years.

6. E. T. A. Hoffman, *Tales*, Continuum: New York, NY, 1982, pp. 163-187.

7. For a popular account of the transatlantic cable, see J. S. Gordon, *A Thread Across the Ocean: The Heroic Story of the Transatlantic Cable*, Walker & Co: New York, NY, 2002.

8. W. Smith, "Effect of Light on Selenium During the Passage of Electricity," *Nature*, **1873**, *7 (20 Feb.)*, 303.

9. A. B. Reeve, *The Silent Bullet*, Grosset & Dunlap: New York, NY, 1910, pp. 157-187.

10. A. G. Bell, "Selenium and the Photophone," *Nature*, **1880**, *22 (23 Sept.)*, 500-503; *Ibid.*, **1880**, *23 (4 Nov.)*, 15-19.

11. A. Korn, *Verfahren zur Fernübertragung von Photographien*, Patent No. 136876, Berlin, 4 Januar, 1902.

12. V. Appleton, *Tom Swift and his Photo Telephone or The Picture that Saved a Fortune*, Grosset & Dunlap: New York, NY, 1914.

13. E. E. Fournier d'Albe, *The Moon-Element: An Introduction to the Wonders of Selenium*, Unwin: London, 1924, pp. 7, 159.

Figure 14. Fournier d'Albe (far left) demonstrating an early model of his "optophone."

book was devoted to the description of Fournier d'Albe's own attempts to develop a device, known as the "optophone" (figure 14), which would allow the blind to read printed books and magazines. Though the optophone, like Bell's photophone, was ultimately a commercial failure, this did not dampen Fournier d'Albe's enthusiasm for the inventive possibilities of selenium cells, as indicated by his concluding paragraph (13):

The utility and promise of the Moon-element are by no means fully revealed as yet. It is unsurpassed in its function of producing electric currents from light. It is the supreme bridge between two of the most vital forms of energy. It enables us to convey our thoughts and our will along the highway of the ether of space. The coming generation will see signs and wonders which at present we can only surmise, but which will eclipse the marvelous results already achieved with the help of the Wonderful Element.

And indeed, coming generations would see such wonders, though few of them were "surmised" by either Fournier d'Albe or his contemporaries. Every teenager with a smart phone now owns their own personal – and portable – version of Tom Swift's photo phone, though its underlying technology has nothing to due with selenium. On the other hand, the most ubiquitous and important modern-day technological application of the photoelectric properties of selenium – the

X
The Marsh Test for Arsenic
The Chemistry of the Telltale Mirror

The King of Poisons

Historically the favorite and most famous of all poisons is arsenic, though the arsenic in question was generally not the pure chemical element itself but rather its oxide, As_2O_3 or diarsenic trioxide, otherwise known with equal inaccuracy as white arsenic. Indeed, since the most common form of this compound is actually composed of discrete As_4O_6 molecules, it should more properly be called tetraarsenic hexaoxide.

For centuries proof of arsenic poisoning was problematic at best. True chemical tests for its presence did not appear until the late 18th century and most of these relied on precipitation of the arsenic as a characteristic colored compound, such as yellow $As_2S_3(s)$ or diarsenic trisulfide (Hahnemann's Test) (1). Unfortunately, when analyzing a sample of stomach fluid, for example, various other stomach contents were often coprecipitated with the arsenic leading to masking of the result and to a corresponding ambiguity in the evidence.

Origins of the Marsh Test

Such a problem was encountered in 1832 when a British chemist in the employ of the Royal Arsenal at Woolwich by the name of James Marsh (figure 1) was
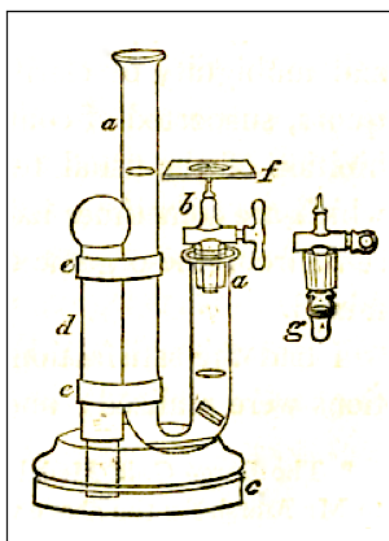

Figure 1. James Marsh (1794-1846).

Figure 2. Marsh's original apparatus as depicted in his paper of 1836.

called upon to give expert testimony at the trial of one John Bodle, who was accused of poisoning his grandfather by putting arsenic in his coffee. Marsh successfully detected arsenic using Hahnemann's test but found that his precipitate deteriorated with time due to the gradual deposition of other material. As a result, the jury was unconvinced and Bodle was found innocent, though he later confessed to the crime.

Frustrated by this experience, Marsh determined to develop a better test for arsenic based on its separation as a volatile gaseous compound rather than as a solid precipitate. He first published his new test in 1836 (2) and, because it addressed an important forensic problem, his paper was rapidly translated into both German (3) and French (4). His original apparatus (figures 2 and 3) consisted of a U-tube with unequal arm lengths and a stopcock fitted to the shorter arm. With the stopcock in the open position, a piece of zinc [Zn] was placed in the shorter arm and the tube filled with dilute sulfuric acid [$H_2(SO_4)$] up to the stopcock in order to displace any air, both reagents having been previously tested to ensure that they were arsenic free. With the stopcock now in the closed position, the

Figure 3. Reproduction of a Marsh apparatus similar to that in figure 2 (Jensen-Thomas Apparatus Collection). A short section of glass tubing is placed in the bend of the U-tube in order to keep the rod of Zn metal in the short arm.

forensic sample to be tested was then added to the liquid. If arsenic was present in the sample, the ensuing reaction would generate a mixture of flammable dihydrogen gas [H_2] and trihydrogen arsenide or arsine gas [H_3As], which would accumulate below the stopcock and force the liquid up the taller arm of the U-tube (5).

Figure 4. Marie-Fortunée Lefarge (1816-1852).

When sufficient gas had formed, the stopcock was opened once again and the gases, under the hydrostatic pressure of the liquid column in the tall arm, were forced out the nozzle where they were ignited and the interior of the resulting flame allowed to play on a square of glazed ceramic or, better still, on the bottom of a glazed ceramic dish filled with cold water. If $H_3As(g)$, and hence arsenic, was present, a black mirror of elemental arsenic would deposit on the bottom of the dish.


Figure 5. Mathieu Joseph Bonaventure Orfila (1787-1853).

Legal Vindication of the Marsh Test

Because the arsenic in the Marsh test was separated from the forensic sample in the form of a gas, the complications that had plagued earlier precipitation tests were avoided and it soon became the definitive procedure for the forensic detection of arsenic. It was first employed in France during the 1840 trial of an attractive young widow by the name of Marie-Fortunée Lefarge (figure 4), who was accused of poisoning her much older husband, Charles, with arsenic that she had allegedly purchased for the purpose of killing rats (6). The trial was closely followed by the French press, especially when several faulty attempts to detect arsenic in Charles' body using the new Marsh test proved negative, only to be subsequently overturned when repeated by the famous toxicologist, Mathieu Orfila (figure 5), who had been originally hired as an expert witness by the defense! In the end Marie was found guilty and the Marsh test both legally and publicly vindicated.

## The Chemistry of the Marsh Test Reconsidered

Rather surprisingly the chemistry underlying this historically important test appears to have been incorrectly rationalized for most of its history. According to this traditional interpretation, the zinc and sulfuric acid first react to produced dihydrogen gas:

$$Zn(s) + H_2(SO_4)(aq) \rightarrow Zn(SO_4)(aq) + H_2(g) \qquad [1]$$
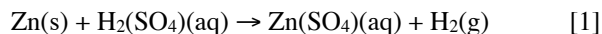
which then reduces the tetraarsenic hexaoxide to trihydrogen arsenide and water (7):

$$12H_2 + As_4O_6(s) \rightarrow 4H_3As + 6H_2O(l) \qquad [2]$$
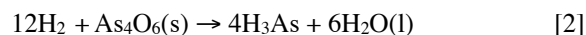
followed by the partial oxidation of the trihydrogen arsenide in the interior of the burning flame:

$$4H_3As(g) + 3O_2(g) \rightarrow As_4(g) + 6H_2O(g) \qquad [3]$$
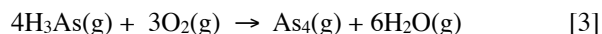
The only problem with this scenario is that, while steps 1 and 3 are both thermodynamically allowed ($\Delta G° = $ -147.2 kJ/mol rx and -1.7 x 10^3 kJ/mol rx respectively), step 2 is thermodynamically disallowed ($\Delta G° = $ +3.63 kJ/mol rx) (8). Indeed, it was known by the early 19th century that $As_4O_6(s)$ cannot be directly reduced to $H_3As(g)$ using $H_2(g)$, though it is apparently reduced when the $H_2(g)$ is generated *in situ* within the Marsh apparatus. This led to the further speculation that freshly generated or "nascent" hydrogen gas differed in some way from regular hydrogen gas, thereby allowing it to undergo reactions not observed for the bulk form of the gas.

While the observation that freshly generated gases are often more reactive than bulk gases is an experimentally verifiable fact, its proper theoretical rationale is a different matter altogether. Thus an historical review of the nascent state concept uncovered a bewildering array of alternative theories, as well as experimental data suggesting that the effect is in fact kinetic rather than thermodynamic in nature (9). Nevertheless, the earliest and most persistent of these rationales, as well as the one most commonly invoked to explain the Marsh reaction in both 19th- and 20th-century textbooks (8), is the theory that freshly generated gases are initially monoatomic and that these transient free atoms only later combine with one another to produce the experimentally observed diatomic gas. Thus reactions 1 and 2 become instead:

$$Zn(s) + H_2(SO_4)(aq) \rightarrow Zn(SO_4)(aq) + 2H(g) \qquad [4]$$

$$24H(g) + As_4O_6(aq) \rightarrow 4H_3As(g) + 6H_2O(l) \qquad [5]$$
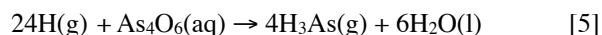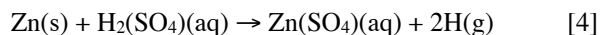
Unlike reaction 2, reaction 5 is thermodynamically allowed ($\Delta G° = $ -2.44 x 10^3 kJ/mol rx). Unfortunately, however, reaction 4, unlike reaction 1, is now thermodynamically disallowed ($\Delta G° = $ +259.3 kJ/mol rx) and thus our thermodynamic objections to the proposed mechanism remain.

From time to time an alternative proposal has appeared in the textbooks in which Zn(s), rather than either $H_2(g)$ or H(g), is considered to be the active reducing agent (9):

$$12Zn(s) + As_4O_6(aq) + 12H_2(SO_4)(aq) \rightarrow$$
$$12Zn(SO_4)(aq) + 4H_3As(g) + 6H_2O(l) \quad [6]$$
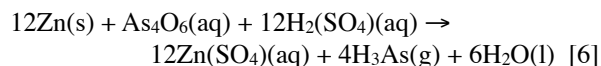
The thermodynamics of this reaction are overwhelmingly favorable ($\Delta G° = $ -1.76 x 10^3 kJ/mol rx) and involve the oxidation of Zn from 0 to II and the reduction of As from III to -III. In this interpretation not only is hydrogen not the active reducing agent, reaction 1 is now relegated to the status of an unavoidable competing side-reaction resulting from the fact that both Zn(s) and $H_2(SO_4)(aq)$ are required to be simultaneously present in the reaction mixture in order to facilitate reaction 6.

Later Developments

The original U-tube apparatus designed by Marsh continued to be sold by apparatus dealers well into the second decade of the 20th century (12). However, in 1837 the famous Swedish chemist, Jöns Berzelius, proposed an alternative version (figures 6-7) in which the sample to be tested was mixed with the Zn(s) and $H_2(SO_4)(aq)$ in either a conventional gas-generating bottle or a two-necked Woulfe bottle and the resulting $H_3As(g)$ passed through a tube that was divided into two sections by a narrow constriction that was strongly heated with an alcohol lamp or gas burner
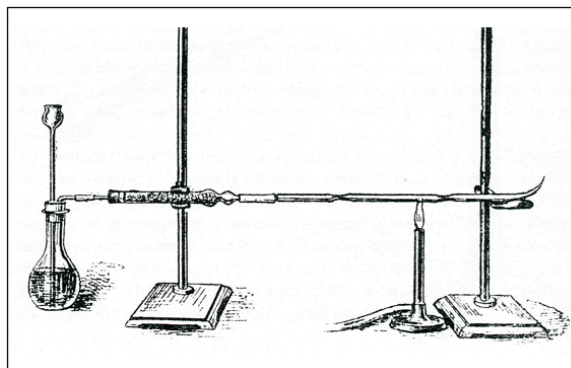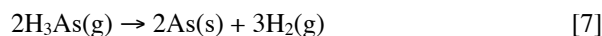

Figure 6. A version of Marsh's apparatus based on modifications introduced by Berzelius in 1837.

Figure 7. A reproduction of Berzelius' modification of the Marsh apparatus similar to that in figure 6 (Jensen-Thomas Apparatus Collection).

(11). The $H_3As(g)$ was decomposed on passing through this heated constriction according to the equation:

$$2H_3As(g) \rightarrow 2As(s) + 3H_2(g) \qquad [7]$$

and the $As(s)$ deposited as a mirror in the second section. The accompanying $H_2(g)$ was still burned off at the end of the tube, presumably to prevent any undecomposed $H_3As(g)$ from escaping into the room. Since reaction 7 is thermodynamically favored at room temperature ($\Delta G° = -137.8$ kJ/mol rx), $H_3As(g)$ must exist only because it is kinetically metastable, thus implying that the purpose of the heat source is to provide the necessary activation energy for its otherwise thermodynamically spontaneous decomposition. Because the decomposition or thermolysis tube could be weighed before and after deposition of the arsenic mirror, Berzelius' modification also allowed for partial quantification of the test. By the 1920s various versions of this alternative – often with a $CaCl_2$ drying tube inserted between the gas generator and the thermolysis tube – had completely displaced Marsh's original apparatus.

Yet a third variation of the Marsh test (figure 8) was to eliminate the thermolysis tube in Berzelius' apparatus and instead connect the gas-generating bottle directly to a simple delivery tube with a turned up end or jet for ignition of the evolved $H_3As(g)$. In this case, the latter was allowed to oxidize completely to $As_4O_6(s)$

$$4H_3As(g) + 6O_2(g) \rightarrow As_4O_6(s) + 6H_2O(l) \qquad [8]$$
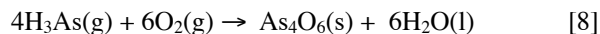
which was then collected in a small test tube held above (rather than within) the flame, followed by confirmation tests using standard precipitation reactions for arsenic. Since the arsenic had been completely separated from the organic constituents of the forensic sample, these tests could now be performed without fear of coprecipitation.

The Marsh Test in Fiction

By the early 20th century the Marsh test was sufficiently well-known so as to make an appearance in several popular detective stories. In particular, it is mentioned in Dorothy L. Sayers' 1930 novel *Strong Poison*, where it is performed by Lord Peter Whimsey's manservant, Bunter. In keeping with the date, the procedure employed is actually Berzelius' thermolysis modification of the original test. Unfortunately Sayers left out some key information on the reagents used and so leaves the reader with the false impression that the test was done in boiling water (14):

In a small apartment usually devoted to Bunter's photographic work and furnished with a sink, a bench and a bunsen burner, stood the apparatus necessary for making a Marsh's test of arsenic. The distilled water was already bubbling gently in the flask, and Bunter lifted the little glass tube which lay across the flame of the burner.

"You will perceive my lord," he observed, "that the apparatus is free from contamination."

... Bunter [then] dropped the white powder into the wide mouth the flask. All five heads eagerly bent

Figure 8. A rather cartoonish circa 1855 etching from the *Illustrated London News* depicting Dr. Alfred Swaine Taylor (on the left) – the so-called "father of British medical jurisprudence" – performing yet a third variation of the Marsh test in which the H_3As is completely oxidized to As_4O_6.

over the apparatus. And presently, definitely, magically, a thin silver stain began to form in the tube where the flame impinged upon it. Second by second it spread and darkened to a deep brownish-black ring with a shining metallic center.

... "Is that arsenic?" breathed Miss Murchison, gently.

"I hope so," said Wimsey, gently detaching the tube and holding it up to the light. "It is either arsenic or antimony."

"Allow me, my lord. The addition of a small quantity of solute chlorinated lime should decide the question beyond reach of cavil,"

He performed this further test amid an anxious silence. The stain dissolved out and vanished under the bleaching solution.

"Then it is arsenic," said Parker.

"Oh yes," said Wimsey nonchalantly, "of course it is arsenic. Didn't I tell you?" His voice wavered a little with suppressed triumph.

Actually a far better description of the Marsh test is given in R. Austin Freeman's 1923 detective novel, *The Cat's Eye*, which features his well-known scientific detective, Dr. John Evelyn Thorndyke (figure 9). The test is performed with the help of Thorndyke's man-servant and laboratory assistant, Polton, on a sample of poisoned chocolate (15, 16):

"And now we will try the most definite and conclusive test of all – Marsh's." He turned to the other apparatus which Polton had made ready, which consisted of a squat bottle with two short necks, through one of which passed a tall glass funnel, and through the other a glass tube fitted with a tap and terminating in a fine jet. The contents of the bottle – lumps of zinc immersed in sulphuric acid – were effervescing briskly, and the tap was turned on to allow the gas to escape through the jet. To the latter Polton now applied a lighted match, and immediately there appeared a little pale violet flame. Picking up a white tile that had been placed in readiness, Thorndyke held it for a moment in the flame and then looked at it.

"You see," said he, "that the tile is quite unsoiled. If there had been the smallest trace of arsenic in the bottle, a dark spot would have appeared on the tile. So we may take it that our chemicals are free from arsenic. Now let us try the solution of the sweet."

He took up the beaker containing the solution of disintegrated chocolate, and poured very slowly, drop by drop, about a teaspoon into the funnel of the bottle. Then, after giving it time to mix thoroughly with the other contents, he once more picked up the tile and held it for an instance in the flame. The result was, to
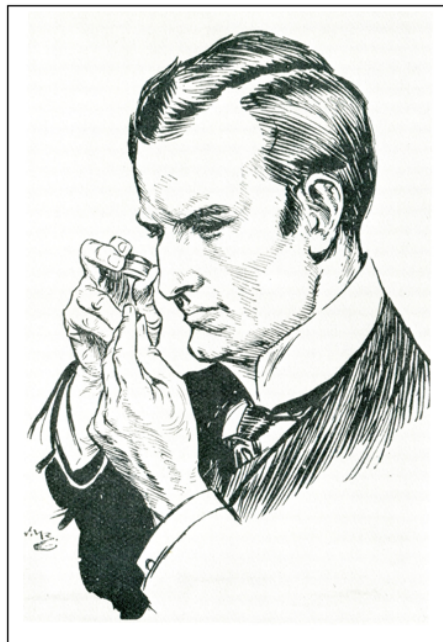

Figure 9. R. Austin Freeman's great scientific detective, Dr. John Evelyn Thorndyke, as depicted in a 1908 drawing from *Pearson's Magazine*.

me, most striking. In the very moment when the tile touched the flame, there appeared on the white surface a circular spot, black, lustrous, and metallic.

"That," said Thorndyke, must be either antimony or arsenic. By its appearance it is obviously metallic arsenic, but still we will make a differential test. If it is arsenic it will dissolve in a solution of chlorinated lime; if it is antimony it will not." He removed a stopper from a bottle labelled "Chlorinated Lime," and poured a little pool of the solution on the tile. Almost immediately the black spot began to fade at the edges, and to grow smaller and fainter until at length it disappeared altogether. "That completes our inquiry," said Thorndyke as he laid down the tile.

This account is actually preceded by a description of various preliminary qualitative tests for arsenic, including its precipitation as yellow diarsenic trisulfide [As_2S_3], as green copper hydrogen arsenite [$CuH(AsO_3)$], and its deposition on copper metal (Reinsch's test). The accuracy of Freeman's descriptions is doubtless due to the fact that he maintained a private workshop/laboratory in his home in which he personally replicated all of the forensic tests performed by his fictional detective (17).

Like its close analog in the periodic table, antimony [Sb], if present in the forensic sample, will also deposit a metallic mirror during the Marsh test and testing of the mirror with the aqueous solution of chlo-

rinated lime or calcium hypochlorite [Ca(OCl)$_2$] used by both Bunter and Thorndyke was necessary in order to distinguish between the two deposits. The net reaction in question would appear to be:

$$4As(s) + 3Ca(OCl)_2(aq) + 2H_2O(l) \rightarrow$$
$$3CaCl_2(aq) + 4H(AsO_2)(aq) \quad [9]$$
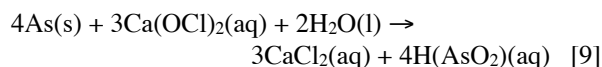
in which arsenic is oxidized from 0 to III and chlorine is reduced from I to -I. However, from a thermodynamic standpoint it is not readily understandable why reaction 9 works for As(s) but the analogous reaction for Sb(s) does not:

$$4Sb(s) + 3Ca(OCl)_2(aq) + 2H_2O(l) \rightarrow$$
$$3CaCl_2(aq) + 4H(SbO_2)(aq) \quad [10]$$
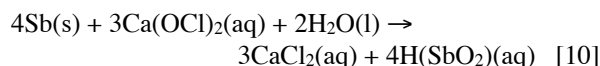
since H(SbO$_2$)(aq) is thermodynamically more stable than H(AsO$_2$)(aq) (8).

Today the Marsh test is largely an historical relic and is unlikely to appear in modern detective novels other than those deliberately set in the past. Like most analytical procedures based on wet chemistry, it was gradually displaced, starting in the 1960s, by more modern instrumental methods of analysis, and especially by the detection of arsenic using either atomic absorption spectrometry or neutron activation analysis (1).

References and Notes

1. Previous historical treatments of the history of arsenic testing include W. A. Campbell, "Some Landmarks in the History of Arsenic Testing," *Chem. Brit.*, **1965**, *1*, 198-201 and R. H. Goldsmith, "The Search for Arsenic," in S. Gerber, R. Saferstein, Eds., *More Chemistry and Crime*, ACS Books: Washington, DC, 1997, pp. 149-168. More superficial accounts appear in P. Macinnis, *Poisons: From Hemlock to Botox and the Killer Bean of Calabar*, Arcade: New York, NY, 2004, pp. 72-73; K. Watson, *Poisoned Lives: English Poisoners and their Victims*, Hambledon & London: London, 2004, pp. 16-20; and J. Emsley, *The Elements of Murder: A History of Poison*, Oxford University Press: Oxford, 2005, pp. 149-151; and J. Parascandola, *King of Poisons: A History of Arsenic*, Potomac Books: Washington, DC, 2012, pp. 10-12.

2. J. Marsh, "An Account of a Method of Separating Small Quantities of Arsenic from Substances with which It May Be Mixed," Edinburgh New Phil. J., 1836, 21, 229-236.

3. J. Marsh, "Beschreibung eines neuen Verfahrens um kleine Quantitäten Arsenik von den Substanzen abzuscheiden, womit er gemischt ist," *Ann. Chem.*, **1837**, *23*, 207-227. This includes two appended editorial commentaries on the paper.

4. J. Marsh, "Arsenic; nouveau procédé pour le découvrir dans les substances auxquelles il est mêlé," *J. Pharm.*, **1837**, *23*, 553-562.

5. There seems to be an ambiguity in the chemical literature as to whether arsine should be represented as trihydrogen arsenide or as arsenic trihydride. Electronegativity scales are not helpful as some give As an EN value less than H (Pauling), some an EN value greater than H (Sanderson) and some an EN value equal to H (Allred-Rochow). However, the assumption of both equations 2 and 6 is that the arsenic is reduced from III to -III which is consistent with the trihydrogen arsenide interpretation.

6. There are many summaries of the Lafarge trial. See, for example, C. J. S. Thompson, *Poison Mysteries in History, Romance and Crime*, Lippincott: Philadelphia, PA, 1924, pp. 273-278. Madame Lafarge's own version of events appears in her autobiography, M. F. Lafarge, *Memoirs of Madame Lafarge Written by Herself*, Carey & Hart: Philadelphia, PA, 1841. Both Thompson and, of course, Lafarge herself contend that she was innocent.

7. As$_4$O$_6$(s) is slightly soluble in water where it hydrolyzes to either H(AsO$_2$)(aq) or H$_3$(AsO$_3$)(aq). However the reaction is very slow, suggesting that the rapid reduction in the Marsh apparatus involves suspended particles of As$_4$O$_6$(s) instead.

8. All thermodynamic data are from A. J. Bard, R. Parsons, J. Jordan, Eds., *Standard Potentials in Aqueous Solution*, Dekker: New York, NY, 1985.

9. W. B. Jensen, "Whatever Happened to the Nascent State?," *Bull. Hist. Chem.*, **1990**, *6*, 26-36.

10. For a recent example involving nascent hydrogen, see N. Wiberg, *Inorganic Chemistry*, Academic Press: New York, NY, 2001, pp. 744-745.

11. C. Bloxam, *Chemistry, Inorganic and Organic, with Experiments*, Lea: Philadelphia, PA, 1873, p. 279.

12. See for example, *Scientific Materials Blue Book: Equipment and Supplies for Chemical, Metallurgical and Biological Laboratories*, Scientific Materials: Pittsburgh, PA, 1919, p. 14, Item 232.

13. J. Berzelius, "Paton's, Marsh's und Simon's Methoden Arsenik zu entdecken," *Pogg. Ann. Phys. Chem.*, **1837**, *42 (2nd series)*, 159-163.

14. D. L. Sayers, *Strong Poison*, Harper & Row: New York, NY, 1930, pp. 304-305, 315-318.

15. R. A. Freeman, *The Cat's Eye*, Burt: New York, NY, 1927, pp. 163-167. First British edition 1923.

16. An even earlier description of the Marsh test occurs in the short story, "The Moabite Cipher," which appears in R. A. Freeman, *John Thorndyke's Cases*, Chatto & Windus: London, 1909. First American edition 1931.

17. N. Donaldson, *In Search of Dr. Thorndyke: The Story of R. Austin Freeman's Great Scientific Investigator and his Creator*, Bowling Green University Popular Press: Bowling Green, OH, 1971, p. 154.