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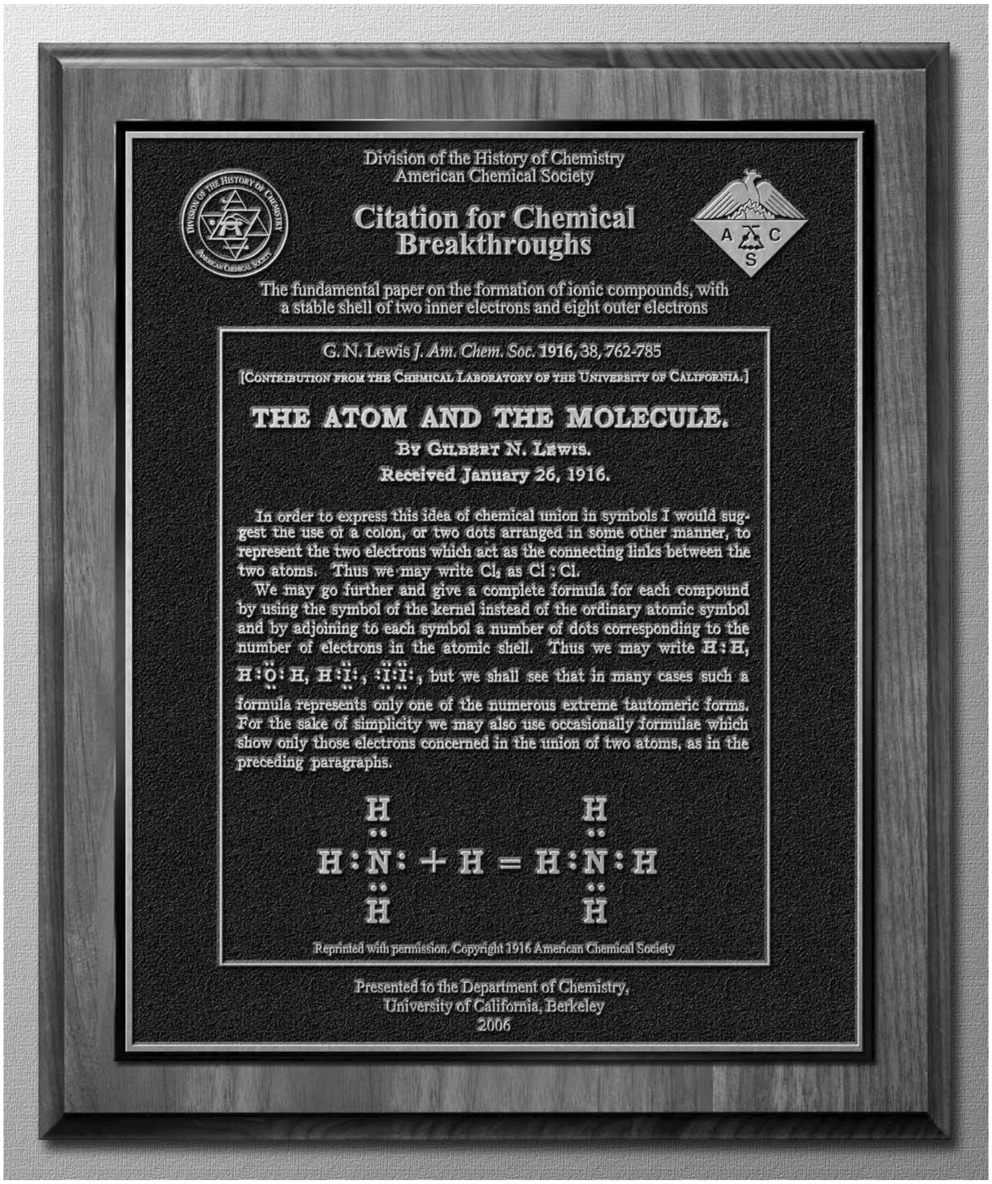

Division of the History of Chemistry
American Chemical Society

Citation for Chemical Breakthroughs

The fundamental paper on the formation of ionic compounds, with
a stable shell of two inner electrons and eight outer electrons

G. N. Lewis *J. Am. Chem. Soc.* 1916, 38, 762-785

[Contribution from the Chemical Laboratory of the University of California.]

THE ATOM AND THE MOLECULE.

By Gilbert N. Lewis.

Received January 26, 1916.

In order to express this idea of chemical union in symbols I would suggest the use of a colon, or two dots arranged in some other manner, to represent the two electrons which act as the connecting links between the two atoms. Thus we may write Cl_2 as $Cl : Cl$.

We may go further and give a complete formula for each compound by using the symbol of the kernel instead of the ordinary atomic symbol and by adjoining to each symbol a number of dots corresponding to the number of electrons in the atomic shell. Thus we may write $H:H$, $H:\overset{..}{\underset{..}{O}}:H$, $H:\overset{..}{\underset{..}{I}}:$, $:\overset{..}{\underset{..}{I}}:\overset{..}{\underset{..}{I}}:$, but we shall see that in many cases such a formula represents only one of the numerous extreme tautomeric forms. For the sake of simplicity we may also use occasionally formulae which show only those electrons concerned in the union of two atoms, as in the preceding paragraphs.

$$\begin{array}{c}H\\..\\H:N:\\..\\H\end{array} + H = \begin{array}{c}H\\..\\H:N:H\\..\\H\end{array}$$

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University of California, Berkeley
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HIST's Citation for Chemical Breakthrough Award

BULLETIN FOR THE HISTORY OF CHEMISTRY

VOLUME 38, CONTENTS

NUMBER 1

REPORT

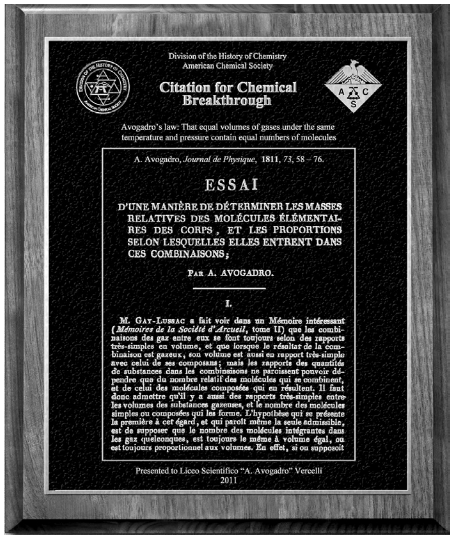
BOOK REVIEWS

REPORT

A Citation for Chemical Breakthrough Award to an Italian High School, the Scientific Liceo Amedeo Avogadro of Vercelli, for Avogadro's 1811 Paper

Teresa Celestino, School of Advanced Studies, University of Camerino, via Sant'Agostino 1, 62032, Camerino (MC), Italy, tercel@chimici.it

On October 20, 2012, the Scientific Liceo Amedeo Avogadro (Amedeo Avogadro High School of Science) of Vercelli, an Italian high school located in Vercelli (about midway between Torino and Milano), received a Citation for Chemical Breakthrough (CCB) award from the ACS Division of the History of Chemistry (HIST). This award honors publications, patents and books that were breakthroughs in chemistry and the molecular sciences. The term "breakthrough" refers to advances that have been revolutionary in concept, broad in scope, and long-term in impact (1). As HIST's only member who resides in Italy, it was my honor and privilege to represent HIST and present the award plaque to the Scientific Liceo Amedeo Avogadro.



Division of the History of Chemistry
American Chemical Society

Citation for Chemical Breakthrough

Avogadro's law: That equal volumes of gases under the same temperature and pressure contain equal numbers of molecules

A. Avogadro, *Journal de Physique*, **1811**, *73*, 58 – 76.

ESSAI

D'UNE MANIÈRE DE DÉTERMINER LES MASSES RELATIVES DES MOLÉCULES ÉLÉMENTAIRES DES CORPS, ET LES PROPORTIONS SELON LESQUELLES ELLES ENTRENT DANS CES COMBINAISONS;

PAR A. AVOGADRO.

I.

M. GAY-LUSSAC a fait voir dans un Mémoire intéressant (*Mémoires de la Société d'Arcueil*, tome II) que les combinaisons des gaz entre eux se font toujours selon des rapports très-simples en volume, et que lorsque le résultat de la combinaison est gazeux, son volume est aussi en rapport très-simple avec celui de ses composans; mais les rapports des quantités de substances dans les combinaisons ne paroissent pouvoir dépendre que du nombre relatif des molécules qui se combinent, et de celui des molécules composées qui en résultent. Il faut donc admettre qu'il y a aussi des rapports très-simples entre les volumes des substances gazeuses, et le nombre des molécules simples ou composées qui les forme. L'hypothèse qui se présente la première à cet égard, et qui paroît même la seule admissible, est de supposer que le nombre des molécules intégrantes dans les gaz quelconques, est toujours le même à volume égal, ou est toujours proportionnel aux volumes. En effet, si on supposoit

Presented to Liceo Scientifico "A. Avogadro" Vercelli
2011

Figure 1. The CCB award plaque for Avogadro's 1811 paper

HIST annually confers CCB awards to institutions from which these breakthrough publications were submitted and published. The first CCB awards were presented in 2006, and the 2012 awardees were recently named. The award consists of an attractive plaque, generally depicting the cover of the book or a portion of the first page of the award paper. More information about the CCB award including photographs of all the award plaques and various award ceremonies can be found on the HIST website (2).

Among the 2011 awardees is Amedeo Avogadro's 1811 paper: "Essai d'une manière de déterminer les masses relatives des molécules des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons" (3). In this paper, Avogadro formulated the famous law bearing his name: Equal volumes of gases at the same temperature and pressure contain the same number of molecules. This paper represents a breakthrough publication because it elucidated a distinction between atoms and molecules. This publication laid one of the most important foundations of chemistry.

HIST decided to give the award and plaque (Figure 1) to an Italian high school, the Scientific Liceo Amedeo Avogadro of Vercelli. In fact, Avogadro conceived the famous law while he was teaching "Positive Philosophy" (Physics and Mathematics) in this institution. (Actually Avogadro had been teaching in a building not a long way away from the place where the high school has been since 1956.) So, for the very first time the CCB award has been presented to a high school.

The Avogadro CCB award ceremony was preceded by a short but highly informative and very well attended symposium. The meeting honoring the great scientist took place in the High School Hall on October 20, 2012, followed by the plaque exposition ceremony. The program (Figure 2) shows the ceremony schedule, the list of speakers and the titles of their contributions.

20th, October 2012,
Aula Magna, Liceo Scientifico " A. Avogadro", Vercelli

Presentation ceremony for plaque received from the History Dpt. of the American Chemical Society to acknowledge the breakthrough of Amedeo Avogadro.

Coordinator: Mrs. Maura Forte, Vice-Headmaster of the Liceo Scientifico
h. 9.00 Welcome addresses by the Civil Authorities
h. 9.15 *Opening speech*,
Professor Paolo Garbarino, Chancellor of the University of "Piemonte Orientale"
h. 9.30 *Exhibition: " Avogadro in his age, in his town " (on the web)*
Mr. Francesco Brugnetta, Teacher at the Liceo
h.9.45 *From Amedeo Avogadro a teaching for the youths*
Mr. Adalberto Codetta Raiteri, Headmaster of the Liceo
h. 10.00 *The Chemistry's Citation for Chemical Breakthrough awards*
Mrs. Teresa Celestino, The Division of the History of Chemistry of American Chemical Society

Transfer to the hall of the Liceo - Plaque exposition - Drinks reception (room 8)

***Figure 2**. Program of the presentation ceremony for Avogadro's 1811 paper*

The opening speech by the Professor Paolo Garbarino, Chancellor of Amedeo Avogadro University of Piemonte Orientale, focused the importance of the great figures of history of science. Undoubtedly Avogadro is a national glory, like Galileo, Volta or Spallanzani. In 2006 the Academy of Sciences of Turin and the University of Piemonte Orientale organized a conference for the 150th anniversary of his death. The speakers highlighted and analyzed various unpublished and little-known papers of this eminent scientist (4).

The speech of the Headmaster, Adalberto Codetta Raiteri, described the scientific and human adventure of Avogadro, focusing on the historical and political context during his life. Avogadro's career developed in a crucial phase of Italian history, over the age of Enlightenment, the Napoleonic era, the Restoration and the Risorgimento (5). The passion of the young Amedeo for physics and chemistry led him away from a long family tradition in the field of law, giving up an easier and prestigious career.

Unfortunately, the encounter between Avogadro and the Italian scientific community was quite problematic: his first papers were rejected by the Academy of Sciences of Turin. Moreover, the political situation prevented him for years from gaining an academic position, so he taught from 1809 to 1819 at the High School of Vercelli, in the middle of the Napoleonic era. Despite the positive impression of the Napoleonic government in science policy, the Restoration penalized especially physics and chemistry, disciplines that played a leading role in the industrial revolution, and thus, disciplines mainly responsible for the political and social disorder according to conservatives.

Avogadro was accused of liberal ideas and lost his professorship at the University of Turin in 1821, just one year after obtaining that position. He regained his position at the same University only in 1833 (6). Thus, Avogadro's life, according to the Headmaster, is an example for young people: despite his genius Avogadro met several obstacles in his career, but he never stopped his research work. Even his scientific law was definitively accepted only many years after its formulation. So the Headmaster invited the students to follow their own passions and dreams, taking the scientist's vicissitudes into account.

During my speech, I explained the purpose of the CCB award and the mechanism by which it is conferred every year. Finally, I discussed the importance of the historical approach in chemistry teaching, and I illustrated these principles by describing some characteristics of the Avogadro's paper. My speech was followed by the plaque exposition.

Thanks to archival research, now we know a lot about Avogadro's scientific activities, but there is still much to discover. Unfortunately, as I pointed out in my presentation, in Italy the history of specific scientific disciplines (for example, physics, biology, geology) is not adequately valued and supported, despite the great intellectual resources available. On the contrary, teaching of general history of science is more common at university level. Cultivating the history of a specific branch of science such as the history of chemistry is also important for its impact on high school teaching practices. Initiatives such this celebration promoted by HIST in a school environment contribute to rekindling students' and teachers' interest in the great Italian historical-scientific heritage. The award plaque, hung in a prominent location near the front door of the school Avogadro's bust (Figure 3), will be a constant reminder of these principles: a small step towards the formation of a next generation of chemists aware of the great cultural value of science.

Students in their last year of school were present in a large number at the conference and seemed to be very interested in the ceremony. The event was been widely reported by several media; journalists belonging to local and national newspapers wrote articles focusing on the reasons of the award given to the school by HIST. The ceremony had great emotional impact on teachers, students, speakers and representatives of the civil and military authorities. A short video of the ceremony is available on the internet (7) as well as some photos (8).

Figure 3. *Avogadro's bust near the award plaque surrounded by the students.*

The Liceo of Vercelli too honored the memory of the great scientist. On October 2011 the high school celebrated the 200th anniversary of the formulation of Avogadro's law, reminding the town of Vercelli of this glorious page of the history of science. On that occasion the high school made a documentary exhibition entitled "Amedeo Avogadro in his Age, in his Town" involving devoted teachers and students. The town's main civic institutions contributed in carrying out the project, and other schools of the town were involved too. The exhibition, presented during the award ceremony, is now on a website created by teachers and students (9). The exhibition was presented by the teacher, Mr. Francesco Brugnetta, while some students, coordinated by their science teacher, reminded the audience some highlights of the nineteenth-century history of chemistry.

In summary, HIST's CCB award program has, quite appropriately, reached out and touched scientists and students and the general population thousands of miles from ACS headquarters in Washington, DC. So much great chemistry was done in countries distant from the United States, even a hundred years prior to the formation of the ACS. The Scientific Liceo Amedeo Avogadro is proud to receive this honor, and I am proud to have been part of the award ceremony.

Acknowledgments

I would like to thank Prof. Jeffrey I. Seeman, who offered me the opportunity to represent HIST, for his careful review of this article, and Prof. Carmen Giunta for its publication. I'm grateful to the Headmaster Adalberto Codetta Raiteri for the welcome I received in his school.

Notes and References

1. See J. I. Seeman, "HIST's Citation for Chemical Breakthrough Awards: The First Paper or the 'Breakthrough' Paper?" *Bull. Hist. Chem.,* **2013**, *38*, 4-6.
2. http://www.scs.illinois.edu/~mainzv/HIST/awards/citations_chem-breakthroughs.php
3. *Journal de physique, de chimie et d'histoire naturelle et des arts*, **1811**, *73*, 58-76. The title translates to "Essay on a Way to Determine the Relative Masses of the Elementary Molecules of Bodies and the Proportions in Which Such Combinations Are Established."
4. Proceedings published in M. Ciardi, Ed., *Il fisico sublime. Amedeo Avogadro e la cultura scientifica del primo Ottocento*, Il Mulino, Bologna, 2007.
5. The relevant Restoration is of the Savoyard monarchy, which ruled Piedmont, Savoy, and Sardinia for many years before Napoleon and from their restoration until the unification of Italy. The term Risorgimento refers to the political and social movements in various Italian states toward national unification—a movement that was underway but not yet accomplished by the time of Avogadro's death.—Ed.
6. Biographical details are taken from M. Ciardi, *Amedeo Avogadro. Una politica per la scienza*, Carocci, Roma, 2006.
7. A five-minute version is available at http://www.youtube.com/watch?v=CtvK93u806E and a 15-minute version at http://www.youtube.com/watch?v=FqwF0IYXq_Q.
8. T. Celestino, "Citation for Chemical Breakthrough Awards," http://www.teresacelestino.net/teresacelestino.net/Album/Pagine/Vercelli_2012.html#grid
9. http://www.liceoscientifico.vc.it/Amedeo_Avogadro/Avogadro.htm

About the Author

Teresa Celestino is a PhD candidate in chemical education at the School of Advanced Studies of the University of Camerino and a member of HIST.

HIST'S CITATION FOR CHEMICAL BREAKTHROUGH AWARDS: THE FIRST PAPER *OR* THE "BREAKTHROUGH" PAPER?

Jeffrey I. Seeman, Department of Chemistry, University of Richmond, jseeman@richmond.edu

In 2006, the Citation for Chemical Breakthrough (CCB) awards were first presented by the Division of the History of Chemistry (HIST) of the American Chemical Society (ACS). As of 2012, 41 awards have recognized breakthrough (1) publications, books and patents in all areas of science served by the ACS. According to HIST's website (http://www.scs.illinois.edu/~mainzv/HIST/awards/citations_chem-breakthroughs.php), "The term 'breakthrough' refers to advances in chemistry that have been revolutionary in concept, broad in scope, and long-term in impact." Full details of the CCB awards can be found on this website along with the names of the awardees, photographs and information about the awardees and the award ceremonies, the names of the award committee members, and nomination information.

The award committee's first step in the selection process for the CCB awardees is rather simple: from a list of nominees (6), the committee members give 10 points to their Number 1 selection, 9 points to their Number 2 selection, and so forth. The nominees with the highest point totals are that year's awardees. The number of awardees per year is determined by vote distribution among other factors.

Unexpectedly but in retrospect, quite reasonably, for some of the awards, one of the most difficult challenges in conducting the CCB award program is determining the actual award-winning publication. For example, during the design of the 2009 CCB award for Christian B. Anfinsen's research, one of the award committee members questioned whether the nominated and selected paper was indeed Anfinsen's scientific breakthrough publication. Anfinsen and his collaborators had published several papers within a short period of time, each of which could have been the breakthrough publication. Which was to be the CCB award-winning publication?

It is generally simple to determine which publication came *first* –by using the date of submission or, lacking that, date of publication. Even here, some journals, especially in the 19th century, did not always include the submission dates. Page number comparisons, or even issue number, may not provide unambiguous data when comparing publications from different journals.

However, knowing the chronology of a series of papers may not always be sufficient to choose the CCB awardee. A much more subtle yet bewildering enigma has arisen on a number of occasions, and not just for pre-1900 publications. In principle, the paper published *first* on a particular subject need not necessarily be *the breakthrough* publication. Which, of several publications, caught the attention of the relevant scientific community? Which caused the stir? Which was read and noticed and consequential? Which changed science forever? First is not always breakthrough!

The CCB award program is fortunate in that it can turn to experts in the field to answer this question. We have relied on individuals who are not specifically historians of chemistry but rather researchers who are experts in the very specific field being honored. In the Anfinsen award instance, we sought out the expertise of several experts in protein and enzyme chemistry to help us identify which *one* of Anfinsen's papers first convinced his peer group that the "native structure of a protein is determined only by the protein's amino acid sequence," as stated on the CCB award plaque (7).

This type of puzzle has reared its curious head several times over the lifetime of the CCB award program. The basis for determination among a group of contending publications is itself worthy of documentation and perhaps even further peer review. The following two articles (8, 9), written by Joseph Gal of the University of Colorado School of Medicine and Norman C. Craig of Oberlin College, respectively, are the first of a series of papers that will explain the basis for selection of one of several publications by the same researcher(s) for a CCB award.

Gal is an expert on Louis Pasteur's chemical research on dissymmetry (i.e., chirality) (10-12). Based on his analysis described fully in this following article, Gal explains why "Mémoire sur la relation qui peut exister entre la forme cristalline de la composition chimique, et sur la cause de la polarisation rotatoire," published in 1848 in the *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* was selected rather than other Pasteur publications that could reasonably have been chosen for a 2012 CCB award.

Similarly, Craig is an expert on Charles M. Hall and has written several papers on Hall's life and career in chemistry. Indeed, Craig was on the faculty of Oberlin College for many years, Oberlin College being the undergraduate school of Hall. Hall made his aluminum invention in a shed in the backyard of his Oberlin, Ohio, home. Based on his analysis described fully in another article published in this issue of the *Bulletin* (9), Hall explains why U. S. Patent 400,766, "Process of Reducing Aluminum by Electrolysis," was selected to receive a 2008 CCB award instead of any of the other four patents issued to Hall on the same day, April 2, 1889.

We marvel that the CCB awards have provided a motivation for chemical and historical scholarship beyond that being honored—in the form of analyses as described herein We hope you will enjoy these in depth evaluations delving into the breakthroughs of chemistry. We anticipate that these articles will provide insights into history and into science and perhaps also into the human side of science. We further note that the formal award presentations themselves bring a level of scholarship and teaching (3, 5, 13) also unanticipated when the concept of this award was first proposed to the Division of History of Chemistry.

References and Notes

1. The CCB award program was first proposed to the HIST Executive Committee at its March 28, 2004, meeting during the 227th ACS National Meeting, Anaheim, CA (2). Two names for the award were proposed, HIST Citation for Chemical Breakthroughs (CCB) and HIST Citation for Chemical Milestones (CCM). The term "Breakthrough" was suggested at that Executive Committee meeting by Mary Virginia Orna and adopted shortly thereafter. The plaques for the first year's awardees read "Citation for Chemical Breakthroughs," and a 2006 article in *Chemical & Engineering News* reporting on the first year's awards cites that name (3). However, during the drafting of a second article on the award program for *Chemical & Engineering News*, Janet S. Dodd, a staff member of *C&EN* and author of the *ACS Style Guide* (4), pointed out that, grammatically, the name ought to be "Citation for Chemical Breakthrough" award (note the omission of the "s" in "Breakthroughs"). That second news article (5) as well as all plaques presented in and subsequent to 2007 and award information have used the revised name. Thus, even the name of the CCB award program has witnessed a degree of ambiguity.
2. V. Mainz, "Minutes of the HIST Executive Committee Meeting - Anaheim, Ca, March 28, 2004," http://www.scs.illinois.edu/~mainzv/HIST/minutes/Minutes/MinutesSpring2004.pdf, accessed March 4, 2013.
3. L. Wang, "Pivotal Publications. New Awards Program Honors Institutions That Have Nurtured Breakthrough Discoveries," *Chem. Eng. News,* **2006**, *84 (July 3)*, 49-50.
4. J. S. Dodd, Ed., *The ACS Style Guide*, American Chemical Society, Washington, DC, 1986.
5. L. Wang, "Landmark Achievements. Award Program Honors Institutions Where Breakthrough Discoveries Occurred," *Chem. Eng. News,* **2007**, *85 (April 30)*, 35.
6. Nominations may be made by anyone and are intentionally designed to be easy to prepare and evaluate. All that is required is a full citation and a justification no longer than 200 words. In fact, one successful nomination, the Watson-Crick 1953 publication in *Nature*, "A Structure for Deoxyribose Nucleic Acid," arrived with a five word supporting statement: "The title says it all."
7. Anfinsen Plaque. http://www.scs.illinois.edu/~mainzv/HIST/awards/Citations/Anfinsen%20plaque.pdf, accessed on March 4, 2013.
8. J. Gal, "Citation for Chemical Breakthrough Awards: Choosing Pasteur's Award-Winning Publication," *Bull. Hist. Chem.,* **2013**, *38*, 7-12.
9. N. C. Craig, "Charles M. Hall's Persistent Quest of Patents for Refining Aluminum Metal by Electrolysis," *Bull. Hist. Chem.*, **2013**, *38*, 13-18.

10. J. Gal, "Louis Pasteur, Language, and Molecular Chirality. I. Background and Dissymmetry," *Chirality,* **2011**, *23*, 1-16.
11. J. Gal, "When Did Louis Pasteur Present His Memoir on the Discovery of Molecular Chirality to the Académie Des Sciences – Analysis of a Discrepancy," *Chirality,* **2008**, *20*, 1072-1084.
12. J. Gal, "Stereochemical Vocabulary for Structures That Are Chiral but Not Asymmetric: History, Analysis, and Proposal for a Rational Terminology," *Chirality,* **2011**, *23*, 647-649.
13. T. Celestino, "A Citation for Chemical Breakthrough Award to an Italian High School, the Scientific Liceo 'Amedeo Avogadro' of Vercelli, for Avogadro's 1811 Paper," *Bull. Hist. Chem.* **2013,** *38*, 1-3.

About the Author

Jeffrey I. Seeman was Chair Elect of HIST from 2003-2004 and Chair from 2005-2006.

2013 HIST Award

The recipient of the 2013 HIST Award of the Division of the History of Chemistry of the American Chemical Society is Professor William R. Newman, Distinguished Professor and Ruth Halls Professor of History and Philosophy of Science, Indiana University, Bloomington, IN. This award is the successor to the Dexter Award (1956-2001) and the Sydney M. Edelstein Award (2002-2009), also administered by the Division of the History of Chemistry.

William Newman was introduced to the history of chemistry by Otto T. Benfey in the 1970s as a student at the University of North Carolina-Greensboro. He did his graduate work at Harvard with the medievalist John Murdoch, also working with the classicist and historian Robert Halleux at the Université de Liège. Newman's doctoral dissertation, finished in 1986, was later published as *The Summa Perfectionis of Pseudo-Geber* (1991), which consisted of an edition, translation, and study of one of the most famous alchemical works of the Middle Ages. Newman demonstrated that this early 14th century Latin alchemical treatise, attributed to Pseudo-Geber, was not a translation of a work of the 8th century Arabic writer, Jabir ibn Hayyan, but an original work by Paul of Taranto. Thus in his doctoral dissertation, Newman laid to rest the Jabir-Geber problem.

Much of Newman's subsequent work has focused on the continuity between alchemy and chemistry in the seventeenth century. Two books, *Gehennical Fire* (1994) and *Alchemy Tried in the Fire* (2002, with L.M. Principe) deal with George Starkey. Newman identified the alchemical writer Eirenaeus Philalethes ("peaceful lover of truth") to be the Harvard-educated chemist George Starkey (1628-1665). Sometimes considered to be America's first scientist, Starkey became Robert Boyle's tutor, Isaac Newton's favorite alchemical author, and a possible influence on the works of John Locke and Gottfried Wilhelm Leibniz. Newman and Principe have advocated the use of the terms "chymistry" and "chymist" to apply to the chemically related work of people such as Newton. Newman's 2004 *Promethean Ambitions* deals with the division between natural and artificial products that has been a problem for chemistry since its origin. His most recent book, *Atoms and Alchemy* (2006), argues that the atomic theories of the nineteenth century were decisively prefigured by a form of chymical atomism that displaced the dominant early modern scholastic matter theory. Newman's novel thesis is that later alchemists were concerned with chemical change in general, not just on the narrowly focused and futile searches for means to transform natural materials into gold. For the last seven years, Newman has devoted most of his time to the Chymistry of Isaac Newton Project (www.chymistry.org), an on-line edition of Newton's alchemical writings hosted by Indiana University. In additional to his appointment in the Indiana University Department of History and Philosophy of Science, he is Director of the Catapult Center for Digital Humanities and Computational Analysis of Texts, also at Indiana University.

The HIST Award consists of an engraved plaque and a check for $1500 and will be presented to Newman at the fall national meeting of the American Chemical Society in Indianapolis in September 2013. Additional information about the award can be found on the HIST website at http://www.scs.illinois.edu/~mainzv/HIST/awards/hist_award.php .

CITATION FOR CHEMICAL BREAKTHROUGH AWARDS: CHOOSING PASTEUR'S AWARD-WINNING PUBLICATION

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Award paper: Louis Pasteur, "Mémoire sur la relation qui peut exister entre la forme cristalline et la composition chimique, et sur la cause de la polarisation rotatoire," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences,* **1848**, *26*, 535-538.

Recipient of award: École normale supérieure, Paris, France.

Year of award: 2012

The Citation for Chemical Breakthrough (CCB) awards are conferred annually by the Division of the History of Chemistry (HIST) of the American Chemical Society. According to HIST's criteria for the awards (http://www.scs.illinois.edu/~mainzv/HIST/awards/citations_chem-breakthroughs.php), "The Citation for Chemical Breakthrough award recognizes breakthrough publications, books and patents worldwide in the field of chemistry. The term 'breakthrough' refers to advances in chemistry that have been revolutionary in concept, broad in scope, and long-term in impact." Each award is made to the department or institution where the breakthrough occurred, not to the individual scientist(s).

Figure 1. Pasteur's official photograph as member of the Académie française. Reproduced from http://academie-francaise.fr/immortels/index.html, courtesy of the Académie française.

In some cases, several publications on a given discovery exist, and the chronologically first disclosure may not be the "breakthrough" article (1). Such a quandary had to be faced recently when the discovery of molecular chirality by Louis Pasteur (1822-1895) was considered for the CCB award (1). Pasteur's discovery is counted among the most important advances in chemistry and constitutes the foundation of stereochemistry (2, 3). Among Pasteur's many publications on chirality (4), three (5, 6, 7) were initially deemed to be contenders for the award. This report presents the analysis that was the basis of the author's recommendation of one of the three publications as Pasteur's *breakthrough* article deserving of the CCB Award.

Introduction

Pasteur (Figure 1), a French chemist, earned a doctor-of-science degree in August 1847 (8) from the University of

Paris based on work he carried out at the École normale supérieure (ENS) in Paris.

After earning his doctorate, Pasteur remained at the ENS until late in 1848 as *agrégé-préparateur* (a sort of laboratory or teaching assistant) in chemistry (8). For laboratory research, late in 1847 or early in 1848 Pasteur began new investigations (9) designed to expand his knowledge of crystallography; later he explained that his motivation for these studies had been his conviction that crystallography could be helpful in chemical research (10). For the new investigations he chose a substance known then as "tartaric acid" [TA], and its salts, because a great deal of crystallographic information on these compounds was available (10). Pasteur's TA ((+)-TA by today's nomenclature), a natural product known by then to be optically active and dextrorotatory, was obtained from the fermenting grape juice during the wine-making process. Nothing was known at the time about the arrangement of atoms in molecules, and therefore (in modern terms) the chemical structure of TA was unknown to Pasteur.

Pasteur also included in his studies a mysterious substance known then as "paratartaric acid" (PTA) or "racemic acid." PTA had been isolated, on a single occasion around 1820, in a factory producing (+)-TA in Alsace, France. PTA was known to be optically inactive and was thought to be an "isomer" of (+)-TA (11), but the nature of its chemical/structural relationship to TA was not understood at the time.

In the spring of 1848 Pasteur found that the sodium ammonium salt of PTA crystallized as a mixture of two types of crystals that were non-superposable mirror-image forms of each other (i.e., enantiomorphous, by today's terminology). One of the crystal types appeared identical to the crystals of the sodium ammonium salt of "ordinary" TA, i.e., (+)-TA. Pasteur manually separated the two crystal types of the PTA salt and measured their optical activity in solution, finding their rotations to be equal (within experimental error) in absolute magnitude but opposite in direction. This observation eventually led him to the realization that the molecules of TA had to be chiral and that PTA was the equimolar combination of the two enantiomers of TA (5, 6, 7, 12, 13).

Pasteur's First Article on Molecular Chirality (*Comptes rendus*) 1848 (5)

The 25-year-old Pasteur read a memoir announcing his discovery to the *Académie des sciences* (Academy of Sciences, Académie henceforth; translations are by the present author) in Paris on May 22nd, 1848 (5, 12). A summary of the lecture was published in the issue of the proceedings of the Académie, the *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* (CR henceforth), for the May 22nd session (5). Translated into English, the title of the article in the CR is "Memoir on the relationship that can exist between crystalline form and chemical composition and on the cause of optical rotation." After the title and the author's name the article is indicated to be an "extrait" (extract, excerpt) of the memoir Pasteur read to the Académie. The *extrait* was prepared by Pasteur (14). The full text of the memoir read by Pasteur to the Académie has not been published and a verbatim transcript of Pasteur's lecture to the Académie has not yet been uncovered, if such a transcript does exist.

The article in the CR, of which an English translation is available (15), was Pasteur's first announcement of his discovery of the resolution of TA. It is short (slightly over three pages) and does not contain the full experimental details. Pasteur begins by pointing out that the many salts of (+)-TA he examined have crystal forms that display great similarity, which he interprets as an indication that a common molecular grouping is shared by these compounds. He then discusses the salts of PTA and points out that while there is a similarity between the (+)-tartrate and paratartrate salts in their basic crystal forms, a fundamental difference between the two series exists, namely, the presence of hemihedral facets (i.e., small surfaces replacing some of the corners or edges of the basic crystal form) in the crystals of the salts of (+)-TA and their absence in the crystals of most of the salts of PTA. He explains that he said "their absence in most of the paratartrates" for a specific reason. That is, he found that the crystals of one of the paratartrates, the sodium ammonium salt, do display hemihedral facets. However, he finds that this salt is a combination of two crystals types, with the hemihedral facets leaning in one direction in some of the crystals and in the opposite direction in the other crystals when the crystals are viewed according to an arbitrary convention. Pasteur then specifies: "Here now is the crystallographic difference between these two types of crystals. They are all hemihedral; but some are hemihedral to the right, others to the left, and the direction of [optical] rotation depends on this dissymmetry." And then a crucial sentence in the article: "Is it not evident by now that the property of certain molecules of rotating the plane of polarization has as its cause, or at least is linked in a most intimate manner to, the dissymmetry of these molecules?"

Pasteur's use of "dissymmetry" and "dissymmetric" in the CR article is critical to the analysis. He applied these terms both to the crystal shapes and to the molecules of the TAs and his use of the terminology was in the general sense of a disruption or degradation of symmetry. He did not mention handedness or non-superposable-mirror-image relationships in the article (and we do not know whether he was more explicit in the actual lecture he delivered to the Académie) (13).

Thus, in the CR article Pasteur proposes that the molecules of (+)- and (-)-TA are *dissymmetric*, i.e., differ in some symmetry properties, the nature of which he did not specify. However, it is likely that he already had the concept of handedness in mind, since a few months later, in the next article (6) contending for the CCB award (see below), he stated that the dissymmetry of the crystals and molecules of the TAs was of the non-superposable-mirror-image type (13).

In summary, the 1848 CR article was Pasteur's first announcement of his resolution of sodium ammonium tartrate; the first recognition of the combination of the two enantiomers in a substance (in equimolar ratio, i.e., a racemate by today's terminology); the first proposal that the basis for the existence of the two optically active TAs can be sought in the differing symmetries of their molecules; and the first proposal that the cause of the optical activity of these substances is in fact the dissymmetry of the molecules. (It is also noteworthy that Pasteur's isolation of (–)-TA from PTA produced the first example (TA) of a substance both of whose enantiomers became known.)

Pasteur's Second Article on Molecular Chirality (*Annales de Chimie et de Physique*) 1848 (6)

Later in 1848, Pasteur published a full paper on the resolution of TA in the *Annales de Chimie et de Physique* (*Annals of Chemistry and Physics*, Annales henceforth). This journal began life as *Annales de Chimie* in 1789 (16). Pasteur's paper in the Annales (as his CR article, see above), was based on a memoir he presented to the Académie. The presentation took place during the session of October 9, 1848, but the issue of the CR for the session contains only the name of the author and the title of the memoir, which was, as translated into English, "Investigations on the relationships that can exist between crystalline form, chemical composition, and the direction of optical rotation" (17). Thus, instead of a printed memoir in the CR, in this case Pasteur published a full paper in the Annales.

Pasteur's article appeared in the October 1848 issue of the Annales (18). The article is 18 pages long and consists of two parts. The first part examines the crystal properties of (+)-TA and a series of its salts as well as some salts of PTA. Pasteur finds hemihedry in (+)-TA and its salts, and first describes the hemihedral crystals as dissymmetric in that the two extremities of the crystal (along the crystal axis) are modified unequally, in violation of Haüy's law of symmetry in crystallography (19), widely believed at the time to govern crystal formation. As for the salts of PTA, Pasteur reports, as in the CR article, the absence of hemihedry in most of them.

In the second part of the article, Pasteur discusses his experiments and findings on the two crystal types of the sodium ammonium salt of PTA. He describes the two types as "dissymmetric crystals facing one another in a mirror." This then is the first time that Pasteur specifically associates the term "dissymmetric" with non-superposable-mirror-image morphology. He then goes on to indicate, also for the first time, that the two TA *molecules* corresponding to the two crystal types of sodium ammonium paratartrate must also have this mirror-image dissymmetry and he points out that the optical rotation by the two acids correlates with their molecular dissymmetry which in turn correlates with the crystal morphology. *Dissymmetry* in the connotation of handedness as specified in the Annales article became Pasteur's standard terminology in both the molecular and crystal-morphology contexts for what we call today *chirality*. (The latter term was coined by Lord Kelvin in 1894, nearly a half-century after Pasteur's discovery of molecular dissymmetry (20).) In fact, "dissymétrie moléculaire" (molecular dissymmetry) became the fundamental term for Pasteur's work on chirality in molecules (13).

In summary, the Annales article (6) contains extensive experimental details while the paper in the CR (5) contains little such information. Another important difference between the two articles is the explicit statement by Pasteur in the Annales paper that the two crystal types of the sodium ammonium salt of PTA (and the crystals of the corresponding free TAs) have handedness and are in fact related as the two hands, i.e., are non-superposable-mirror-image forms of each other. In addition, a critical new element in the Annales article is the explicit recognition by Pasteur that the *molecules* of the two optically active TAs are chiral and are related as enantiomers (by today's terminology).

Pasteur's Retrospective Article on Molecular Chirality (*Leçons de Chimie*) 1861 (7)

By the late 1850s, Pasteur had abandoned his work on chirality and embarked on his eventually celebrated work in microbiology and infectious diseases (21). However, on January 20th and February 3rd, 1860, he presented two lectures to the Société chimique de Paris (Chemical Society of Paris, CSP) in which he reviewed and analyzed his extensive work of about 10 years on molecular and crystal dissymmetry. (There were two separate lectures due to time constraints). Pasteur's lectures were published as a single article in the original French in 1861 as part of a collection of lectures to the CSP (7). An English translation (divided into two separate articles corresponding to the two lectures) was published in 1862 (22, 23).

The article based on Pasteur's two lectures constitutes an important exposition of his work on molecular chirality. In its originally published form it is 42 pages long and is divided into two sections entitled Lecture 1 and Lecture 2, respectively. Pasteur begins Lecture 1 by reviewing some of the phenomena underlying his studies of molecular dissymmetry, including polarized light, optical rotation, and crystal hemihedrism. He then describes in great detail his studies of the crystallography of the tartrates, his resolution of sodium ammonium paratartrate, and his isolation of the two (*dextro*- and *levo*-rotatory, respectively) free TAs starting from the sodium ammonium salt of PTA.

In the final section of Lecture 1, Pasteur provides a detailed and lucid interpretation of his findings. He emphasizes that the two optically active TAs are isomeric by virtue of a difference in the arrangement of the atoms in the molecules, and explains that this difference is of the non-superposable-mirror-image type. Importantly, he asks whether this mirror-image dissymmetry may be the result of a helical or a tetrahedral arrangement of the atoms in the molecules. He also states that molecular dissymmetry is the cause of the formation of dissymmetric hemihedral crystals and is also the cause of optical rotation by substances in the non-crystalline state (e.g., in solution, in the liquid phase, etc.).

In Lecture 2, Pasteur considers the presence of molecular dissymmetry in some compounds and its absence in others. He concludes that (a) all the "products of the laboratory" (i.e., wholly synthetic substances) and the inorganic compounds are not dissymmetric, and (b) the majority of the organic natural substances, those that are essential to life, are dissymmetric. He points out that all the latter compounds are optically active in the non-crystalline state, which he states to be a necessary and sufficient property for the indication of molecular dissymmetry. Pasteur points out that molecular dissymmetry is the only known absolute demarcation between life and inanimate matter, and wonders about the universal forces that induce dissymmetry in organic natural substances in plants and animals. In the final section of Lecture 2 Pasteur extends his observations on molecular dissymmetry in substances derived from living organisms by describing his discovery that (+)-TA is metabolized with considerable preference over (–)-TA when PTA is incubated with a microorganism (21, 24).

In summary, in addition to the material also included in the two 1848 papers (5, 6), the 1861 article (7) contains an extensive discussion of the background underlying Pasteur's discovery and also includes an examination of the origins of molecular chirality in natural products; importantly, in this article Pasteur suggests that the basis of molecular dissymmetry may be a helical or tetrahedral arrangement of the atoms in the molecules.

Overall Analysis and Recommendation

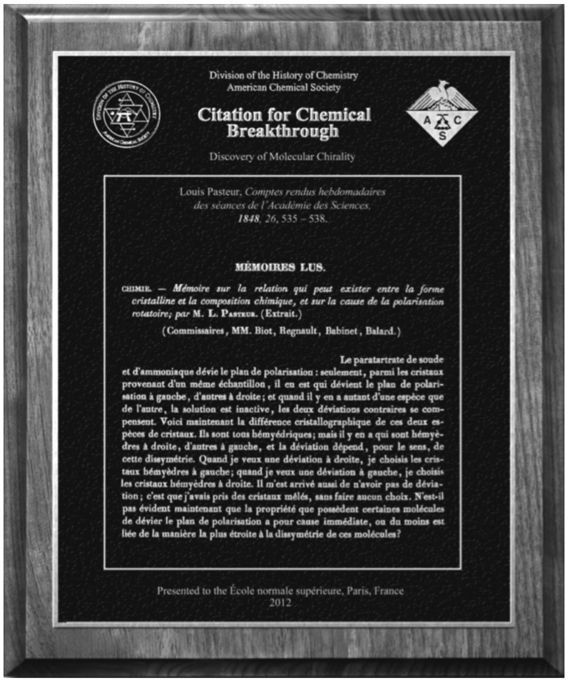
Of the three contending Pasteur publications (CR (5), Annales (6), and *Leçons de Chimie* (7)), which is the "breakthrough" paper? All three articles are important documents of Pasteur's discovery, and all three have often been cited in the literature; only a few such citations can be mentioned here (25-31). However, all three articles also have unique aspects and elements.

Clearly, the CR article (5) was first: it appeared no later than May 29th, 1848, i.e., one week after Pasteur's lecture to the Académie (32). The CR, an important publication by a leading institution of science, the Académie, contained scientific articles from a large variety of fields and was widely distributed (33). The CR article was brief and did not go into chemical or experimental details. (Brevity was a requirement for publishing in the CR (32).) On the other hand, the succinct and uncomplicated presentation in the CR made for a focused and clear article that was understandable by readers from a variety of backgrounds. The article reported entirely new and revolutionary observations with crucial implications for molecular structure. The first formulations of molecular-structural theory appeared about 10 years after Pasteur's discovery of 1848 (34), but even at the time of Pasteur's announcement of molecular dissymmetry, the question of the arrangements of atoms in molecules was of interest in a variety of fields, e.g., chemistry, crystallography, physics, etc. Moreover, until Pasteur's announcement in the CR (5), there had been no explanation for optical rotation by substances in the non-crystalline state.

French (Parisian) chemistry in the 19th century was troubled by certain "pathologies," including a "culture of celebrity" (35). Nevertheless, the system functioned well in many respects (35), and the novelty and importance of the discovery announced in the CR by the young and unknown Pasteur did attract the attention of Parisian scientific circles (36). He soon received significant recognition, including from renowned scientists such as the chemist Louis Jacques Thenard (1777-1857) (37) and the physicist Jean-Baptiste Biot (1774-1862) (36).

Pasteur's article (6) in the Annales, a respected journal of the period (16), had the great merit of containing the first written statement by Pasteur that his findings meant that the molecules of (+)- and (–)-TA must be dissymmetric (i.e., chiral, by today's terminology), and Pasteur's insight was clearly of great importance in the history of chemistry. (As we have seen, in the CR article Pasteur did refer to the TA molecules as "dissymmetric" but did not explicitly mention handedness). However, the Annales article described in considerable detail the crystallographic characteristics of a great many substances, material that would have been meaningful to (and readable by) only a relatively few individuals. Indeed, the large amount of such detail somewhat "dilutes" Pasteur's statements in the article concerning molecular chirality. Moreover, the readership of the Annales consisted primarily of chemists and physicists, and it did not have the wide interest and dissemination that the CR enjoyed (16, 33). Overall, the Annales article did not make the clear, stunning, and broad impact that Pasteur's concentrated first announcement in the CR achieved.

Pasteur's retrospective article of 1861 (7) has the merit of containing a detailed, well-organized, and lucid account of the background and the discovery. It also contains the suggestion of a helical or tetrahedral atomic arrangement as the potential explanation of molecular chirality, truly revolutionary insights by Pasteur that preceded van 't Hoff's (38) and LeBel's (39) proposals for the tetrahedral asymmetric carbon atom by well over a decade. Nevertheless, since the article (7) appeared 13 years after Pasteur's discovery, it did not cause the "sensation" that the CR article had produced. In addition, the 1861 article contains a great deal of material beyond the TA resolution and the concept of molecular chirality: as mentioned above, the article deals at length with the biological origins of molecular chirality, and while this aspect is recognized today as highly important (40), the focused announcement of the CR article seems, at least to the present author, more in line with the aims and criteria of the CCB award.



Division of the History of Chemistry
American Chemical Society

Citation for Chemical Breakthrough

Discovery of Molecular Chirality

Louis Pasteur, *Comptes rendus hebdomadaires des séances de l'Académie des Sciences.* *1848, 26*, 535 – 538.

MÉMOIRES LUS.

CHIMIE. — *Mémoire sur la relation qui peut exister entre la forme cristalline et la composition chimique, et sur la cause de la polarisation rotatoire; par* M. L. PASTEUR. (Extrait.)

(Commissaires, MM. Biot, Regnault, Babinet, Balard.)

Le paratartrate de soude et d'ammoniaque dévie le plan de polarisation : seulement, parmi les cristaux provenant d'un même échantillon, il en est qui dévient le plan de polarisation à gauche, d'autres à droite ; et quand il y en a autant d'une espèce que de l'autre, la solution est inactive, les deux déviations contraires se compensent. Voici maintenant la différence cristallographique de ces deux espèces de cristaux. Ils sont tous hémyédriques; mais il y en a qui sont hémyèdres à droite, d'autres à gauche, et la déviation dépend, pour le sens, de cette dissymétrie. Quand je veux une déviation à droite, je choisis les cristaux hémyèdres à gauche; quand je veux une déviation à gauche, je choisis les cristaux hémyèdres à droite. Il m'est arrivé aussi de n'avoir pas de déviation ; c'est que j'avais pris des cristaux mêlés, sans faire aucun choix. N'est-il pas évident maintenant que la propriété que possèdent certaines molécules de dévier le plan de polarisation a pour cause immédiate, ou du moins est liée de la manière la plus étroite à la dissymétrie de ces molécules?

Presented to the École normale supérieure, Paris, France
2012

***Figure 2**. The plaque of the CCB award to the ENS.*

Overall, then, for all the reasons laid out above, the CR article (5) was my recommendation as Pasteur's breakthrough publication (1), and was the final choice for a CCB award made to the ENS in Paris. The CCB award includes a high-quality plaque to be placed at a site selected by the recipient near the office or laboratory where the breakthrough was achieved. The plaque for the award to the ENS for Pasteur's discovery is shown in Figure 2.

Acknowledgments

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About the Author

Joseph Gal, a member of the editorial board of the journal *Chirality*, has long been interested in Pasteur's work on chirality and has published a number of articles on this subject.

CHARLES M. HALL'S PERSISTENT QUEST OF PATENTS FOR REFINING ALUMINUM METAL BY ELECTROLYSIS

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Introduction

In a single day, April 2, 1889, Charles M. Hall was awarded five patents for his discovery of the electrolysis process for extracting aluminum metal from aluminum oxide. To celebrate Hall's breakthrough achievement—ultimately, the commercial production of aluminum—under the Citation for Chemical Breakthrough (CCB) program of the Division of the History of Chemistry of the American Chemical Society, it was necessary to select the most important patent for display on the plaque (1). All five patents were carefully reviewed, as were the circumstances of the applications for the patents. As part of this evaluation, several fundamental questions were examined: Why were five patents issued and how do they differ from each other? Was more at stake than an inventor attempting to make the patent claims as broad as possible? The evidence brought out in this paper reveals that problems with the original process propelled Hall's determined investigation of alternative formulations of electrolyte baths and different cell designs.

Helpful reviews of the Hall patents are in the papers of Seabury C. Mastick (2) and Lloyd Van Doren (3), who were patent attorneys. For a full account of Hall's life and his work on aluminum metallurgy see the writings of Holmes, Edwards, and Craig (4-6).

Demonstrating the Hall Process

To give substance to Hall's original small-scale process and to make tangible the problems he encountered, a modern story helps. For a lecture demonstration celebrating the 100th anniversary of Hall's discovery, which had occurred on February 23, 1886, I began practicing the original tabletop process in early January 1986. The process involved electrolysis of alumina (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6) (7). The (+) anode was a graphite (carbon) rod, and a graphite crucible served as the (–) cathode. I had confidently offered to do this presentation because of having helped my 9-year-old daughter, Julie, do the process for a school project in 1970. Soon it was apparent that aluminum metal was not being produced. Furthermore, upon reexamination, the shiny bits that Julie had harvested in 1970 proved not to be aluminum metal. Lowering the temperature below the 1000°C melting point of the cryolite solvent, which was also the upper limit of the available electric pot furnace, seemed a possible remedy. A phase diagram for the aluminum fluoride/sodium fluoride system showed that additional aluminum fluoride lowered the melting point of the solvent without compromising the solubility of aluminum oxide (8). Adding aluminum fluoride to the mix solved the problem of making aluminum metal for the centennial lecture demonstration. Figure 1 shows a small graphite crucible, after sawing it in half, of the type used in the lecture demonstration and by Hall. Shiny halves of small pellets of aluminum metal are in the bottom of the crucible. Telling the story about having to rediscover the extra, unpublicized ingredient helped make the centennial lecture demonstration contemporary and fully engaging for the audience. (At the time, I had not studied the patents.)

***Figure 1**. A graphite crucible cut in half following a modern demonstration run on the small scale. Halves of shiny aluminum globules are in the bottom of the crucible.*

Although the lecture demonstration was rescued for February 1986, I learned in subsequent presentations of this demonstration that I had been lucky and that the small-scale process was far from being dependable. With much help from Dr. Lewis V. McCarty in the late 1990s, many experiments were performed in an attempt to identify the problems with the small-scale process. We had limited success in doing so.

Working on the Small Scale

How does the account of doing lecture demonstrations of the Hall process relate to Hall's path to the patents that became the foundation of Alcoa and the whole aluminum industry? My troubled experience with the small-scale process confirmed the unpredictability that dogged Hall's work in refining the method and helped explain why a series of modifications of the original patent application were submitted separately. Hall worked tirelessly for two and one-half years to improve his original process and to convince investors to support him. When Hall began work at the nascent Pittsburgh Reduction Company (later Alcoa) in the late summer of 1888, he moved immediately to a larger scale. Once he scaled up the process, the difficulties largely vanished. It is also likely that changing within a few months from the use of the original method of external heating to only internal resistive heating helped solve the problems.

Hall's first financial support for developing the process came from Judge Henry Baldwin and a Mr. Brown of Alston, MA, located across the Charles River from Cambridge. These "Boston backers" were recruited by Charles Hall's brother, George, but they did not sustain their support beyond the fall of 1886 because of problems with the method.

Hall's second financial backers were the brothers Eugene and Alfred Cowles of Cleveland, OH (9). They were making a copper-aluminum *alloy* with the process of electrothermy by putting a large electric current through a mixture of aluminum oxide, copper, and graphite. Their company was named the Cowles Electric Smelting Company. They agreed to support Hall's work on developing the electrolysis process to extract pure aluminum and assigned him to their plant at Lockport, NY, where waterpower generated large electric currents. Hall worked at Lockport for a year until the Cowles terminated the agreement in July 1888 (10). They concluded that Hall's uncertain process to make pure aluminum was not competitive with electrothermy for making alloys. The next month Hall joined Alfred Hunt and his fellow investors in Pittsburgh in forming a new company.

Applications for Patents

Hall submitted his first application for a patent on July 9, 1886, four and one-half months after making his original discovery. In a report from the patent examiner in October 1886, Hall learned that Paul L. T. Héroult had received a patent in France on April 23, 1886, for a comparable invention and had applied for a US patent on May 22, 1886. US patent law gave precedence to an American inventor who could prove that he had reduced his process to practice within a two-year period prior to the date of application of the foreigner for a US patent. Hall established precedence for his February 23 discovery through a patent interference proceeding. This demonstration was made with two postmarked technical letters he had mailed to his brother, George, on February 23 and 24, 1886, immediately after his first successful production of aluminum metal and through testimony of Hall and four witnesses on October 24, 1887 (11). One of the witnesses was Professor Frank F. Jewett, Hall's mentor at Oberlin College. Included in Hall's testimony was the phrase, "and I added some aluminum fluoride." This ingredient was not reported in any of the secondary accounts of Hall's original discovery. However, see the discussion of the patents below. I first saw the record of the patent interference testimony in early February 1986 after independently finding the beneficial effect of adding aluminum fluoride to the cryolite solvent.

The Five Patents

Hall's applications for the first two patents, a division of the original patent, were overseen by Robert L. Fenwick of the Washington, D.C., law firm of Mason, Fenwick, and Lawrence. Financial support for the initial patent application came from the Boston backers in the summer of 1886. Familiar signatures on the other patents show that the same law firm represented Hall's interests throughout the patent process.

For each patent the following summaries contain the patent number, the filing date and associated serial number, the number of figures, the title of the patent, and the principal claims for each patent (12). The patents use "aluminium," as "aluminum" was still called in the United States in the 1880s. All five patents refer to the method of external heating in a gasoline-fired oven. In the commercial process in the spring of 1889, Hall replaced external heating entirely with internal resistive heating by a large electric current. His use of internal heating became the basis for legal disputes with the Cowles brothers in the 1890s and early 1900s. They claimed internal heating was an application of their process of electrothermy, learned by Hall in Lockport. Because the patent No. 400,766 is the basic patent, it is put first in the list. This patent contained the substance of the first patent filed and was closest to the method employed in industrial practice. It was used on the CCB plaque. All five patents were issued on April 2, 1889.

It is unclear who bore the cost of the three patents filed in 1888. However, the dates are such that Alfred Hunt of the Pittsburgh Reduction Company probably paid for them. It is also unclear who paid any added cost for the submission of the divided patent No. 400,664 in February 1887. At that time, Hall did not have secure financial backers.

No. 400,766. July 9, 1886, Serial No. 207,601. Two figures. "Process of Reducing Aluminium by Electrolysis." **Basic Patent.**

Figure 2 is a reproduction of the page with the two figures accompanying this patent. The top figure shows two separate electrode rods in the melt and the gasoline-fired burner used to heat the pot. Crucibles in both figures were made from iron shells lined with graphite. The bottom figure anticipates the commercial process by having a graphite liner of the pot serve as the negative cathode. Under the figures are the signatures of George E. Hall, Hall's brother, and Robert L. Fenwick, the lawyer, as witnesses. The name of the Mason, Fenwick, and Lawrence law firm appears below Hall's signature.

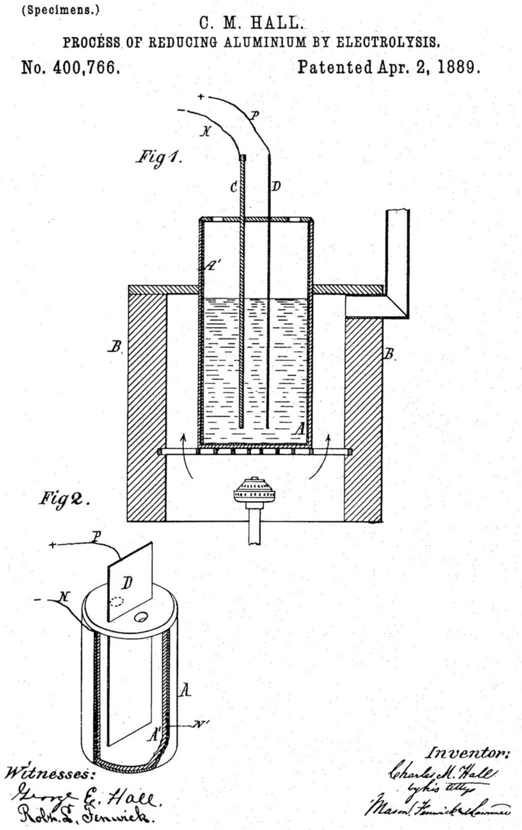

***Figure 2**. Two figures in patent No. 400,766.*

The solvent mixture was specified as $Na_2Al_2F_8$ or $2NaF{\bullet}2AlF_3$ (13), which can be re-expressed as two moles of AlF_3 for each mole of Na_3AlF_6 (cryolite). Thus, this patent called for a substantial excess of aluminum fluoride. Aluminum oxide was dissolved in the molten solvent mixture and added as consumed in the electrolysis. The negative electrode (C in Figure 2) was made of graphite unless an alloy was intended to form with a metal electrode. When electrodes such as copper were used as the positive electrode (D in Figure 2), oxygen gas was released at the anode. When carbon was used as the positive electrode, the electrode was gradually consumed by production of "carbonic [acid] oxide (CO_2)." The option of using lithium fluoride, or fluorides of other metals more electropositive than aluminum, in place of some of the sodium fluoride to lower the melting point of the solvent was included. The source of electricity was a "dynamo-electric machine or other suitable source" giving a voltage of 4-6 V and a high current. Liquid aluminum, being denser than the solvent, sank to the bottom of the pot, where it was protected from reoxidation.

The final content of this patent differed substantially from the original submission. After 30 written communications between the Patent Office and Hall, the final formulation of the patent was reached.

No. 400,664. July 9, 1886, Serial No. 207,601. Divided and the new application filed February 2, 1887, Serial No. 226,206. Three figures. "Process of Reducing Aluminium from its Fluoride Salts by Electrolysis."

The same initial serial number, 207,601, and the "divided" descriptor confirm that this patent was part of the original submission. The essential difference from patent No. 400,766 was use of potassium fluoride and aluminum fluoride with the composition of $K_2Al_2F_8$ instead of sodium fluoride and aluminum fluoride for the solvent. Replacing some of the potassium fluoride component with lithium fluoride made the bath lower melting and a better solvent for aluminum oxide. The first two figures for this patent were similar to those in No. 400,766. The third figure included a tube at the bottom of the crucible for drawing off molten aluminum metal. Cells in all three figures had graphite liners in crucibles made of iron or another metal. The graphite liners in the second and third figures served as the negative electrode. Use of non-carbonaceous anodes (+) was emphasized.

No. 400,665. August 17, 1888, Serial No. 282,954. One figure. "Manufacture of Aluminium."

This patent concerned new developments beyond the original application. The cell design, as shown in Figure 3, differed significantly from the other patents in having a cover and a barrier made of graphite dividing one electrode area from the other near the surface of the melt. The divider was needed because liquid aluminum floated on the dense electrolyte composed of the alkaline earth metal fluoride solvents, as specified in this patent. The cover prevented rapid reoxidation of the aluminum metal by atmospheric oxygen, and the divider prevented reoxidation of the aluminum by contact with the anode. The principal claim in this patent was for electrolytes that avoided the formation of a "black substance" with its concomitant increase in resistance and voltage during extended electrolysis. With sodium- or potassium-based electrolytes, the solvent system had to be renewed periodically. New electrolytes included $CaAl_2F_8$, which involved an excess of AlF_3, as well as $SrAl_2F_8$ and $BaAl_2F_8$ and stoichiometrically balanced $Ca_3Al_2F_{12}$. All of these solvents had the advantage of being lower melting than the cryolite-based solvents and of making continuous operation possible. When alloys were made with a metallic cathode (–), the alloys were dense enough to sink to the bottom. If two-thirds of the weight of the solvent was replaced with $K_2Al_2F_8$, the solvent had a low enough density for molten aluminum to sink to the bottom. The barrier and cover were no longer necessary.

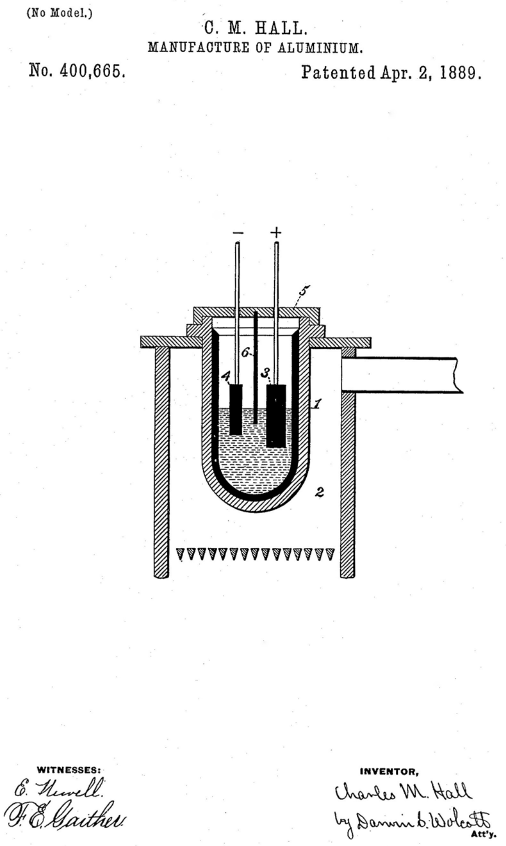

Figure 3. *The figure in patent No. 400,665.*

This patent described the "artificial" preparation of aluminum fluoride from hydrated alumina and hydrofluoric acid, which is nasty chemistry because of the hazardous nature of hydrofluoric acid. The aluminum oxide was also described as being "artificially" prepared, presumably from alum [$KAl(SO_4)_2$].

No. 400,666. August 17, 1888 Serial No. 282,955. One figure. "Process of Electrolyzing Crude Salts of Aluminium."

This patent, a companion to 400,665, described further improvements for avoiding the formation of the black substance accompanied by an increase in resistance that occurred with sodium- and potassium-based solvents. The variation was a solvent composed of $Na_2Al_2F_8$ + $CaAl_2F_8$, which was sufficiently low in density to allow molten aluminum to sink to the bottom of the crucible. No cover or barrier between the electrodes was needed. In addition, a few percent of calcium chloride was added, which, due to volatility, had to be resupplied periodically. Continuous operation was affirmed.

No. 400,667. September 21, 1888, Serial No. 286,034. No figure. "Process of Electrolyzing Fused Salts of Aluminium."

Little difference exists between this patent and Nos. 400,665 and 400,666, filed a month earlier. As in the previous two, the emphasis was on achieving continuous operation without replacing the solvent. Tests were described for when to supply additional calcium chloride. These tests were observing a rise in voltage and an increase in the CO/CO_2 ratio. No method for determining this ratio was supplied. Absorption of CO_2 gas in base, leaving CO gas to be measured volumetrically, would have sufficed.

Had I studied the patents before doing the lecture demonstration, I would have known from the outset to add aluminum fluoride to the cryolite solvent.

The account of the essentials of the multiple patents shows that Hall was preoccupied with overcoming various difficulties by changing solvent composition and cell construction before he had the resources to run the process on a larger scale. This interpretation of the goal of Hall's intense work during the 1886-1888 development period and the multiplicity of patents concerned with improving the reliability of the process was confirmed in the detailed prospectus that Hall wrote on July 10, 1888 (14) and by Van Doren (3). This prospectus was written to convince Alfred Hunt to found a company that was soon named Pittsburgh Reduction Company. Most of the additional methods described in the patents were not needed because when the process was scaled up the difficulties largely disappeared. Switching over to internal resistive heating by a strong electric current also simplified the process, managing the contents of the cell, and prolonging the life of the cell.

The industrial process is substantially the same as that described in patent No. 400,766, the patent with the earliest filing date. Thus, *despite it having the higher number*, this patent was the appropriate one to honor by a CCB award. This plaque honoring Charles Hall and his achievement is shown in Figure 4 (15). The figure on the plaque is a slight rearrangement of the figure (Figure 2) that was on patent No. 400,766.

***Figure 4**. The display on the plaques presented to Oberlin College and the Oberlin Heritage Center for the Citation for Chemical Breakthrough.*

Today, the Hall-Héroult process, as it became known in the twentieth century, has been scaled up by orders of magnitude and is largely automated. Computer control of the current, of the distance between electrodes, of the addition of aluminum oxide, and of the addition of aluminum fluoride and some calcium fluoride gives maximum efficiency in the use of electric power and materials. Today, a representative composition of the solution (in mol) is 1.0 Na_3AlF_6, 0.34 AlF_3, 0.17 CaF_2, and 0.13 Al_2O_3. A modern smelter has hundreds of pots running in series for roughly a year's lifetime each. Figure 5 is a photograph of a small part of the massive pot line of the new Alcoa plant at the Fjardaál smelter in Iceland, where electricity from geothermal energy is abundant. The scale-up and continuity of operation are breathtaking in comparison with the original tabletop process. The robustness and reliability of the industrial process is a long way from the uncertainties that Charles Hall faced during the period of development. For the most part the multiplicity of patents proved to be unnecessary.

Acknowledgment

I am grateful to Maurice Laparra, president of the Institute for the History of Aluminium in Paris for the information about the composition of today's electrolyte solution and for his hosting of a tour of the huge, new aluminum smelter at Dunkerque, France.

Figure 5*. A small part of the pot line in the Alcoa aluminum smelter at Fjardaál, Iceland. 2008 photograph. Image used courtesy of Alcoa Inc.*

References and Notes

1. Presentation of the CCB plaque by the Division of the History of Chemistry to Oberlin College and to the Oberlin Heritage Center citing Charles M. Hall's principal patent, February 23, 2009. For a broader introduction to the challenge "first" or "breakthrough" as this distinction relates to the CCB award program, see: J. I. Seeman, "HIST's Citation for Chemical Breakthrough Awards: The 'First' *or* the 'Breakthrough' Paper?" *Bull. Hist. Chem.,* **2013,** *38*, 4-6.
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7. J. Walker, "Retracing the Steps by which Aluminum Metal was Initially Purified back in 1886," The Amateur Scientist, *Sci. Am.*, August **1986**, *255*(2), 116-119.
8. J. D. Edwards, F. S. Frary, and Z. Jeffries, *The Aluminum Industry*, Vol 1, *Aluminum and its Production*, McGraw-Hill, New York, 1930, p 287.
9. A. Cowles, *The True Story of Aluminum*, Henry Regnery, Chicago, 1958.
10. Ref. 5, p 78.
11. United States Patent Office Publication, including testimony on the interference between Charles M. Hall and P. L V. [*sic*] Héroult, 1887. Oberlin College Archives.
12. Copies of these patents are available through the website of the US Patent Office or Oberlin College Archives.
13. The use of the formula $Na_2Al_2F_8$ and similar formulas in the other patents was puzzling. It is not the simplest formula, which is $NaAlF_4$. In the prospectus (13) written for Hunt, Hall consistently used "Al_2." Thus, Hall must have regarded Al_2 as the fundamental unit of the element aluminum, as reflected in $Na_2Al_2F_8$.
14. C. M. Hall, Prospectus written for Alfred Hunt, July 10, 1888. Oberlin College Archives.
15. Identical plaques were presented to Oberlin College and the Oberlin Heritage Center. The college's plaque is located near the aluminum statue of Charles M. Hall in the Department of Chemistry and Biochemistry. The plaque at the Oberlin Heritage Center is in the woodshed attached to the Jewett House, where there is a recreation of Hall's workplace.

About the Author

Norman C. Craig is Emeritus Biggs Professor of Natural Science in the Department of Chemistry and Biochemistry at Oberlin College, Oberlin, OH 44074. He has been a student of the work of Charles M. Hall, a 1885 graduate of Oberlin College. Craig has written papers and has given a number of presentations on Hall's life and work. He has an article about Julia Hall, Hall's older sister, in *Chemical Heritage*. He has also written about the history of chemistry at Oberlin College in the *Bulletin*.

WILHELM HEINTZ (1817-1880) AND THE CHEMISTRY OF THE FATTY ACIDS (1)

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Introduction

In 1855, Otto Erdmann, the editor of the *Journal für praktische Chemie*, asked Wilhelm Heintz at the University of Halle to submit a review article summarizing his lengthy investigation of the fats and fatty acids. Beginning in the mid-1840s, Heintz had subjected these compounds to their most thorough investigation since Michel Eugène Chevreul thirty years earlier, and he redefined the criteria for identifying them as chemical species. Spurred by difficulties in purifying fats isolated from human fatty tissue, Heintz's research program demonstrated convincingly that well established fatty acids long thought to be pure were in fact mixtures of other known fatty acids. Heintz argued, furthermore, that a sharp melting point after repeated crystallization could no longer serve as a sufficient criterion for their purity and introduced a new method for establishing the purity of the fatty acids (2).

Although little known today, Wilhelm Heintz was an extremely productive chemist during the nineteenth century. At the time of his death in 1880, Heintz had authored over 200 publications, primarily in physiological chemistry, but also on mineral analysis, improved techniques for elemental analysis, and organic chemistry. His relative obscurity perhaps derives from a number of factors, including his position at Halle, one of the smaller, less prestigious universities in Germany, where he did not have the resources to direct a large research group. His only significant student was Johannes Wislicenus (1835-1902), to whom we owe the only major account of Heintz's life (3). Heintz also emphasized primarily empirical investigation and wrote little on theoretical matters except during a short dispute in 1864 with Vladimir Markovnikov on the constitution of the ethyl glycol amides, when he was among the first chemists to use Aleksandr Butlerov's new term "chemical structure" (4). Nearly all of Heintz's published work consisted of journal articles, and he published only one book, a textbook of animal chemistry, in 1853 (5).

Wilhelm Heintz

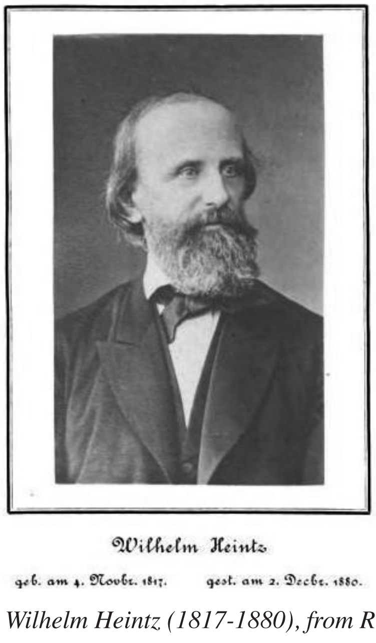

***Figure 1**. Wilhelm Heintz (1817-1880), from Ref. 3.*

Heintz was born in Berlin, the son of a businessman, and followed an unusual path to a university career in chemistry. He was initially apprenticed to a pharmacist, but soon decided against a career as a pharmacist in favor of chemistry. Since he had not completed his education at the Gymnasium for normal entrance to the university, Heintz prepared for and passed the matriculation exam in October 1840, when he immediately enrolled at the University of Berlin (6). He attended lectures from J. H. F. Link in pharmacy and natural history, Heinrich Dove in physics, Eilhard Mitserlich and Heinrich Rose in chemistry, and Johannes Müller in physiology. He became friends with many of Müller's students, and in January of 1845, he was the only chemist among the cofounders of the *Deutsche physikalische Gesellschaft zu Berlin* with Emil du Bois Reymond, Ernst Brücke, Karl Knoblauch, Wilhem Beetz and Gustav Karsten. During this time, he also met and became friends with Hermann Helmholtz, and by the late 1840s, had established himself as a significant member of the Berlin circle of up and coming physical scientists, including DuBois-Reymond and Helmholtz.

Heintz worked in Rose's laboratory, studying inorganic compounds such as alumina and iron oxide, asbestos, properties of glass in the electroscope, and dyestuffs. For his dissertation, which he completed in February of 1844, Heintz turned to saccharic acid (7). Although he did not formally complete a *Habilitationsschrift*, by late 1845, Heintz already had thirteen publications and a small private laboratory in his parents' house where he offered instruction in qualitative analysis to a small number of students. He was therefore granted the *venia docendi* (the right to lecture at the university) by ministerial dispensation, and in 1846 Heintz was appointed to the medical faculty as a lecturer in physiological and animal chemistry at the institute of clinical medicine directed by Johann Lukas Schönlein (1793-1864) at the Charité hospital in Berlin (8).

Throughout his career, Heintz's major interest was in physiological and animal chemistry, especially the chemical composition of animal fluids. Between 1845 and 1850, he published 26 papers that described novel methods for isolating and identifying components of various animal fluids, especially human urine. He introduced a new method for the quantitative determination of urea in normal and diseased urine by measuring the quantity of ammonia formed by decomposition, discovered the presence of creatine in urine and studied the composition of urine sediments (9). In other papers, he described methods for determining the composition of ash residue from bones and animal substances, characterized stomach acid, analyzed the composition of the fluid found in a hydantoin cyst, and the milk from the "cow tree" of Venezuela (10). On the basis of this work, Heintz was called to the University of Halle in 1851 to succeed Richard Marchand, where he remained until his death in 1880.

Heintz's Fat Kingdom

When he moved to Halle, Heintz turned his attention to the chemistry of the animal fats, or the "fat kingdom" (*Fettreich*) as he affectionately called it. The animal fats had first been extensively studied nearly forty years earlier by Chevreul, who published his results first as a series of papers in the *Annales de chimie* and then in an 1823 book, *Chemical Research on the Fatty Bodies of Animal Origin* (*Recherches chimiques sur les corps gras d'origine animale*) (11). Chevreul separated animal fats into distinct compounds with a definite composition. He found that saponifying each of these animal fats formed a "sweet principle" to which he gave the name "glycerin" that combined with a few common fatty acids that he named stearic, oleic, and margaric acids. Chevreul also found spermaceti to saponify, but instead of the "sweet principle," it contained a substance that resembled alcohol, but with a significantly higher molecular weight, which he called "Ethal," that combined with various fatty acids to form spermaceti. He also isolated another fatty substance that he could not saponify that he named cholesterine (cholesterol). Chevreul used a variety of novel techniques, including elemental analysis, fractional solution and crystallization. He also used the melting point both to identify and judge the purity of the fats and fatty acids he isolated. Highly admired at the time, Chevreul showed that the fats were subject to systematic chemical analysis and obeyed the laws of chemical combination (2). Chevreul's work provided the basis for further investigation of fats and oils, and when Heintz entered the field, chemists had identified many new fats and fatty acids, all defined by their melting point and chemical composition. Furthermore, in 1853, the young Marcelin Berthelot further demonstrated by synthesis that fats are triglycerides, when he combined glycerine with various combinations of three fatty acids (12).

Heintz became interested in the fatty acids through his friend, the physiologist Ernst Brücke, who had worked in his laboratory during the 1840s with a project on the composition of human fat. Brücke had assumed that human fat consisted of the fats margarin and olein, and should therefore produce margaric acid on saponification, but he had repeatedly obtained a fatty acid with a melting point below that of margaric acid. Brücke would abandon this project sometime in the mid-1840s, before he left Berlin in 1848 for the University of Königsberg, but the line of investigation resulting from Brücke's unexpected difficulty would eventually, as Heintz wrote in 1855, "make questionable the existence of all the [fatty acids] as chemically pure bodies" (13). Heintz published the results of this research between 1851 and 1857 in a series of lengthy articles in his preferred journal, *Poggendorff's Annalen der Physik und Chemie*. As Wislicenus noted, Heintz's articles gave a "clear picture of Heintz's working style," and he reported carefully the "path followed by experimental investigation" without sparing the reader any detours and errors along the way (14).

Heintz's own narrative suggests that he continued Brücke's project nearly immediately, even though his first full publication on fats did not appear until 1851 (15). Brücke's difficulties suggested to Heintz that human fat must contain an additional solid fat that on saponification produced an additional solid fatty acid that could not be separated from margaric acid by "simple crystallization" (*bloßes Umkrystallization*) (16). Heintz slowly cooled a sample of human fat below 0°C, separating any solidified fats from the remaining liquid, and eventually concluded that human fat consisted of a mixture of at least six different fats, including margarin, palmitin, olein, and a new fat he named anthropin. Saponification of the margarin prepared from human fat produced margaric acid, but the composition and melting points of these acids suggested they were still impure.

> This circumstance connected with the fact that the previously applied methods of separating fatty acids applied to human fat has not once resulted in the pure preparation of any of the fatty acids, compelled me to seek another separation method. I have had a lengthy, repeated struggle to use the ordinary, conventional separation techniques on the fatty acids, but always with no success, as [should be] expected, because it is well known how extraordinarily similarly, one could almost say identically, the compounds of the various fatty acids behave with the same foundation towards means of resolution (17).

Heintz's frustration finally eased in 1848, when he encountered an article by Liebig on a new method for separating valeric, butyric and acetic acids by conversion to their salts with sodium carbonate followed by distillation (18). In any mixture of these three acids, Liebig found that butyric and valeric acid distilled first, always leaving the acetic acid behind, even though it had the lowest boiling point of the three components. Heintz explained this—as Liebig had not—by suggesting that the butyric and valeric radicals had a lesser affinity for the sodium, allowing the separation to take place (19).

> This train of thought led me to test the idea if it would not be possible simply to separate such substances (*Körper*) from one another by their degree of affinity, when their properties are so similar, both in a pure state (*im freien Zustand*) and when combined with other substances, that they were previously inseparable or only partially separable. I thought right away about the solid fatty acids, with which I have occupied myself for so long without success, precisely because the previously applied methods were quite imperfect.

The fatty acids could not easily be distilled, but Heintz could take advantage of the differential solubility of their salts, and he settled on treating the fatty acids with lead acetate. He would later use magnesium and barium salts, but the method remained the same (13). Heintz dissolved the fatty acid in minimal hot alcohol and slowly added a solution of lead acetate in approximately half the stoichiometric amount. On cooling, the fatty acid with the greatest affinity for lead precipitated as the lead salt. The precipitate was then filtered and acidified to yield the acid, and the filtrate treated again with lead acetate. This process was repeated until the melting points of the obtained fatty acids remained constant (20). Heintz found that he could separate mixtures of three or more acids by this method, and the results suggested that mutton tallow and spermaceti were more complicated mixtures than earlier assumed. Heintz noted that the "quality" (*Güte*) of this method was justified by the isolation of a new fatty acid from anthropin that he named anthropic acid (*Anthropinsäure*).

In 1852 Heintz extended these preliminary results. Because he had found human fat to contain margaric, palmitic and anthropic acids, he expected sheep tallow to have a similar composition because it contained similar fats. His results were confirmed, but in an unexpected way. In the attempt to isolate anthropic acid from saponified mutton tallow, Heintz found that the melting point continually increased on repeated recrystallization of the fraction, and in several of the recrystallizations, he noticed the precipitation of small amounts of margaric and stearic acid. "The results of these experiments," Heintz wrote, "finally gave me the notion that anthropic acid, despite its great ability to crystallize, may be a mixture of stearic and margaric acid" (21). Heintz therefore mixed stearic acid with varying amounts of margaric acid, and noticed that even a small amount of stearic acid changed the appearance of the margaric acid crystals, which eventually entirely lost their crystalline properties. A solid mixture of 11 parts margaric acid and 6 parts stearic acid appeared "exactly like the acid I had named anthropic acid," and had the same melting point (22). "Pure" anthropic acid was therefore simply a mixture of stearic and margaric acids.

Furthermore, Heintz noted that palmitic acid seemed to be ubiquitous when handling anthropic acid, such that he "could not resist the suspicion" (*der Vermuthung nicht mehr erwehren*) that margaric acid itself was nothing more than a mixture of stearic and palmitic acid. Heintz found that a mixture of 7 parts palmitic acid and 5 parts stearic acid resulted in a compound, "which in all of its properties, especially in the crystalline form as it solidifies and in the melting point, coincides with anthropic acid." A mixture of ten parts palmitic acid and one part stearic acid, "possessed *all the properties* of margaric acid," in both melting point and crystalline form (23). As the portion of stearic acid increased, the melting point continued to decrease to a minimum, when it increased again and assumed the appearance of anthropic acid. "This experiment with palmitic and stearic acid with different origins has been repeated so often," Heintz wrote, "that I can no longer doubt [these results]" (24).

These results completely changed the composition of both human fat and mutton tallow. The fats anthropin and margarin did not exist. Human fat consisted only of stearin and palmitin, which contained palmitic and stearic acids, and human and mutton fat differed only in the proportion of stearin and palmitin. The results also cast doubt on the composition of spermaceti, which Heintz had shown earlier to consist of ethal and six fatty acids, including margaric acid. (25).

Spermaceti, the Rule of Four, and Melting Point Depression

Before returning to spermaceti, Heintz turned to the fatty acids contained in butter. Already in 1844, Joseph Lerch had identified four fatty acids in butter (26):

Buttersäure (butyric acid): $C_8H_8O_4$

Capronsäure (capronic acid): $C_{12}H_{12}O_4$

Caprylsäure (caprylic acid): $C_{16}H_{16}O_4$

Caprinsäure (capric acid): $C_{20}H_{16}O_4$

Heintz isolated four more fatty acids, doubling the number in butter to eight, and noted that palmitic acid was present in the greatest quantity:

Myristic acid: $C_{28}H_{28}O_4$

Palmitic acid: $C_{32}H_{32}O_4$

Stearic acid: $C_{36}H_{36}O_4$

Arachidic acid (*Butinsäure*): $C_{40}H_{40}O_4$

Heintz noted that the composition of these acids seemed to follow a general law, "that the saponification products of fats contain only those acids whose number of carbon atoms is divisible by four" (27). This implied that any known fatty acid that did not follow this law would be a mixture of fatty acids that did. This was true for margaric and anthropic acids (both with 34 carbons). It also suggested that some fatty acids created by saponification of spermaceti, cetyl acid, with 30 carbons, and cocinic acid, with 26 carbon atoms, must be mixtures of other fatty acids that obeyed the "law of four," and Heintz obtained ten pounds of spermaceti to investigate further (28).

Heintz's results on spermaceti appeared as a two-part article in 1854. He collected the fatty acids separated from the ethal and submitted them to fractional precipitation, slowly adding ethanol and removing the resulting precipitate in twenty fractions. Because it "would be an endless task" (*endlose Arbeit*) to subject each of these fractions individually to additional fractional crystallization, Heintz combined fractions with similar melting points for crystallization. This work proved painstaking; Heintz recrystallized the solids from the first six fractions fifteen times, until the amount was too small to continue. The earliest fractions from the initial precipitation produced the acids with the highest melting points, and in subsequent fractions the melting points decreased. From the stable melting points of the acids from the various combined fractions, Heintz concluded that spermaceti contained only four fatty acids that fully confirmed his rule of four (29):

Stearic acid ($C_{36}H_{136}O_4$): m.p. 69.2°

Palmitic acid ($C_{32}H_{32}O_4$): m.p. 62°

Myristic acid ($C_{28}H_{28}O_4$): m.p. 53.8°

Lauric acid (*Laurostearinsäure*, $C_{24}H_{24}O_4$): m.p. 43.6°

There remained, however, a single fraction with a melting point of 32.3°, lower than pure lauric acid. This suggested a fifth component with a lower melting point, but acids isolated from the subsequent fractions had a higher melting point, making this fraction an exception to Heintz's general observation that all the later fractions contained acids with lower melting points. This "left only the suspicion" that this fraction was another mixture of two fatty acids in the correct proportion to produce a lowered, but sharp melting point, just as the mixture of palmitic and stearic acid had produced margaric acid. Heintz therefore systematically mixed the following pairs of the four fatty acids in various proportions to determine their melting point:

Stearic/palmitic acids (C_{36}/C_{32})

Palmitic/myristic acids (C_{32}/C_{28})

Myristic/lauric acids (C_{28}/C_{24})

Stearic/myristic acids (C_{36}/C_{28})

Palmitic/lauric acids (C_{32}/C_{24})

Stearic/lauric acids (C_{36}/C_{24})

The melting points for the various combinations suggested that "analogous mixtures of different acids behave in a completely analogous way" (30). For mixtures of acids that differed in composition by four carbon atoms (the first three combinations above), a mixture of 70% of the acid with the lower carbon content and 30% of the acid with the higher carbon content always resulted in the lowest melting point. Furthermore, the melting point of palmitic acid was lowered by the same amount if mixed with the same proportion of either stearic acid (containing four more carbon atoms) or myristic acid (containing four fewer carbon atoms) acids. The same was true for myristic acid. Mixtures consisting of two acids that differed by eight or twelve carbons followed a similar rule. If the melting point was plotted against composition, Heintz wrote (31),

> in all cases the curve will first sink below [the value of] the lower melting compound, and then turns upward, cutting the abscissa and then slowly climbing above it. This curve remains almost the same for every two acids that differ by four or eight carbons. But the greater the difference of composition of the two acids, the sooner the curve reaches its the lowest point.

But this new law still did not explain the fraction that melted at 32.3°C. Heintz now suspected that this could be a mixture of three acids that increased by four carbon units in sequence (such as stearic, palmitic and myristic acids). Heintz took a fixed mixture of palmitic and myristic acid and combined it with varying amounts of stearic acid, and another fixed mixture of myristic and lauric acid with varying amounts of palmitic acid. The melting points of these mixtures "fully confirmed" Heintz's initial suspicions, as one of these mixtures proved to have a melting point of 32.2°C.

Heintz concluded that the law he had established in his study of butter had general consequences, and the fatty acids in spermaceti also followed the "rule of four." There was no need to postulate a fifth fatty acid, and all four acids present contained a multiple of four carbon atoms. Heintz went on to list the many known fatty acids that did not fit the "rule of four" and suggested that they must be mixtures of known acids. By 1855, therefore, Heintz had reached two major conclusions: 1) fats consisted of a small number of fatty acids, and that these acids always contained a multiple of four carbon atoms, and 2) that mixtures of fatty acids produced a lowered melting point that sometimes remained quite sharp, giving a false sense of their purity. Furthermore, the degree of melting point depression followed a general law, according to the proportion of fatty acids that differed in composition by four carbon atoms. In 1857, Heintz completed his investigation by synthesizing the "true" margaric acid with 34 carbon atoms and found its properties very different from the original margaric acid (32).

Heintz recognized that the presence of a sharp melting point in these mixtures could be due to a new pure chemical compound created on mixing the acids, but he rejected this possibility for two reasons. First, the mixtures with the lowest possible melting point did not appear to have a unique form when they solidified, and they appeared completely uncrystalline. The only exception to this was, not surprisingly, margaric acid, which, according to Heintz, produced long needles on crystallization, and "possesses a much greater ability to crystallize" (*besitzt viel grössere Krystallisationsfähigkeit*) than either pure stearic or palmitic acid (33). Heintz's second argument is complex and difficult to follow, but in essence he suggested that the proportions required to produce the lowest possible melting point did not "correspond to a weight proportion (*Gewichtsverhältniß*) of simple molecular numbers (*Atomzahlen*)" (34). The possibility of creating a new compound on mixing fatty acids seemed even more unlikely when Heintz considered that three fatty acids could mix to lower the melting point even further. "It is therefore certain," wrote Heintz, "that the physical behavior of the molecules (*Atome*) alone is the reason for the observed phenomena" (35).

Simple Substances, Melting Points and Chemical Species

Heintz's work on fats was only a fraction of his total research output, but it reflects his general emphasis on the empirical investigation of animal fluids with little reliance on theory beyond calculating molecular formulas. It certainly was his most significant and enduring accomplishment, even if his name is no longer recognized today. Separating these acids was painstaking work, with melting points that often differed only a fraction of a degree. Accounts of Heintz's work acknowledged his "astonishing perseverance" and "great virtuosity with which he manipulated his method." An 1881 commenter in *Nature* remarked that Heintz's work "form[s] essentially the basis of our present knowledge of the fats and the fatty acids" (36). Heintz's painstaking work on differentiating the fatty acids also resembles Emil Fischer's more famous later investigation of the isomeric sugars. Yet, unlike Fischer, who had van 't Hoff's theory to guide him on the total number of possible stereoisomeric sugars, Heintz had no theoretical guidance as to how many fatty acids there could be until he derived the rule of four.

Heintz's research on fatty acids illustrates a number of issues in nineteenth century chemistry. First, consider Heintz's technique for separating the fatty acids and the criteria for chemical identity–how do chemists identify a unique chemical species? In his 1854 paper on spermaceti, Heintz concluded that the long accepted method for preparing pure compounds, repeated recrystallization until the melting point no longer changed, was no longer adequate. Heintz wrote in 1854 (37)

> Until my work no other means of purification was recognized other than recrystallization. If the melting point by repetition of this operation no longer changed, it was safe to conclude the purity of the acid. My investigations have demonstrated that this conclusion is not correct under all conditions. But I have previously learned a method for the case when recrystallization does not suffice to establish an acid's purity, and with its assistance, [I] demonstrated that margaric, cetyl and anthropic acids are mixtures.

In other words, "simple crystallization" (*bloß Umkrystallization*) could not guarantee the formation of a single pure compound, no matter how uniform and regular the crystals appeared to be, or how sharp and unchanging the melting point. The only way to assure purity, according to Heintz was repeated fractional precipitation of the fatty acids to reach a constant melting point.

In 1823, echoing Lavoisier, Chevreul had written that the identity of any chemical species is "based on experiment and should not be considered as absolute but purely as the result of the means employed" (38). Heintz's method of fractional precipitation demonstrated that margaric and anthropic acid were no longer "simple substances," in Lavoisier's sense of the term. Heintz himself was fairly surprised at the appearance of yet another new separation method, remarking that (39)

> since chemistry became a science, it was the most enthusiastic goal of everyone who set it as their life's work, to complete and increase the methods of investigation. One would hardly think that even now it is still possible to devise methods that are entirely new in their principles.

As a sign that Heintz thought his fractional precipitation method was significant, his first 1851 paper on the fatty acids discussed exclusively the origins and effectiveness of this new method.

Another significant result of Heintz's work was what he termed the "law" of melting point depression, an extensive quantification of the effect of impurities on melting points. In his 1823 book, Chevreul had compiled an extensive table that displayed a regular increase in melting point in mixtures of oleic and margaric acids. Although he did not find a mixture with the lowest possible melting point, Chevreul demonstrated that the melting points gradually increased from approximately 0°C (99% oleic acid) to 55°C (99% margaric acid) (40). Heintz did not mention Chevreul's table, but was directly influenced by Johann Gottlieb's 1846 paper on the fatty acids isolated from goose fat. Gottlieb had saponified goose fat and isolated both stearic acid (*Talgsäure*) and margaric acid, but he was initially confused, because his first fraction melted at 58°C, a value below the melting point of both stearic and margaric acids. Gottlieb therefore deliberately mixed the two acids and found that the melting point was often below 60°C, and compiled a table of melting points as a function of composition to avoid errors and correlate the melting point with composition (41). Whereas Gottlieb had only mixed stearic and margaric acids, Heintz expanded Gottlieb's results significantly by determining the melting points of various combinations of stearic, palmitic, lauric and myristic acids, and deriving a general law describing the relationship between composition and the maximum melting point depression (42). Both Gottlieb and Heintz drew an explicit analogy between the melting point depression in fatty acids and a similar phenomenon that occurred in mixtures of certain metals. Heintz noted (43)

> The mixing of two metals often results in a significant lowering of the melting point, and if a third [metal] is added, the melting point often goes significantly lower. I remember here especially the mixture of metals reported by Rose, Newton, and Lichtenberg, made of lead, tin, and bismuth, that melts in boiling water.

Heintz's use of melting points to identify fatty acids as chemical species raises broader questions about the general adoption of melting points as an identification technique in chemistry. In his 1851 paper on the composition of human fat, Heintz described his careful measurement of the temperature of fat as it solidified around the bulb of a thermometer, determining the freezing temperature when the liquid fat became transparent. He also determined the melting point of the same fat in a capillary tube, and then measured the temperature at which it re-solidified on cooling (44).

On two other occasions, in 1852 and 1855, Heintz described in detail his method for determining accurate melting points. His thermometer was made by the prominent glassblower Heinrich Geisler, and had a small bulb (10 □ 4 mm), allowing it quickly to assume the surrounding temperature. The scale was divided into 1/5°C increments, and allowed him to establish temperatures within 1/20°C with the naked eye (45). To take a melting point, Heintz first melted the acid in a water bath and sucked some of the molten solid into a "capillary tube with the thinnest possible walls, made from already thin-walled gas inlet tube." The acid solidified in the capillary tube and it was then attached to the thermometer such that it touched the bulb. The assembly was then placed in a beaker (*Becherglas*) full of water and the temperature gradually increased to the moment when the acid became transparent where the capillary touched the bulb of the thermometer. This temperature was then the melting point of the acid (46).

Heintz emphasized that it was important to have a fully calibrated, accurate thermometer, since small differences in melting point could indicate a substantial difference in the purity of the sample, and that no other methods would be sufficient for determining purity of the fatty acids, for "otherwise agreement with my results will be difficult to obtain, and the melting point might indicate a pure acid, when it certainly is not" (47). Heintz's detailed description of his melting point technique would seem to indicate its novelty, and Wislicenus and Richard Meyer suggested later that Heintz was among the first chemists to use the constancy of the melting point as a criterion for a compound's purity (48). But this is clearly not true, as Heintz himself explicitly noted that the accepted technique for identifying purity of the fatty acids was repeated crystallization until a constant melting point was reached (49).

The origins of the melting point as an accepted standard for chemical species identification remain unclear. Melting points for inorganic compounds do appear in textbooks fairly early. In the first volume of his 1821 *Lehrbuch*, Berzelius listed the melting points of mercury, wax, tin, lead, copper and iron, and in his 1844 textbook, Eilhard Mitserlich listed the melting points of sulfur, selenium and phosphorous (50). The first use of melting points for organic compounds is more difficult to determine. Chevreul himself, of course, recorded specific melting points as identifying properties for the fats and fatty acids, and in their 1832 paper on the benzoyl radical, Liebig and Wöhler casually mention the melting point of benzamide as 115°C (51). It may be that fatty acids were routinely characterized by melting point following Chevreul's example, and chemists used melting points for other organic compounds only irregularly.

Literature references to early techniques for measuring melting points seem to be even more obscure than the first literature appearance of melting points. Berzelius, Mitserlich, Liebig and Wohler, and Chevreul did not describe their technique for measuring melting points, or even discuss it as a novel means of identification, suggesting that melting points were already used for identification by the 1820s, and the technique for measurement was not unusual enough to discuss. On the other hand, Heintz thought his technique for measuring melting points original enough to describe in detail twice (52). Heintz therefore appears to belong to an existing tradition of measuring and using melting points, but we are still far from understanding the process by which this technique, and its counterpart the boiling point, became standardized among chemists for defining a chemical species (53).

References and Notes

1. Presented at the 244th National Meeting of the American Chemical Society, Philadelphia, PA, August 19, 2012, HIST 2.
2. A. B. Costa, *Michel Eugène Chevreul, Pioneer of Organic Chemistry,* Wisconsin State Historical Society, Madison, WI, 1962. Costa briefly described Heintz's work on the fats (pp 74-76), but did not provide a significant analysis of its origins or Heintz's train of thought.
3. J. Wislicenus, "Wilhelm Heintz," *Berichte,* **1883**, *16*, 3121-3140.

4. H. M. Leicester, “Kekulé, Butlerov, Markovnikov: Controversies on Chemical Structure from 1860 to 1870,” in O. T. Benfey, Ed., *Kekulé Centennial*, American Chemical Society, Washington, DC, 1966, pp 13-23 (pp. 18-19); W. Heintz, “Zur Lehre der chemischen Structur,” *Zeit. Chem.,* **1865**, *8*, 408; Ref. 3, 3134.
5. W. Heintz, *Lehrbuch der Zoochemie,* Reimer, Berlin, 1853. *Zoochemie* was the first and only book in a planned series on physiogical chemistry (3). Heintz’s only other contribution to a book was with his assistant Wilhelm Bär on the elemental composition of fuels for Phillip Wilhelm Brix’s 1853 volume on the caloric power of fuels in Prussia: P. W. Brix and W. Heintz, *Untersuchungen über die Heizkraft der Wichtigeren Brennstoffe des Preußischen Staats,* Ernst and Cohn, Berlin, 1853.
6. Ref. 3, p 3122.
7. W. Heintz, *De acido saccharico eiusque salibus,* Schlesinger, Berolini, 1844.
8. R. Meyer, *Vorlesungen über die Geschichte der Chemie,* Akademische Verlagsgesellschaft, Leipzig, 1922, p 165; Ref. 3, p 3124.
9. W. Heintz, “Ammoniakgehalt des Harnes,” *Zeit. ges. Naturw.,* **1855**, *5*, 366-369; W. Heintz, “Auffindung des Kreatins im Harne,” *Ann. Chem.,* **1847**, *70*, 466-480; W. Heintz, “Rechtfertigung der Methode, den Harnstoff aus der Quantität des aus ihm erzeugten Ammoniaks zu bestimmen,” *J. prakt. Chem.,* **1847**, *41*, 282-284; W. Heintz, “Über die harnsauren Sedimente,” *Ann. Chem.,* **1845**, *55*, 45-78; W. Heintz, “Über die quantitative Bestimmung des Harnstoffs, des Kalis und Ammoniaks im Harne,” *Pogg. Ann. Phys. Chem.,* **1845**, *66*, 114-160.
10. W. Heintz, “Quantitative Bestimmung der Aschenbestandtheile thierischer Substanzen I,” *Pogg. Ann. Phys. Chem.,* **1847**, *72*, 113-155; W. Heintz, “Quantitative Bestimmung der Aschenbestandtheile thierischer Substanzen II,” *Pogg. Ann. Phys. Chem.,* **1848**, *73*, 455-461; W. Heintz, “Untersuchung des flüssigen Inhalts der Echinococcenbälge (Hydatinbälge) einer Frau Echinococcenflüssigkeit,” *Jenaische Ann. Phys. Med.,* **1850**, *1*, 180-191; W. Heintz, “Zusammensetzung der Knochenerde,” *Pogg. Ann. Phys. Chem.,* **1849**, *77*, 267-287; W. Heintz, “Bestimmung des Harnstoffs im Harn und Zusammensetzung des salpetersauren Harnstoffs,” *Berichte der Berliner Akademie,* **1845**, 277-282.
11. M. E. Chevreul, *Recherches chimiques sur les corps gras d’origine animale,* Levrault, Paris, 1823. M. E. Chevreul, *A Chemical Study of Oils and Fats of Animal Origin,* translated by G. R. List and J. Wisniak. AOCS Press, Urbana, 2009. On Chevreul, see Costa, Ref. 2, and A. J. Dijkstra, “How Chevreul (1786-1889) Based His Conclusions on His Analytical Results,” *Oleagineux, Corps Gras, Lipides*, **2009**, *16*, 8-13.
12. A. J. Rocke, *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry*, MIT Press, Cambridge, MA, 2000. pp 200-201.
13. W. Heintz, “Ueber die Fette,” *J. prakt. Chem.,* **1855**, *66*, 1-51, p 3. A slightly modified version appeared later in the *Zeitschrift für die gesammten Naturwissenschaften*. W. Heintz, “Über die Fette,” *Z. ges. Naturw., 6,* **1855**, 279-307.
14. Ref. 3, p 3131. “klare Anschauung von der Art, wie Heintz arbeitete,” ... “Experimentaluntersuchung verfolgten Weg.”
15. Heintz’s earliest communication on the fats, concerning tallow, appeared in 1849 in the proceedings of the Prussian Academy. W. Heintz, “Beobachtungen über das Schmelzen von Stearin aus Hammeltalg,” *Monatsberichte der Königlich Preußischen Akademie der Wissenschaften zu Berlin,* **1849**, 222.
16. W. Heintz, “Ueber die Zusammensetzung des Menschenfetts,” *Pogg. Ann. Phys. Chem.,* **1851**, *84*, 238-261, p 239.
17. Ibid., p 244. “Dieser Umstand verbunden mit dem, dass die bisher angewendete Methode der Scheidung der fetten Säuren, auf die aus dem Menschenfett gewonnenen angewendet, nicht einmal die Reindarstellung auch nur *einer* derselben gestaltet, nöthigte mich, nach einer andern Trennungsmethode derselben zu forschen Lange und vielfach habe ich mich bemüht, die gewöhnlich gebräuchlichen Principien der Scheidung auf die feiten Säuren anzuwenden, aber stets ohne Erfolg, wie zu erwarten, weil ja bekannt ist, wie außerordentlich ähnlich, man möchte fast sagen gleich, sich die Verbindungen der verschiedenen feiten Säuren mit derselben Basis gegen Auflösungsmittel verhalten.”
18. J. Liebig, “Ueber die Trennung einiger Säuren der Reihe $(CH)_nO_4$,” *Ann. Chem.,* **1849**, *71*, 355-357.
19. W. Heintz, “Ueber eine neue allgemeine Trennungsmethode solcher Körper, welche sich in ihren Eigenschaften sehr nahe stehen,” *Pogg. Ann. Phys. Chem.,* **1851**, *84*, 221-237, pp 225-226. “Diese Gedankenfolge, deren allgemeines Resultat also das war, dass bei jener von Liebig angegebenen Scheidungsmethode der Verwandtschaftsgrad von wesentlichstem Einfluss ist, führte mich auf die Idee zu versuchen, ob es nicht gelingen sollte, eben durch den Grad der Verwandtschaft solche Körper von einander zu trennen, deren Eigenschaften sowohl, wenn sie sich im freien Zustande befinden, als wenn sie an andere Substanzen gebunden sind, sich so nahe kommen, dass man sie bisher nicht oder nur unvollkommen zu scheiden vermochte. Ich dachte hierbei zunächst an die festen fetten Säuren, mit denen ich mich schon seit längerer Zeit erfolglos beschäftigte eben weil die bis dahin angewendeten Methoden so höchst unvollkommen waren.”
20. Ref. 19, pp 226-227.
21. W. Heintz, “Über die Zusammensetzung des Hammeltalgs, des Menschenfetts und des Wallraths,” *Pogg. Ann. Phys. Chem.,* **1852**, *87*, 553-587, pp 571-572. “Diese Resultate meiner Versuche brachten mich endlich auf den Gedanken, dass die Anthropinsäure ungeachtet ihrer grossen Fähigkeit zu krystallisiren, ein Gemenge von Stearinsäure und Margarinsäure seyn möchte.” Heintz noted that had the amounts of anthropic acid from human fat been greater, he would have noticed it was a

mixture much earlier. It was the quantities of anthropic acid from mutton tallow that allowed him to determine that it produced two fractions with similar melting points but different compositions.

22. Ibid., p 572. "durchaus wie die Säure, die ich Anthropinsäure genannt hatte."
23. Ibid., p 573. "welches in *allen Eigenschaften*, namentlich in der Art zu krystallisiren, wenn es aus dem geschmolzenen Zustande in den festen übergeht, und im Schmelzpunkt, der bei 56°,3 C. liegt, mit der Anthropinsäure übereinstimmt." Heintz's emphasis.
24. Ibid., p 574. "Dieser Versuch ist mit Palmitinsäure und Stearinsäure von verschiedenem Ursprung so oft wiederholt worden, dass ich ihn nicht mehr bezweifeln kann."
25. W. Heintz, "Über den Wallrath," *Pogg. Ann. Phys. Chem.,* **1852**, *87*, 21-44, 267-293.
26. J. Lerch, "Ueber die flüchtigen Säuren der Butter," *Ann. Chem.,* **1844**, *49*, 212-31. Formulas are given using Heintz's atomic weights, where C = 6 and O = 8.
27. W. Heintz, "Über die Butter," *Pogg. Ann. Phys. Chem.,* **1853**, *90*, 137-165, p 162 "daß in den Verseifungsprodukten der Fette überhaupt nur solche Säuren vorkommen, deren Kohlenstoffatomzahl durch 4 theilbar ist." This corresponds to the modern "law" that naturally occurring fatty acids usually exist in multiples of two, although modern methods have detected small quantities of fatty acids with an odd number of carbon atoms.
28. Ibid., p 163.
29. W. Heintz, "Über den Wallrath," *Pogg. Ann. Phys. Chem.,* **1854**, *92*, 429-451; 588-612, pp 440-441. Myristic acid was first isolated from nutmeg by Lyon Playfair in 1841, but Heintz renamed it. L. Playfair, "Ueber das feste Fett der Muskatbutter," *Ann. Chem.,* **1841**, *37*, 152-164.
30. Heintz, Ref. 29, p 591. "analoge Gemische der verschiedenen Säuren vollkommen analog verhalten."
31. Heintz, Ref. 29, p 593. "Will man den Einfluss der Mischung auf den Schmelzpunkt der Säuregemische durch Curven ausdrücken, und verlegt man zu dem Ende den Anfangspunkt derselben von der leichter schmelzenden Säure ausgehend, in die Abscisse, so wird in allen Fällen die Curve zuerst unter dieselbe herabsinken, dann sich wieder nach oben wenden, die Abscisse schneiden und nun allmälig über dieselbe hinaussteigen. Diese Curve bleibt für je zwei Säuren, die sich um C_4H_4 und die sich um C_8H_8 unterscheiden, nahezu dieselbe. Je grösser aber der Unterschied der Zusammensetzung: der beiden Säuren ist, um so früher tritt der tiefste Punkt der Curven ein."
32. W. Heintz, "Ueber die Margarinsäure," *Pogg. Ann. Phys. Chem.,* **1857**, 257-289. Modern methods have detected small amounts of a naturally occurring fatty acid with 17 carbons.
33. Ref. 13, p 7.
34. Heintz, Ref. 29, p 595. "Es müßten ferner die Verhältnisse, in welchen die beiden Säuren gemischt werden müssen, um ein Gemisch darzustellen, das einen möglichst niedrigen Schmelzpunkt besitzt, dem Gewichtsverhältniß einfacher Atomzahlen entsprechen, was ebenfalls nicht zutrifft." Heintz is using the word "Atom" here in the modern sense of "molecule."
35. Ref. 13, p 17. "Es ist demnach zweifellos, dass nicht in der Bildung chemischer Verbindungen, sondern in dem physikalischen Verhalten der Atome allein der Grund für die beobachteten Erscheinungen gesucht werden muss."
36. "erstaunlicher Ausdauer" Wislicenus, Ref. 3, p 3126. "… hohe Virtuosität, zu welcher er die Handhabung [manipulation] dieses Verfahrens ausbildete," E. v. Meyer, in E. Korschelt, et al., *Handwörterbuch der Naturwissenschaften*, vol. 5, Fischer, Jena, 1914, p 300. T. H. N., "Wilhelm Heintz," *Nature,* **1881**, 245-246, p 245.
37. Heintz, Ref. 29, p 598. "Bis zu meinen Arbeiten hat man aber kein anderes Reinigungsmittel gekannt, als das Umkrystallisiren. Wenn der Schmelzpunkt durch Wiederholung dieser Operation sich nicht mehr änderte, so glaubte man auf die Reinheit der Säure schliessen zu dürfen. Dass dieser Schluss nicht unter allen Umständen richtig ist, haben meine Untersuchungen dargethan. Ich habe aber schon früher ein Mittel kennen gelehrt, um in dem Falle, wenn das des Umkrystallisirens nicht ausreicht, sich doch von der Reinheit einer Säure zu überzeugen, und mit Hülfe desselben die Gemischtheit der Margarinsäure, Aethalsäure, Anthropinsäure dargethan."
    Heintz, Ref. 13, p 3. "Man hatte bis dahin für die Reinheit einer fetten Säure nur das eine Merkzeichen, dass durch Umkrystallisiren ihr Schmelzpunkt nicht mehr erhöht werden konnte."
38. Ref. 11, p 301. This passage was emphasized by Chevreul.
39. Ref. 19, p 221. "Seitdem die Chemie sich zu einer Wissenschaft zu erheben anfing, war es das eifrigste Bestreben aller derer, welche sie zu fördern zu ihrem Lebensziele setzten, die Methoden der Untersuchung zu vervollkommnen und zu vermehren. Man sollte daher kaum glauben, dass jetzt noch es möglich ist, eine in ihrem Principe gänzlich neue Methode zu ersinnen."
40. Ref. 11, 82-83. The melting point of oleic acid is 13-14°C, and therefore a liquid at room temperature.
41. J. Gottlieb, "Untersuchung Des Gänsefettes und der Oelsäure," *Ann. Chem.,* **1846**, *57*, 33-67, pp 34-37.
42. Although he did not use the term, Heintz is describing what today is called the eutectic point of a mixture.
43. Heintz, Ref. 29, p 597-598. "Die fetten Säuren verhalten sich daher durchaus ähnlich wie die Metalle. Durch Vermischen von zwei Metallen sinkt der Schmelzpunkt oft bedeutend und wenn noch ein drittes hinzugesetzt wird, so geht der Schmelzpunkt häufig von Neuem bedeutend herunter. Ich erinnere hier nur an das Rose'sche, Newton'sche, Lichtenberg'sche Metallgemisch, das aus Blei, Zinn und Wismuth bestehend, im kochenden Wasser schmilzt." Unfortunately, neither Heintz nor Gottlieb gave a literature citation for this curious phenomenon.
44. Ref. 16, p 239. "Wurde etwas desselben auf einer Thermometerkugel geschmelzt, so war es beim allmäligen Erkalten noch bei 50° C. dünnflüssig, wurde aber allmälig immer dicklicher, überzog sich bei 46° C. mit einer Haut,

floss bei 45° C. nicht mehr, wurde aber erst bei 42°-43° C. trübe und undurchsichtig. Diese Erscheinung wiederholte sich vollkommen mit einer neu dargestellten Portion dieses Fettes. Wurde dagegen sein Schmelzpunkt bestimmt, indem man es in einem Capillarrohr unter Wasser erhitzte, so wurde es erst bei 53° C. flüssig, die geschmolzene Masse trübte sich jedoch erst wieder bei 44° C."

45. Ref. 21, p 583.
46. Ref. 13, p 23. "möglichst dünnwandiges Capillarrohr, das man durch schnelles Ausziehen eines schon dünnwandigen Gasleitungsrohrs erhält." Heintz did not use the modern standard of reporting a melting point range.
47. Ibid. "sonst eine Uebereinstimmung mit meinen Resultaten schwerlich erzielt werden würde, und man daher nach dem Schmelzpunkt eine Säure für rein halten würde, die es keineswegs ist."
48. Meyer, Ref. 8, p 165. Wislicenus, Ref. 2, p 3126.
49. W. Heintz, "Über die Fette," *Zeit. ges. Naturw.,* **1855**, *6*, 279-307, p 280
50. E. Mitserlich, *Lehrbuch der Chemie,* Mittler, Berlin, 1844, pp 50, 61, and 64; J. Berzelius, *Lehrbuch der Chemie,* 6 vols. Vol. 1, Macken, Reutlingen, 1821, pp 38-39.
51. Liebig and Wöhler wrote simply: "At 115°C [benzamide] melts to a water-like liquid, which congeals by cooling to a large-leaved crystalline mass, …" J. Liebig and F. Wöhler, "Untersuchungen über des Radikal der Benzoesäure," *Ann. Pharm.,* **1832**, *3*, 249-287, translated in O. T. Benfey, Ed., *Classics in the Theory of Chemical Combination*, Dover Publications, New York, 1963, p 29. Timmermans implies that Liebig and Wöhler were the first to use the melting point, although he does not present a systematic study of the literature. J. Timmermans, *The Concept of Species in Chemistry,* translated by R. Oesper, Chemical Publication Company, New York, 1963. See also W. B. Jensen, "Melting Points and the Characterization of Organic Compounds," *J. Chem. Educ.,* **2009**, *86*, 22-23.
52. Heintz's description of his melting point technique is the earliest I have seen, although almost certainly there must be earlier descriptions. Later descriptions of melting point apparatus include J. Piccard, "Zur Bestimmung Des Schmelzpunkts," *Berichte,* **1875**, *8*, 687-689, and C. F. Roth, "Ein neuer Apparat zur Bestimmung von Schmelzpunkten," *Berichte,* **1886**, *19*, 1970-1973. In 1893, Walther Nernst wrote a comprehensive survey on boiling and melting points, but did not extensively discuss techniques. W. Nernst and A. Hesse, *Siede- und Schmelzpunkt, ihre Theorie und praktische Verwerthung mit besonderer Berücksichtigung organischer Verbindungen,* Vieweg, Braunschweig, 1893.
53. The most comprehensive studies of thermometry are by Chang and Middleton, but neither discusses the melting point. H. Chang, *Inventing Temperature: Measurement and Scientific Progress,* Oxford University Press, New York, 2004. W. E. K. Middleton, *A History of the Thermometer and Its Use in Meteorology,* Johns Hopkins University Press, Baltimore, 1966. For an excellent discussion of chemical species identity, see J. Schummer, "The iImpact of iInstrumentation on cChemical sSpecies iIdentity from cChemical sSubstances to mMolecular sSpecies," in P. J. T. Morris, Ed., *From Classical to Modern Chemistry: The Instrumental Revolution*, edited by P. J. T. Morris, pp. 188-211, Chemical Heritage Foundation, Philadelphia, 2002.

About the Author

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150 YEARS AFTER THEIR EMERGENCE: A NEW LOOK AT LOSCHMIDT'S REPRESENTATIONS OF BENZENE

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Abstract

A new examination of structures that Loschmidt considered for benzene derivatives, notably naphthalene and "rings" doubly bonded to O or triply bonded to N, show conclusively that Loschmidt did not view benzene as a planar ring of six carbon atoms.

Introduction

August Kekulé has long been credited with several major contributions to structural organic chemistry: recognizing the tetravalence of carbon (1857) (1,2); recognizing that carbon atoms combine with one another to form chains (1858) (3); and recognizing the structure of benzene (1865) (4), in the view of Japp, the "crowning achievement of the doctrine of the linking of atoms" (5). Kekulé's work on benzene provided a major stimulus to research in aromatic chemistry, causing an unprecedented growth in this field; it coincided with an explosive growth in the application of aromatic compounds, e.g., as synthetic dyes (6), pharmaceuticals (7), or explosives (8). The majority of Kekulé's contemporaries gave him credit for major accomplishments and, in essence, attributed to him the birth of structural organic chemistry.

Contemporary critics included the formidable Hermann Kolbe (9), and the science historian Ernst von Meyer (Kolbe's son in-law): Kolbe voiced opposition to Kekulé's theories, because, in the summary of Alan Rocke, they were "at once too empirical and too speculative" (10); von Meyer criticized Kekulé for not giving credit to Frankland for the concept of valence or to Kolbe or for his many contributions (11).

More recent criticism has its roots in the work of Kekulé's biographer and successor on the Chair in Bonn, Richard Anschütz. While compiling material for his two-volume Kekulé biography (12), Anschütz found references to Couper (13), who had developed the idea of linking carbon atoms independent of Kekulé; he also noticed a footnote in Kekulé's 1865 paper concerning structural formulae by Loschmidt. This 1861 article (14) had been published outside of the established chemical literature and was not readily available. Anschütz noted that Loschmidt's booklet was hard to read (15); therefore, he had the entire work reprinted (16) with copious comments, including 208 footnotes with many references (Loschmidt's paper didn't cite any literature), and with several "improved," i.e., revised structures. Most importantly he inserted the formulae into the text, making the work much easier to read.

In the 1980s new criticism arose from two quarters: Wotiz and Rudofsky attacked Kekulé's priority claims in general, and the benzene structure in particular (17); and Wiswesser, having discovered the work of Loschmidt, hailed him as a "forgotten genius" (18). This criticism reached its climax in *The Kekulé Riddle* (19), a 1993 volume with 19 contributions under the motto "Pravda vítêzí" ("truth prevails"). Coincidentally, in 1995 a symposium was held to commemorate the centennial of Loschmidt's death, in which 33 papers addressed his contributions to chemistry and physics (20).

The recent criticism of Kekulé focuses on a range of questions: (a) does Kekulé deserve credit for recognizing the tetravalency of carbon, C = 12 (1,2), or does Kolbe, who implied tetravalency for the double-equivalent, C_2 (C = 6), just barely later (21)? (b) Does Kekulé deserve credit for realizing that carbon atoms can form chains (2,3) or does Couper (13), who developed the concept independently, whose formulae were "nearer to our present formulae" (5), and who "intended them to be constitutional formulae (5)? (c) Did Loschmidt (14) conceive a cyclic structure for benzene four years before Kekulé? And (d) was Kekulé inspired by dreams (22) or did he fashion his benzene structure after a pictogram of Loschmidt's and fraudulently invent dreams to support his priority claims (17)?

In this paper I will review these issues, in particular the formulae that Loschmidt offered for benzene and selected derivatives to weigh whether they support the claim that Loschmidt viewed benzene as a cyclic array of six carbon atoms. An evaluation of the structures provides strong arguments that Loschmidt did not consider the nature of benzene in such terms. Some of these arguments, as far as I am aware, have not been advanced before.

Tetravalence of Carbon and Linking of Carbon Atoms

In considering the first two points, recognizing the tetravalency of carbon (1) and realizing that carbon atoms can form chains (2,3), the opinion of Kekulé's contemporary Ernst von Meyer, is illuminating. Meyer's *Geschichte der organischen Chemie* (11), according to R. E. Oesper, is "among the late works that can rightfully be considered to be fairly complete" (23). Meyer (correctly) credited Frankland (24) with the concept of a specific valence for different atoms (25). He viewed Kekulé's train of thoughts that led to the conclusion that carbon is tetravalent "almost identical" ("fast der gleiche") to Frankland's. Thus, he was unwilling to credit Kekulé with a *major* accomplishment in this area. Frankland (obviously) agreed with this conclusion; in his *Experimental Researches* (26) he correctly claimed credit for the general concept of valence: "This hypothesis ...constitutes the basis of what has since been called the doctrine of atomicity or equivalence of elements; and it was, so far as I am aware, the first announcement of this doctrine." It is hard to argue with the view pronounced by von Meyer or Frankland.

Still, von Meyer conceded that the scientific community was slow in reaching the obvious conclusion, and that a "specific valence of carbon had remained unformulated for an extended period of time" ("blieb die bestimmte Auffassung seiner Valenz längere Zeit unausgesprochen") (25). The merit of having enunciated the tetravalence of carbon he accorded to Kekulé. Recent claims that Couper had "proposed the tetravalence of carbon" before Kekulé (15) are without merit as Kekulé's 1957 paper (1a) was published a full year before Couper's (13). Obviously, Loschmidt cannot be credited with having derived the tetravalency of carbon because his paper (14) appeared several years after Kekulé's (1) as well as Couper's (13), at a time when new insights were gained in rapid succession (27).

Concerning the linking of carbon atoms, von Meyer gave Kekulé credit for having developed this concept and, thereby, having advanced structural theory (25):

> Kekulé's merit ... lies in the fact that he tried to understand the way in which two or more carbon atoms link with each other and saturate their affinities. (Kekulé's Verdienst ... muß darin gesucht werden daß er der Frage nach der Art wie sich zwei und mehr Kohlenstoffatome miteinander verbinden und ihre Affinitäten sättigen auf den Grund zu gehen suchte.)

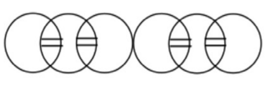
In the area of recognizing the ability of carbon atoms to form chains, both von Meyer (28) and Japp (5) argued that Couper deserves a share of the credit for having recognized this concept independently. Apparently, Couper's work was not completely unknown in the 1890s, although, obviously, it was to Anschütz. A century later Bader (15) and Rocke (27) provided evidence that Couper gave his manuscript to Wurtz for presentation to the French Académie before Kekulé's paper was published. Bader's statement to the effect that "Wurtz failed to do that" (present Couper's paper before the Academie) is, of course, correct; one should note, though, that Wurtz was not a member in 1858. In any event, Couper's papers (13) appeared after Kekulé's 1858 paper (3).

Loschmidt's Benzene Formulae and Their Meaning

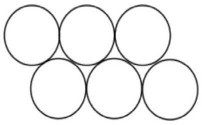
Dr Jos. Loschmidt

Figure 1*. Johann Joseph Loschmidt, best known as a physicist for his 1865 estimate of the size of air molecules and for the determination of the number of molecules in a macroscopic sample. His contributions to organic chemistry were published outside of the scientific mainstream of his time and were essentially ignored by his contemporaries.*

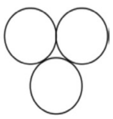
In 1861 J. J. Loschmidt (Figure 1) published a compilation of structures that allowed the direct visualization of the constitution of molecules, i.e., the connectivity of their atoms. This monograph (14) shows a detailed knowledge and deep understanding of many aspects of organic chemistry, though it does not contain a single reference. Among the numerous compounds for which Loschmidt offered structures, he recognized that benzene posed an especially difficult structural problem. He considered two structures in detail, describing them in 131 and 120 words, respectively. The first structure (29), 1,2,4,5-hexatetraene (bisallene, L 181), had been considered previously by Couper (13), and would "materialize" only more than 100 years later (30); the second structure was composed of fused three-membered rings without double bonds; tetracyclo[$3.1.0.0^{1,4}.0^{2,4}$]hexane, as current IUPAC nomenclature would name it, has yet to "materialize." Loschmidt recognized that the known reactivity of benzene was incompatible with formula L 181; therefore he favored the tetracyclic structure, L 182.



L 181



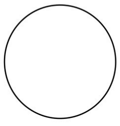
L 182



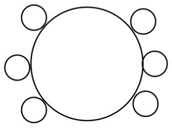
L 68

He thought the "compressed" nature ("Verdichtung") of benzene less important, but considered the layered nature ("Schichtung") its key feature. He viewed this formula as a doubled allyl nucleus ("doppelte Allylkern"), i.e., composed of two fragments of L 68, an array he offered as an alternative structure for propylene and allyl derivatives.

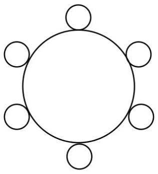
Alas, Loschmidt refrained from taking a firm position on the details of the benzene structure because he didn't think that the available results ("nach dem bis jetzt vorliegenden") supported formula L 182 unambiguously. Accordingly, he chose a non-committal formula, representing the benzene nucleus as a "hexavalent element" ("sechsstelliges Element") (L 184) and benzene as L 185, describing the provisional character of this structure in a mere twenty words. In this context one should note that structure **1**, shown on the cover of *The Kekulé Riddle* (19) and a similar structure offered by M. Kohn (31) are deceptive adaptations without precedent in Loschmidt's work.



L 184



L 185



1

As Schiemenz (32,33) and Heilbronner and Hafner (34) have pointed out, the key to Loschmidt's benzene structure lies in his understanding of the term "element." In the introductory pages of his booklet (35) Loschmidt unambiguously defined the "atom" as the center of a sphere, represented by a circle, i.e., its projection onto a plane. By this clear definition the circle in structures L 184 and L 185 represents an "atom," not a "ring of six carbon atoms." Significantly, this is exactly how Anschütz saw Loschmidt's structures (36): "in contrast to Kekulé he [Loschmidt] considered the benzene nucleus an array that behaves as a hexavalent element" ("im Gegensatz zu Kekulé sah er [Loschmidt] in dem Benzolkern ein Gebilde das sich wie ein sechswertiges Element verhält").

Loschmidt's contemporaries either ignored or didn't know of Loschmidt's booklet. Textbooks of the second half of the 19th century did not cite Loschmidt's work (11, 27-39); only when Anschütz became editor of von Richter's text (40) were Loschmidt's formulae incorporated. However, Anschütz emphasized: "He does not address the equivalence of the six benzene hydrogens, it was incompatible with the assumption that benzene consists of two allyl-(trimethylene) rings ..." ("Ueber die

Gleichwertigkeit der sechs Benzolwasserstoffatome sagt er [Loschmidt] nichts aus, sie war bei der Annahme, dass das Benzol aus zwei geschichteten Allyl-(Trimethylen) Ringen besteht, ausgeschlossen ...") Carl Graebe concluded: "His work was essentially ignored and has had no impact on the development of organic chemistry." ("Seine Ausführungen [sind] so gut wie unbeachtet geblieben und haben auf die Entwicklung der organischen Chemie keinen Einfluss ausgeübt" (41).) Half a century later A. J. Ihde called Loschmidt's work "an unheralded attempt to establish the theoretical foundations of structural chemistry ...because of its limited circulation [it] was never widely known" (42).

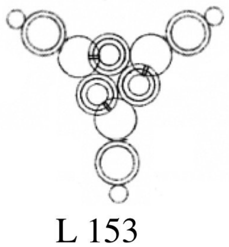
Beginning in the 1980s some authors (15,17,18,43) have chosen to ignore Loschmidt's definition (and that of his 20th-century discoverer, Anschütz) and interpret the circle in L 184 as a ring of six carbons. If this assertion could be supported, Kekulé's benzene structure of 1865 (4) would be a decided second to Loschmidt's (14) and the commonly held historical view surely would have to be revised. However, the revisionist arguments have been met by several well-reasoned, thorough, and (at least to this author) convincing challenges.

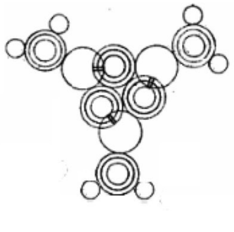
G. Schiemenz followed the developing arguments for Loschmidt's priority in detail, beginning with Anschütz's revision, and summarized the results as "the birth of a legend" (32). He also surveyed the use of spheres for atoms in the mid-1800s and concluded that Loschmidt's structures were not exceptional (33). Heilbronner and Hafner reviewed the development of structural chemistry in the 19th century (34); concerning Loschmidt's benzene formula, and its recent interpretation as representing a ring of six carbons, they concluded: "it is hard to understand how an unambiguous statement [by Loschmidt] could be misunderstood so completely" (34) [by the authors of Refs. 15, 17, 18, and 43]. Rocke analyzed the use of structural images in the development of structural chemistry and concluded that Kekulé, and not Loschmidt, made significant contributions to the foundation of structural chemistry, including the benzene structure (27). The weight of these rebuttals appears strong, even overwhelming. Yet they have not silenced the revisionist view; in fact, new authors support this view (44,45), even if without additional arguments.

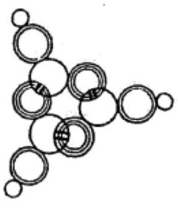
In a possibly vain attempt, to stem this tide, I wish to add to the argument in favor of Kekulé's achievement; this attempt is based solely on Loschmidt's structures and on the language he uses to describe them. In my view the priority claims in favor of Loschmidt are an interesting case of scientific anachronism. Loschmidt's contemporaries were not prepared to see a connection between a circle (his "hexavalent element") and an aromatic structure (even if they had studied the booklet in any detail); neither Anschütz nor Graebe viewed Loschmidt's non-committal circle as a ring structure. Could it be that a half-century of exposure to the circle, that Robinson introduced in 1925 as a symbol of aromaticity (46), conditioned Loschmidt's champions for their conclusion (15,17,18,43-45) and that their response could be seen as an example of a conditioned reflex?

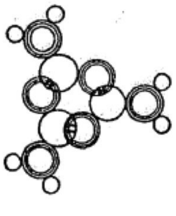
The principal argument advanced in this paper against Loschmidt having conceived benzene as "a ring of six carbons" is based on the language Loschmidt uses to present structures L 184 and L 185. Loschmidt clearly conceded that it was "impossible to derive an unambiguous result from the available information ("ist es nach dem bis jetzt Vorliegenden unmöglich, hierüber zu einem definitiven Resultat zu gelangen"). Therefore, he postponed (held "in suspenso") assigning a structure and chose a non-committal symbol. Loschmidt used the subjunctive (Konjunktiv) "*as if it were* a hexavalent element" ("*als ob er* ein sechsstelliges Element *wäre*") [emphasis added] and fell short of using the affirmative indicative mode (Indikativ), such as, "Benzol hat die Ringstruktur 184" ("benzene has the ring structure 184"). Having refrained from assigning a structure he chose the circle (L 184) as a temporary representation without implying a relationship to the actual structure.

As a further argument we point to the failure to show the individual atoms. Loschmidt discussed and depicted the linear tetraene, L 181, and the tetracyclic benzene formula, L 182, in detail; he showed compounds, such as cyanuric acid, L 153, and melamine, L 154, as well as eleven of their derivatives as six-atom arrays. (Structures A 153 and A 154, reminiscent of Kekulé's cyclohexatriene structure, are revisions created by Anschütz (16).) Loschmidt also showed all six individual carbon atoms for the perceived six-membered ring of "diethylenedi-

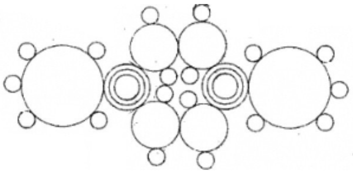

L 153


L 154

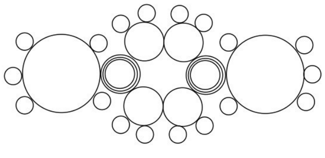

A 153


A 154

phenyl diamine," L 237 (also "cleaned up" by Anschütz).

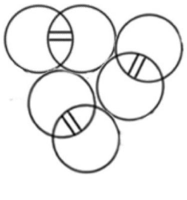


L 237

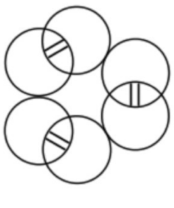


A 237

It appears inconceivable that Loschmidt would have failed to describe and depict the unprecedented planar cyclic benzene structure in similar detail, had he actually conceived of it. He surely would have given the revolutionary ring structure a more detailed pictogram, perhaps formula **2**, akin to L 153 and L 154, perhaps even a cyclohexatriene formula, **3**. The absence of any such formula for benzene argues strongly against Loschmidt understanding benzene as a planar monocycle.



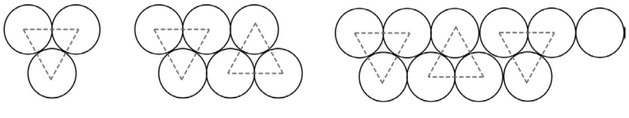
2



3

Furthermore, we note that Loschmidt did not comment on the arrangement of the carbon atoms in this "element"; he referred to the six-carbon unit as an "atom complex Є_{6}," not once as a "ring." Only in the discussion of the cyclic allyl structure, L 68, did he call a cyclic structure the "akzeptabelste Supposition" ("the most acceptable proposal") for phenyl. However, there can be little doubt that the term "cyclic" refers to the cyclic allyl subunit (L 68) of the "doubled allyl" structure (L 182) and not to a benzene monocycle. He did discuss the putative "para"-isomer of benzene ("known" at the time, but soon discarded as erroneous); Loschmidt assumed for the "Kern" (nucleus) of para-benzene a "somewhat changed configuration." This fact again supports the view that he saw benzene as a six-carbon cluster (with unspecified configuration).

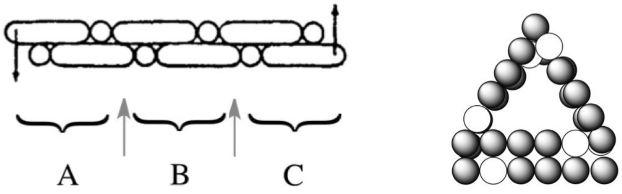
Elaborating on his preferred benzene constitution, L 182, Loschmidt considered two unsaturated Є-10 compounds, naphthalene ($\text{Є}_{10}H_{8}$) and "terpentin" ($\text{Є}_{10}H_{16}$); he recognized the terpene as "related to the vinyl function" and naphthalene as related to benzene. Alas, the relationship he envisioned between benzene and naphthalene does not support his understanding of benzene as a ring of six carbons. In analogy to the "layered" benzene, L 182, he considered naphthalene to be a "verdreifachtes" (threefold) allyl system, bearing a methyl group (L 183; Figure 2). In essence, he viewed naphthalene, as a homologue of toluene, the methyl-substituted "doubled allyl." The proposed naphthalene structure, L 183, is irreconcilable with the notion of benzene as a "ring of six carbon atoms."



L 68 L 182 L 183

Figure 2. Loschmidt's representation of cyclic allyl, benzene nucleus, and naphthalene nucleus; the dashed lines have been added to emphasize the "layered" "allyl" units.

To contemporaries wrestling with understanding the various structural representations of molecules, Loschmidt's preferred "layered" benzene formula (L182) may have been reminiscent of a structure that Kekulé offered for benzene in his textbook (47), in essence a three-dimensional cyclic version of the "benzine" (**4**) of his original publication (4) (Figure 3). Rotating the segments A and C around the C–C single bonds (denoted by red arrows) by 120° and –120°, respectively, results in the triangular structure, **5**, where Kekulé's two black arrows (in structure **4**) form the final C–C bond closing the ring. Of course, it is obvious to today's reader that the perceived two-layer structure is an artefact of the "sausage" structures used by Kekulé.

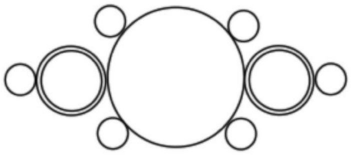


4 **5**

***Figure 3**. Two pictograms offered by Kekulé for benzene (4a,47). The first structure is dissected into two-carbon units; rotation of segments A and C by 120° and –120°, respectively, around the single bonds (above the light arrows) allows the free valences (black arrows) to form the final C–C bond, closing the ring. In the second structure Kekulé's "sausage" C atoms are shown as linear arrays of four filled circles, H atoms as single open circles.*

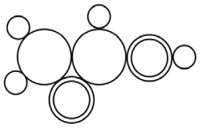
Benzene Derivatives: Number of Isomers and Bonding to Di- and Trivalent Atoms

In the final section we probe Loschmidt's views of the benzene structure by his treatment of isomeric substituted benzenes and in the connection of di- and trivalent elements to benzene. Loschmidt did not comment on the symmetry of his "atom complex $\in_6$;" he mentioned the possibility of isomerism, but not the number of possible isomers or the relative position of the substituents relative to each other. For example, he represented the two known isomeric "modifications" of "phenylglycol," $\in_6H_4Hd_2$ [Hd = OH], pyrocatechol (1,2-) and hydroquinone (1,4-), by the identical formula, L 188, in a streamlined "default" notation. Heilbronner and Hafner have pointed out, that (in nearly one hundred of his schemata), Loschmidt simply alternated the "Aufsätze" (substituents), =O, –H, etc., between "up" and "down" to achieve streamlined ("sterisch möglichst gestreckt") formulae (34).

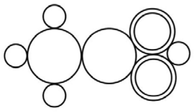


L 188

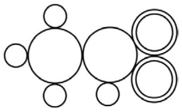
In the context of isomerism, we mention that Noe and Bader (43a) took exception to Kekulé's comment in a letter to Erlenmeyer, referring to "Loschmidt's Konfusionsformeln." Given the crowded Formeltafeln and, viewing just one example early in Loschmidt's paper, it perhaps is not too hard to understand the reaction of the cautious Kekulé (48). The pictograms considered for acetic acid include three structures, which in modern IUPAC nomenclature would be called oxiranol (L 23a) and dioxirane derivatives (L 23b and L (23b)), respectively. Loschmidt excluded the strained species as possible formulae for acetic acid, but expressly supported their presence in other carboxylic acids, specifically maleic acid.



L 23a

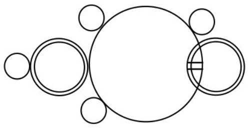


L 23b

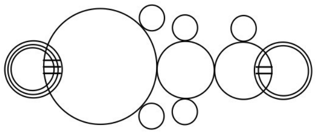


L (23b)

Less than four years after Loschmidt's publication Kekulé understood that the benzene ring could form only single bonds to (divalent) oxygen and (trivalent) nitrogen (47). In contrast, Loschmidt repeatedly depicted atoms doubly or triply bonded to the "atom complex $\in_6$," i.e., in the formulae assigned to a total of twenty compounds containing as many as three "$\in_6$ nuclei" with doubly- or triply-bonded atoms. We choose the formulae for "benzoquinone" (L 189) and "indigo" (L 270) as examples.

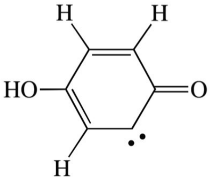


L 189



L 270

To accept the claim (15,17,18,40) that structures L 184 and L 185 represent a "ring of six carbon atoms" means to accept the presence of di-, tri-, and pentavalent carbons in formulae L 189 and L 270, which correspond to structures **7** and **8**, respectively. Structure **7** could be the first carbene, one year before Geuther's alkaline hydrolysis of chloroform (49). Structure **8** could be a carbene next to a pentavalent carbon next to an alkenyl free radical, almost forty years before Moses Gomberg's triphenylmethyl (50).



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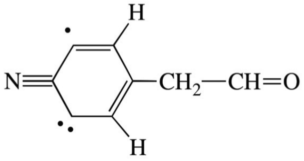
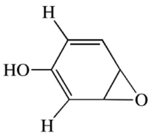


8

Replacing the CO double bond in **7** by two CO single bonds would yield a benzene oxide, **9**, but that clearly does not correspond to Loschmidt's pictogram, as it would ignore the specific double bond, one of Loschmidt's principal firsts in depicting organic structures. Similarly, converting the specific CN triple bond in **8** to a CN double plus a CN single bond or to three CN single bonds, would either yield a bicyclic azirene with an adjacent sigma radical, **10**, or an azabicyclobutane bridged by an allyl radical, **11**, respectively; again, neither **10** nor **11** reflects the pictogram, L 270.



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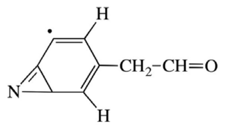

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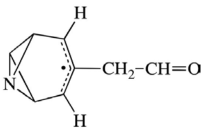

11

Admittedly, the structure of indigo posed a serious puzzle to 19th century investigators; it took another twenty years to solve (51), a very long period of time in an era when the science of organic chemistry was developing rapidly.

Conclusion

In summary, I question the interpretation of Loschmidt's spherical benzene structure as a ring of six carbons for several reasons: (a) Loschmidt clearly favored the "layered" "doubled-allyl" structure (L 182); (b) the "triple-allyl" structure envisioned for naphthalene (L 183) supports this assignment; (c) his language clearly shows that the "cyclic" structure, L 185, was chosen as a noncommittal alternative because there was no clear evidence for structure L 181; (d) Loschmidt referred to the six-carbon unit as "atom complex $\in_6$," not as a "ring"; (e) given the detail in which Loschmidt *described* structures L 182, and the detail in which he *depicted* cyanuric acid, L 153, and melamine, L 154, as well as eleven of their derivatives, it is inconceivable that he wouldn't have described the revolutionary cyclic benzene structure in similar detail; and (f) he depicted over twenty cases of double and triple bonds to the "atom complex $\in_6$." I believe that the sum of these arguments show conclusively that Loschmidt did not view benzene as a planar molecule with six equivalent carbons and six equivalent hydrogen atoms.

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GEORGE DOWNING LIVEING AND THE ORIGINS OF CHEMICAL THERMODYNAMICS IN GREAT BRITAIN

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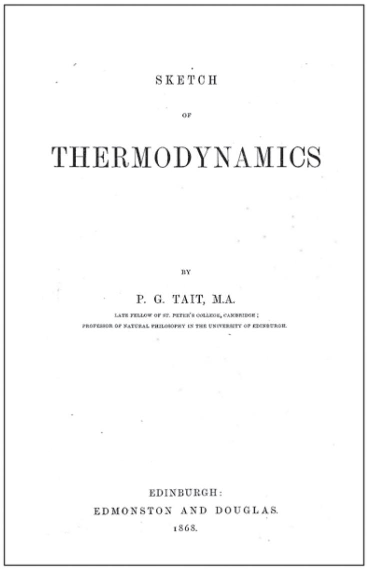
Though the history of thermodynamics, as it relates to both engineering and physics, is well documented in both the journal and monograph literature (1-3), the same is not equally true of the history of its specific applications to the field of chemistry (4). In an attempt to fill this lacuna, the author has recently published English translations and commentaries on the work of both the Austrian chemist and physicist, Leopold Pfaundler, who was the first to apply the newly emerging kinetic theory of gases to chemical rates and equilibria in 1867 (5-6), and the German chemist, August Horstmann, who was the first to apply Clausius's entropy function to the rationalization of chemical equilibria in 1873 (7-8). In keeping with this program, the present paper is concerned with a distinctive British attempt to base the early teaching of chemical thermodynamics on the use of William Thomson's concept of energy dissipation rather than on Rudolf Clausius' more familiar entropy function, as reflected in the pioneering contributions of the British chemist, George Downing Liveing (9-10).

Energy Dissipation versus Entropy Increase

The first English-language textbook on thermodynamics (Figure 1) was published by the Scottish physicist, Peter Guthrie Tait (Figure 2), in 1868 under the title *Sketch of Thermodynamics* (11). In actual fact, this small volume of only 128 pages consisted primarily of a slightly revised reprint of two popular articles on heat and energy that Tait had published four years earlier in the *North British Review,* plus an additional, far more mathematical, chapter on thermodynamics proper, and was intended for classroom use by his students at the University of Edinburgh.



SKETCH
OF
THERMODYNAMICS

BY
P. G. TAIT, M.A.
LATE FELLOW OF ST. PETER'S COLLEGE, CAMBRIDGE;
PROFESSOR OF NATURAL PHILOSOPHY IN THE UNIVERSITY OF EDINBURGH.

EDINBURGH:
EDMONSTON AND DOUGLAS.
1868.

Figure 1. *Title page of Tait's 1868 monograph on thermodynamics (11) (Oesper Collections).*

***Figure 2**. An etching of Peter Guthrie Tait (1831-1901) lecturing on the subject of electrostatics (Oesper Collections).*

In his first two chapters Tait had adopted a largely historical approach and, as a result, had managed to ignite two historical debates over issues of priority (12). The first of these involved the law of the conservation of energy and the relative merits of the contributions of the German physician, Robert Mayer, versus those of the Englishman, James Joule, with Tait, not surprisingly, coming down decisively in favor of Joule. This would elicit a defense of the claims of Mayer by both Hermann von Helmholtz and John Tyndall and, if I am to judge from a spirited conversation I had with a visiting British physicist some years ago, this debate is still going strong among determined Anglophiles.

The second debate involved the relative merits of two competing formulations of the second law of thermodynamics. The first of these, by Tait's colleague and frequent collaborator, William Thomson or Lord Kelvin (Figure 3), was first formulated in 1852 and was based on the concept that in all spontaneously occurring natural processes a certain portion of the useful energy was necessarily irreversibly dissipated or degraded into isothermal heat, leading to the further conclusion that the universe, once its reserve of available energy was exhausted, would undergo a so-called "heat death" (13):

> 1. There is at present in the material world a universal tendency to the dissipation of mechanical energy.
>
> 2. Any restoration of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life or subject to the will of an animated creature.
>
> 3. Within a finite period of time past the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject.

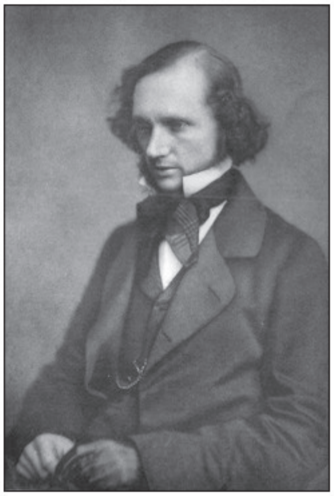


***Figure 3**. William Thomson (1824-1907) as he appeared in 1852, the year he proposed the principle of energy dissipation (Oesper Collections).*

Though, in his original formulation, Thomson had made reference only to the dissipation of mechanical energy, by 1864 Tait had generalized this to include all forms of useful energy, whether mechanical, chemical, electrical or gravitational, and had enshrined it as one of the three underlying principles of the science of energy (11):

> The Theory of Energy, as at present developed, contemplates its Conservation, Transformation, and Dissipation.

The second approach was due to the German physicist, Rudolf Clausius. In his 1850 memoir on heat, Clausius had reconciled Carnot's original theory of heat engines with the newly emerging principle of the conservation of energy and the mutual interconversion of heat and work. In so doing, he had shown that only a portion of the heat passing through the temperature gradient of a heat engine was converted into work, with the remainder being ejected as waste heat at the lower temperature. It was only in 1854 that Clausius reformulated his results using the ratio of heat to absolute temperature or Q/T as a convenient quantitative measure of what he called the system's "equivalence value of transformation," and only in 1865 that he finally gave this ratio the name of *entropy* and assigned it a distinct symbol (S), leading to his often quoted summary of our currently accepted versions of the two laws of thermodynamics, as distinct from Tait's earlier three principles of energy (14):

> *Die Energie der Welt ist constant.*
>
> *Die Entropie der Welt strebt einem Maximum zu.*

Perhaps the best overall evaluation of the relative merits of these two contributions was given by Horstmann, who had studied under Clausius, in his famous paper of 1873 on the application of the entropy concept to chemical equilibrium, in which he argued that, while Thomson was the first to qualitatively state the underlying physical basis of the second law of thermodynamics, it was Clausius who first gave it a proper mathematical formulation via his entropy function (7):

> W. Thomson was the first to take note of one of the consequences of the mechanical theory of heat—namely that the entire world is continuously approaching, via the totality of all natural processes, a limiting state in which further change is impossible. Repose and death will then reign over all and the end of the world will have arrived. Clausius knew how to give this conclusion a mathematical form by constructing a quantity—the entropy—which increases during all natural changes but which cannot be decreased by any known force of nature. The limiting state is, therefore, reached when the entropy of the world is as large as possible.

As might be expected, Tait, with his distinctly British bias, overwhelmingly favored Thomson's dissipation approach over Clausius's entropy approach and would even go so far as to appropriate Clausius's term to describe the opposite of Thomson's concept. Tait, observed a later biographer, "was always ready to put on his armor and place lance in rest for the cause of British science" (15). Believing that the word entropy was Greek for "transformation capacity," Tait argued it should be used to describe the amount of available energy remaining in a system, rather than its loss. Once this energy was dissipated and the system no longer possessed the capacity for further change, its transformation capacity or entropy would be at a minimum rather than at a maximum, as argued by Clausius. Hence Tait proposed reversing both the sign and meaning of Clausius's original entropy function (11):

> It is very desirable to have a word to express the *Availability* for work of the heat in a given magazine; a term for that possession, the opposite of which is called *Dissipation*. Unfortunately the excellent word *Entropy*, which Clausius has introduced in this connexion, is applied by him to the negative of the idea we most naturally wish to express. It would only confuse the student if we were to endeavor to invent another term for our purpose. But the necessity for some such term will be obvious from the beautiful examples which follow. And we have taken the liberty of using the term Entropy in this altered sense. ... The entropy of the universe tends continually to zero.

Tait's rationale for this linguistic kidnapping was hardly convincing, since, despite his claim that inventing his own term would prove confusing to students, he had in fact already done so earlier in the paragraph when he chose to highlight the word "Availability." In addition, as we will soon see, his proposed revision of Clausius's terminology would have unfortunate consequences for the early development of chemical thermodynamics in Great Britain.

Dissipation and Chemical Equilibrium

Though Tait mentioned chemical reactions in his treatise, most of his passing references had to do with their use in constructing voltaic cells and examples of the application of the conservation of energy. Little or nothing was said on the subject of dissipation and chemical equilibrium. Indeed, it was not until 1875 that this subject was finally raised by Lord Rayleigh (Figure 4) in the course of a popular lecture delivered at the Royal Institution (16):

> The chemical bearings of the theory of dissipation are very important, but have not hitherto received much attention. A chemical transformation is impossible if its occurrence would involve the opposite of dissipation (for which there is no convenient word); but it is not true, on the other hand, that a transformation which would involve dissipation must necessarily take place. Otherwise, the existence of explosives like gunpowder would be impossible.

What is of particular interest in this quote is Rayleigh's explicit recognition of the importance in chemical phenomena of what is now called "kinetic metastability"—the realization that energy dissipation is a necessary, but not a sufficient, condition for a given chemical reaction to occur.

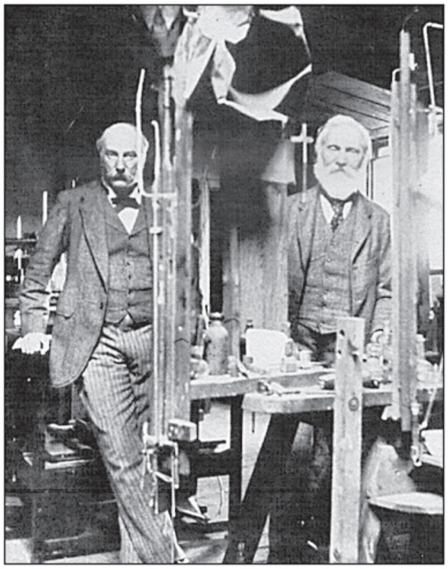


***Figure 4**. Lord Rayleigh (left) and Lord Kelvin (right) consulting in later life in Rayleigh's private laboratory (Oesper Collections).*

Rayleigh then went on to rather oddly argue that the supposed widespread absence of reversibility in chemical reactions had so far hampered the application of thermodynamics to chemistry—odd because reversible chemical reactions are quite common in gaseous and liquid solution systems, and in electrochemical systems. In any case, energy dissipation must accompany all spontaneous chemical reactions, reversible or otherwise (16):

> The difficulty in applying thermodynamical principles to chemistry arises from the fact that chemical transformations cannot generally be supposed to take place in a reversible manner, even though unlimited time be allowed. Some progress has, however, recently been made, and the experiments of Debray on the influence of pressure on the evolution of carbonic anhydride [i.e., carbon dioxide] from chalk [i.e., calcium carbonate] throw considerable light on the matter.

He then concluded his lecture with a few remarks on the role of contraction and expansion in altering the degree of energy dissipation for a given chemical reaction.

It was not until 1882 that the relevance of such topics as energy conservation and dissipation, the mechanical theory of heat, and the kinetic theory of gases to the theory of chemical reactions were once again brought to the attention of the British scientific community—this time via an address on "Chemical Dynamics" given in Southampton at the August meeting of the British Association for the Advancement of Science (BAAS) by the Cambridge chemist, George Downing Liveing (Figure 5), in his capacity as President of the Chemical Section of the Association (17):

> If I were asked in what direction chemical science had of late been making the most important advances, I should reply that it was in the attempt to place the dynamics of chemistry on a satisfactory basis, to render an account of the various phenomena of chemical action on the same mechanical principles as are acknowledged in other branches of physics.

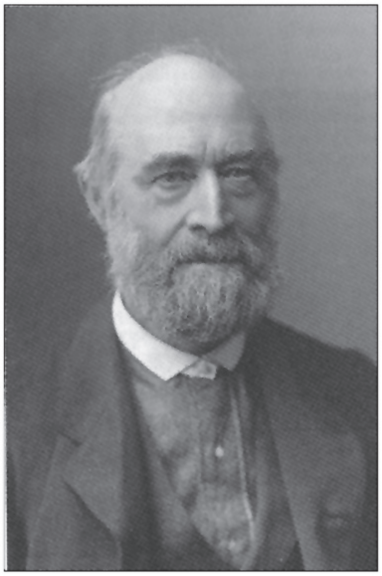


***Figure 5**. George Downing Liveing (1827-1924) (Oesper Collections).*

Liveing then briefly summarized just what these universal mechanical principles were (17):

> The kinetic theory of gases has analyzed for us the different motions of the molecules in a mass of matter and has facilitated the conception of the part which heat plays in chemical actions. Hence we have had of late several attempts to reduce to a form susceptible of mathematical calculation the problems of chemistry. Most of these attempts have proceeded on the well-known mechanical principle that the change of *vis viva* of a system, in passing from an initial to a final configuration, is independent of the intermediate stages through which it may have passed provided the external conditions are unaltered; and on the principle of the dissipation of energy, that is to say,

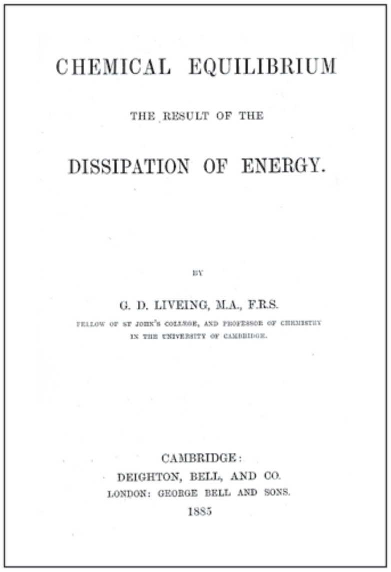
> on the condition that the state of the system, if it be a stable one, must be such that the energy run down in reaching it is a maximum.

Citing the recent work of Gibbs, Berthelot, Thomsen, and Deville as examples of this progress, Liveing then called attention to the almost negligible impact that this work had so far had on the average chemistry textbook (17):

> But how far can we say that mechanical principles are actually recognized as the true basis of rational chemistry? So far as I know no chemist denies that this is so, and yet how little do our textbooks, even the most recent and the most highly reputed, show the predominance of this idea! How very small a portion of such books is taken up with it, how much seems to utterly ignore it or to be couched in language antagonistic to it!

At this point Liveing diverged from his initial theme and spent the remainder of his address (indeed the majority) discussing recent advances in his research specialty of spectroscopy and their bearing on such issues as Prout's hypothesis and the unity of matter and the origins and renewal of the sun's ultimate source of energy.

This address appears to have been a resume of a course on chemical thermodynamics that Liveing had either already given, or was planning to give, to his students at Cambridge—the full contents of which were finally published three years later in the form of a small booklet (Figure 6) of only 97 pages entitled, with startling directness, *Chemical Equilibrium the Result of the Dissipation of Energy* (18). This is, to the best of my knowledge, the first English-language monograph to deal specifically with chemical thermodynamics, rather than with either thermochemistry or engineering thermodynamics, and the only such monograph to explicitly adopt an approach based on Thomson's energy dissipation principle rather than on Clausius's entropy function.



CHEMICAL EQUILIBRIUM

THE RESULT OF THE

DISSIPATION OF ENERGY.

BY

G. D. LIVEING, M.A., F.R.S.

FELLOW OF ST JOHN'S COLLEGE, AND PROFESSOR OF CHEMISTRY
IN THE UNIVERSITY OF CAMBRIDGE.

CAMBRIDGE:
DEIGHTON, BELL, AND CO.
LONDON: GEORGE BELL AND SONS.
1885

***Figure 6**. The title page of Liveing's 1885 monograph on chemical thermodynamics (18) (Oesper Collections).*

Unhappily, it is also very difficult reading for the modern chemist, not because it is crammed with complex mathematics or because it talks of energy dissipation rather than entropy changes, but for precisely the opposite reason. In actuality the book contains virtually no mathematical equations whatsoever and, though it describes a great many chemical reactions, it also contains very few balanced chemical equations. Likewise, though reference is made to various experimental setups, no figures of apparatus appear and, though each chapter addresses multiple topics, there are no section headers or numbered paragraphs to mark the passage from one subject to another. The modern reader, who takes for granted these conventions for summarizing and organizing technical material—conventions already widely used by the 1880s—will quickly discover that their absence, coupled with an almost total reliance on verbal description only, imposes a great burden on both one's memory and attention span.

The book is divided into six brief chapters and also contains a lithograph of typical line spectra and a photographic plate of three complex spectra. The first chapter, entitled "Introduction," verbally defines energy dissipation and discusses various mechanisms for the process, including heat conduction and variations in rarefaction and condensation due to changes of state (taken in the broad sense to also include both mixing and adsorption). It concludes with a summary of the criteria for establishing that energy dissipation has occurred (18):

> 1. The system can be returned to its initial state only through addition of available energy from an external source.
>
> 2. For small perturbations at least, the system returns to its final state of maximum dissipation when the external energy sources are removed.

The second chapter is entitled "Equilibrium in Dissociation," and attempts to dispel the older belief, based on the caloric theory, that heat is a repulsive force which acts in opposition to chemical affinity. The reason compounds eventually dissociate upon heating is not because the repulsion of the added heat finally overwhelms the attractions of the internal bonds, nor because, in keeping with the newer mechanical theory of heat, the increasing violence of the intramolecular vibrations finally break the internal bonds. Rather it is because the net increase in the number of independently moving species formed upon dissociation is more able to effectively dissipate the system's internal kinetic energy.

The third chapter, entitled "Termination of Reactions," contains the only diagram in the booklet and depicts the gravitational potential of a rolling ball (Figure 7). Though admittedly not a direct representation of the actual potential of a chemical reaction system, Liveing nevertheless uses this diagram as an analogy to describe the changes in the potential energy of several example chemical reactions, and thus it is arguably the first known example of the use of a potential energy surface to analyze chemical reactivity. Its primary use by Liveing was to discuss the issue of successive reactions.

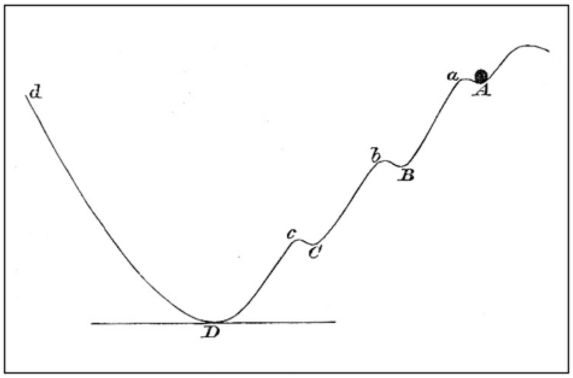


Figure 7. *The two-dimensional potential energy surface used by Liveing to illustrate the existence of metastable states (A, B, C) and activation barriers (a, b, c) (Oesper Collections).*

As early as 1793 the French chemist, Antoine Fourcroy, had enunciated the principle that, if a set of reactants was able to form more than one alternative set of products, the least stable set was produced first and only subsequently converted into the more stable set (19). This same principle was repeated again by Gay-Lussac in 1842 (20) and again by Ostwald in 1897 under the guise of "the law of successive reactions" (21). In terms of Liveing's potential energy surface of 1885, the initial reactants are represented by position *A* and the successive products by positions *B*, *C,* and *D*. Whether the system stops at one of these local minima (*B* or *C*) or proceeds all the way to the true minimum (*D*) depends on how rapidly it dissipates its kinetic energy. If the dissipation is rapid, the system will stop at either *B* or *C* because it will lack sufficient kinetic energy to surmount the intervening potential energy maxima (*b* and *c*). If, however, it is slow, then the system may retain sufficient kinetic energy to surmount these barriers and will then proceed all the way to the true minimum (*D*).

In our modern terminology, points *a*, *b*, and *c* correspond to activation barriers, and in the first scenario *B* and *C* correspond to kinetically metastable products and *D* to the true thermodynamic product, whereas in the second scenario *B* and *C* correspond to reaction intermediates. However, not only did Liveing lack our modern terminology, he also failed to make a clear distinction between the kinetic and thermodynamic aspects of chemical reactivity, so his analysis is only partially correct by modern standards.

The final issue addressed by Liveing in this chapter was the question of whether a chemical reaction will proceed all the way to completion or will come to equilibrium before completion. In Pfaundler's kinetic approach of 1867 equilibrium was the result of the dynamic equalization of the forward and reverse reaction rates, whereas in Horstmann's entropy approach of 1873 it was a consequence of the competitive demands of the reactants versus the products with respect to maximization of their individual entropies of dilution. Since he did not deal with the question of reaction rates, Liveing's rationale is, not surprisingly, most closely related to that of Horstmann. If gases are generated in a reaction, their accumulation in a closed container creates a pressure which can be used to perform useful work. Likewise, the increase in the concentrations of any dissolved products in a solution can also be used to perform useful work (e.g., in an electrochemical cell). The resulting accumulations of potential energy eventually limit the ability of the system to dissipate its kinetic energy and thus bring the reactions in question to equilibrium before completion. On the other hand, removal of the products from the system via precipitation, or by allowing any product gases to escape into the environment, has the opposite effect and allows the reactions in question to proceed to completion. Unfortunately, this purely verbal rationale via a series of special cases lacks the generality of Horstmann's approach and is further compounded by the absence of any mathematical expressions for equilibrium constants.

The fourth chapter is entitled "The Nascent State." This term was first introduced by Priestley in the 18th century and refers to the observation that gases chemically generated *in situ* within a reaction system are frequently far more reactive than when the same gases are bubbled into the reaction system from an external source. A remarkably large number of rationales have been offered for this phenomenon over the years (22), the most popular of which was the hypothesis that chemically generated gases, such as hydrogen, were initially formed in a monoatomic state, whereas the fully formed gases from the external source were diatomic. The chapter is essentially an attack on this idea based on the argument that the initial formation of such high potential energy products as free atoms, without any corresponding mechanism for energy dissipation, is impossible.

Liveing's failure to properly distinguish between the kinetic and thermodynamic aspects of chemical reactions and his lack of an adequate vocabulary for this purpose are nowhere more apparent than in chapter five of his booklet entitled "The Passage from One State of Equilibrium to Another." The first part deals largely with the role of external energy sources in stimulating the passage of a reaction system from a high-potential metastable state to a lower-potential thermodynamically stable state, such as the role of light in initiating the violently explosive reaction between dihydrogen and dichlorine gas:

$$h\nu + H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad [1]$$

In other words, it deals with what we now call activation energy. This would have been an ideal topic for the potential energy diagram introduced in chapter three. But instead of referring this energy requirement back to the energy maxima in his earlier diagram, Liveing instead talks about these stimuli as "opening a new channel for energy dissipation," Also included among his examples are many that would today be classified as catalytic, though he does not employ this term.

The second part discusses the synthesis of metastable compounds or "explosives" from reactants of lower potential energy. Liveing suggests that this happens in one of two ways—either the reactants are first promoted to a higher potential, which lies above rather than below that of the desired products, via addition of external energy, as in the electrical excitation of dioxygen gas in the synthesis of metastable ozone:

$$\Delta E_{el} + 3O_2(g) \rightarrow 2O_3(g) \qquad [2]$$

or the high potential metastable product is formed along with a low potential energy by-product, such that the combined change leads to the required net energy dissipation, as in the synthesis of metastable nitrogen triiodide along with ammonium iodide as the thermodynamically stable by-product.

$$5NH_3(aq) + 3I_2(s) \rightarrow NI_3{\bullet}NH_3(s) + 3(NH_4)I(s) \qquad [3]$$

Again, though these arguments cry out for representation on his earlier potential energy surface, no use is made of it.

Just as the second chapter contained an attack on the outdated concept of heat as a repulsive force, so the sixth and final chapter, entitled "Theoretical View of the Nature of Chemical Combination," contains an attack on the Newtonian concept of chemical affinity as a specific force of interatomic attraction. Here Liveing extends the concept of energy dissipation from a macroscopic reaction system to an individual molecule, arguing that dissipation leads to an equalization of the kinetic energies of all of the atoms within a molecule. This, in turn, leads to a synchronization of their motions and it is this synchronization, rather than specific forces of attraction, which allow the atoms to move together as a single cohesive molecular unit (18):

> The consideration of the conditions of chemical equilibrium points to the conclusion that chemical combination is not due to any bonds which have to be untied from one union before they can be tied together again in a new one, nor yet to any special forces of chemical affinity peculiar to each element and "satisfied," whatever that may mean, or disappearing in its combinations; but that it consists rather in a harmony of the motions of the combined atoms in virtue of which they move and vibrate together, and that such harmony is brought about by the general force of nature which compels to an equal distribution of energy throughout the universe.

The resulting complex of harmonized vibrations found in a typical molecule can change on heating, leading, in turn, to changes in atomic valence and spectra (whence the relevance of spectroscopy and the attached plates of spectra) and are probably best envisioned using William Thomson's vortex atom rather than the hard billiard-ball atoms of Dalton and the kinetic theory of gases, though Liveing provides no specific examples.

What these conclusions reveal is that Liveing had little sympathy for the entire 19th-century program of synthetic organic chemistry and its accompanying edifice of structural formulas, which he viewed as historical anachronisms based on outdated ideas concerning chemical affinity—a position that was much more explicit in his earlier BAAS address of 1882 (17):

> Moreover, we still find in many of our textbooks the old statical notion of chemical combination stereotyped in pictures of molecules. I do not, of course, mean to accuse the distinguished inventors of graphic formulae of meaning to depict molecules, for I believe they would agree with me in thinking

> that these diagrams do not any more nearly represent actual molecules than they represent the solar system; but unfortunately we cannot prevent beginners from regarding them as pictures, and molding their ideas upon them. They present something easily grasped by the infant mind, and schoolmasters are fond of them; but only those who have each year to combat a fresh crop of misconceptions, and false mechanical notions engendered by them, can be aware of how much they hinder, I won't say the advance, but the spread of real chemical science.

Nor was Liveing alone in these assumptions. As revealed by the work of McGucken, the Thomson vortex atom was something of a fad among spectroscopists of this period (23) and the idea that valence and chemical combination were really a consequence of synchronized atomic motions forms the climax of Lothar Meyer's 1892 textbook, *Outlines of Theoretical Chemistry* (24):

> We have gradually receded from the idea of a static state of equilibrium of the atoms brought about by their powers of affinity, and we now consider the atoms, and the molecules which are built up of atoms, as particles in an active state of movement. Their relations to each other are essentially determined by the magnitude and form of their movements. Chemical theories grow more and more kinetic, and although, partly from habit and partly from want of a better expedient, the existence of an attractive force between atoms is frequently assumed in explaining chemical phenomena, this only happens in the conviction that this hypothetical affinity is merely an expression for the real, though imperfectly known, cause of the internal cohesion of chemical compounds.

Similar ideas concerning a kinetic interpretation of both chemical affinity and valence were still being advocated by the American chemist, Francis Venable, as late as 1904 (25).

Evaluation

By this point it should be apparent to the modern reader that Liveing's unique approach to chemical thermodynamics proved to be a dead end and that his booklet had no intellectual successors. Indeed, an argument can be made that it was already outdated by the time of its appearance. The ground-breaking work of both Horstmann (1873) and Gibbs (1874), which had already laid a proper mathematical foundation for chemical thermodynamics—couched explicitly in terms of Clausius's entropy function in the case of Horstmann and indirectly, via free-energy functions, in the case of Gibbs—were already more than a decade old by the time Liveing's book appeared, and Pfaundler's kinetic molecular rationale of both chemical rates and equilibria (1867) was even older.

Interestingly, in the preface to his booklet, Liveing revealed that he was well aware of the work of both Horstmann and Gibbs, though one suspects that he had mastered neither. His excuse for not employing Gibbs's approach was that it was too mathematical for the average student (an interesting claim given the supposed mathematical prowess of the typical Cambridge undergraduate), though much of the problem was really due to Gibbs's terse prose style and could have easily been compensated for by a good teacher.

Liveing's reason for rejecting the entropy approach of Horstmann is even more interesting (17):

> I regret that I have been obliged to abandon in this essay the use of the very expressive word "entropy" coined by Clausius. I have done so because it has been used by Clerk Maxwell with a meaning different from that which Clausius intended to express by it, and as Clerk Maxwell's elementary treatises are in the hands of most students of chemistry, I did not wish to run the risk of a misunderstanding of the word.

What Liveing is referring to in this quote is James Clerk Maxwell's textbook, *Theory of Heat*, which was first published in 1871 and in many subsequent editions (26). In the first edition Maxwell had adopted Tait's earlier suggestion that the term entropy be used to denote the amount of available energy left in a system, rather than in the sense originally intended by Clausius. However, by 1875 Maxwell, as a result of having read Gibbs, had caught his mistake and had corrected it (27):

> In former editions of this book the meaning of the term Entropy, as introduced by Clausius, was erroneously stated ... the book then proceeded to use the term as equivalent to the available energy; thus introducing great confusion into the language of thermodynamics. In this edition I have endeavored to use the word Entropy according to its original definition by Clausius.

Thus we find that the excuse cited by Liveing had actually been obviated more than a decade earlier. There is no doubt that Maxwell's textbook was used at Cambridge. According to Liveing's successor as Professor of Chemistry, William Jackson Pope, Liveing himself had taught the course on heat before Maxwell's arrival at Cambridge as the Cavendish Professor of Physics in 1871 and had even played a role in Maxwell's hiring (28). But by 1885 Maxwell's textbook had passed through at least eight editions and the idea that most Cambridge undergraduates were still using the first edition is either implausible or provides us with an unintended insight into the degree to which used textbooks were recycled by students of the period.

Ironically, the true predecessors of our current textbook tradition in chemical thermodynamics were making an appearance within the same time frame as Liveing's small booklet and include both Jacobus van't Hoff's 1884 monograph, *Études de dynamique chimique* (29) and Pierre Duhem's 1886 monograph, *Le potentiel thermodynamique et ses applications à la mécanique chimique et à l'étude des phénomènes électriques* (30). As suggested by its title, Duhem's approach was based on the use of Gibbs's chemical potential and was the first of a series of books on chemical thermodynamics that he would write over the next two decades, culminating in his 1902 textbook *Thermodynamique et chimie*, the only one to be translated into English (31).

Justly celebrated as the first modern monograph on chemical kinetics, van't Hoff's book also concluded with a section on chemical thermodynamics based on the concept of equilibrium as an equalization of the forward and reverse phenomenological reaction rates. Although heavily influenced by the work of Horstmann, whose writings on thermodynamics he would later edit (32, 33), van't Hoff unfortunately chose to abandon Horstmann's explicit use of the entropy function and opted instead for an approach based on *Arbeit* or useful work in which the role of entropy was implicit rather than explicit. His work was extremely influential in molding the teaching of chemical thermodynamics for the next 40 years but also condemned it to the use of such artificial devices as reversible cycles, osmotic-pressure membranes, and adiabatic pistons. Only with the publication in 1923 of the famous textbook of Lewis and Randall was this pseudo-engineering approach finally eclipsed and the subject once again returned to the purity of Gibbs (9).

A Modern Reconciliation

In modern terms, the entire hiatus prompted by Tait's ill-advised attempt to redefine entropy can be summarized by the fundamental relationship:

$$\Delta G = -T\Delta S_{\text{tot}} \qquad [4]$$

where ΔG is the Gibbs free-energy change for the reaction system, ΔS_{tot} is the total entropy change for both the reaction system and its surroundings, and T is the absolute temperature. Essentially ΔG is the modern equivalent of what Tait meant by "Availability" and, like it, tends to zero as one approaches equilibrium. This was the term that Tait wished to rename entropy—a proposal that entailed not only a change in the meaning and sign of the total entropy as originally defined by Clausius, but also, taking T into account, a change in its fundamental physical dimensions as well. $T\Delta S_{\text{tot}}$, on the other hand, when taken in Clausius's original sense, is a good measure of the energy dissipated by the system at the temperature in question and likewise tends to zero as one approaches equilibrium. As dissipation increases, availability decreases (34).

Unfortunately the term "dissipation," though having uses in modern engineering thermodynamics, seldom appears today in the literature on chemical thermodynamics. However, when used in Thomson's original sense, it has been argued that it is a far better interpretation of the physical meaning of entropy than either disorder or information (10, 35-36). Neither information nor disorder are true causal agents like energy, and entropy is essentially a descriptor for how the energy of a system is distributed. Modern quantum statistics teaches us that movement from a low entropy state to a high entropy state corresponds to a dilution or dissipation of the system's kinetic energy content over an ever greater number of accessible quantum levels. Though increased molecular disorder is frequently, though not invariably, an *indicator* that the system has acquired a greater capacity to disperse its energy, it is not entropy in and of itself. Likewise, the idea that entropy is linked with information is actually based on a formal mathematical isomorphism rather than on a true physical isomorphism, and opens the entire concept to the charge of being subjective (37-38). Had Tait chosen to equate Thomson's dissipation with Clausius's entropy, rather than with available energy, this entire unfortunate episode in the history of chemical thermodynamics might have been avoided.

Biographical Background

Having outlined and evaluated Liveing's contributions to the teaching of chemical thermodynamics, it is only fitting that, in conclusion, something should also be said about his life and career in general. George Downing Liveing (Figure 8) was born on 21 December 1827 in Nayland, a small English village on the Suffolk bank of the River Stour, the eldest son of Edward Liveing and Catherine Downing (28, 39-43). His father was a surgeon by profession and his mother the daughter of a London barrister. In 1845, at age 18, Liveing entered St. John's College of Cambridge University as a pensioner, where he would remain in various capacities until his death 79 years later on 26 December 1924 at age 97.

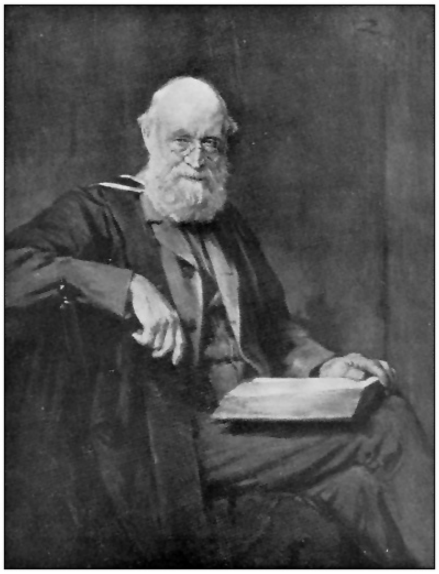


Figure 8*. Liveing as he appeared in later life in the full tide of Cambridge honors (Oesper Collections).*

Matriculating at St. John's in 1846, Liveing was awarded his B.A. in 1850 along with the position of 11th Wrangler in the Mathematical Tripos. Continuing on with postgraduate work at St. John's, he was awarded a first class with distinction in chemistry and mineralogy in the Natural Sciences Tripos of 1851, followed by work in the chemical laboratories of August Hofmann at the Royal College of Chemistry in London and Karl Rammelsberg in Berlin.

On his return from Berlin in 1852, he began teaching a practical course in chemistry for medical students in a primitive laboratory which he had outfitted at his own expense in a small cottage on the west side of Corn Exchange Street. However, in 1853 he received not only an M.A. from St. John's, but also appointment as a fellow of the college and an official lectureship in chemistry, along with a teaching laboratory which the College built for him behind New Court—the first of its kind at Cambridge.

By 1860 Liveing was able to supplement his position at St. John's through his appointment as Professor of Chemistry at the Staff College in Camberley and at the Royal Military College in Sandhurst, and in 1861 he was finally appointed as full Professor of Chemistry at Cambridge upon the death of the Reverend James Cummings, who had held the position since 1815. From this point on, he became involved in a continuous campaign to improve and expand the student laboratory facilities at Cambridge.

One of several plans for a chemical laboratory proposed during this period, but subsequently rejected by Liveing, reveals just how leery and unfamiliar the University was with the requirements of experimental chemistry (40):

> The laboratory is to be constructed underground and is to be capable of resisting violent explosions and to be as little flammable as possible.

Just how rare the opportunity for actual hands-on laboratory work was in these early years may be gauged from Lord Rayleigh's recollections of his experiences as a student at Cambridge in the 1860s, as later recounted by his son (44):

> In 1867 he took a course of qualitative chemical analysis (test-tubing as it is now often called) under Professor Liveing. This was, I think, the only laboratory instruction of any kind which he could get at Cambridge. I have dwelt in detail on the difficulty he found in getting experimental instruction, because it was a subject he often spoke of in telling me of his early years of manhood. "It wasted three or four years of my life."

In 1888 Liveing's efforts finally paid off with the completion of the Pembroke Street University Laboratories, described at the time as "one of the finest facilities in the Kingdom" (42). But even then, as one biographer noted, Liveing's laboratory stipend was only (28)

> ... 100£ per annum, paid by the government and subject to a deduction of Treasury fees amounting to four guineas. As he has said himself, men in those days had to devote their means as well as their wits to the service of the University.

In keeping with this remark, Liveing was forced, until his retirement two decades later, to finance (28)

> ... the chemical laboratory as a private venture, and informed me that he declined to submit his accounts, when challenged in later years by the suggestion that he had been drawing a large revenue, because he was ashamed to disclose to his colleagues how large a sum he had thus contributed from his own resources.

The retirement in question finally came in 1908 at age 80, on which occasion Liveing was also awarded an honorary Sc.D. Elected a Fellow of the Royal Society in 1879, he was also a recipient of its Davy Medal in 1901, served as President of St John's College from 1911-1924, and as corresponding secretary to two successive University Chancellors.

Liveing could be terse and abrupt with those who irritated him, either by invading the privacy of his personal workroom or by violating the strict working rules of the new University Laboratories—attributes which won him the nickname of "Red Precipitate" among the undergraduates. As recalled by a former colleague (41):

> Liveing had a great objection to being interrupted when at work in his private room in the Laboratory. One day I was asked by a man whether he could see the Professor and where was his private room. My reply was that the Professor did not see people except by appointment, but there was his room ... I could do no more than point to the door behind which the Professor worked and wait. I heard three taps on the door, a voice "Come in," a louder voice "Get out!," and a shutting of the door. I retreated with discretion. He was indeed extraordinarily terse in his conversation; not exactly abrupt or curt, but sometimes very monosyllabic. Like Captain Cuttle, he did not "waste language as some do."

On the other hand, Liveing could also be "a very entertaining companion" when he chose to be and especially when one succeeded in tapping his remarkable memory of past events, which remained intact until the end (42):

> He had a remarkable memory, talked freely of the men and events of the past, but would write no reminiscences. "I never look back," he said, "I always look forward."

In a similar vein, Pope recalled after Liveing's death in 1924 that (28):

> In his conversation, always sprightly and vivacious, Liveing seemed often trying to translate our later knowledge into terms of the science of seventy years ago. As befitted one who belonged to the age when the collection of facts was the main objective of science, he was apprehensive as concerned the vast theoretical flights of modern physics and chemistry ... In talking with Liveing and hearing his statement of long obsolete chemical views, one began to realize the difference between the science of seventy years ago and that of today, and to speculate on what our survivors seventy years hence will think of the science of the future. At the same time, and although an authority on older chemical knowledge, Liveing always maintained an excellent appreciation of recent progress.

After all, as Pope emphasized, here was a man who had completed his chemical training (28)

> ... before Frankland had stated the doctrine of valency and before Kekulé had devised the structural formulae of the chemist. Liveing had been the personal friend of Dr. Whewell, the great Master of Trinity, W. H. Miller, the founder of our present system of crystallographic nomenclature, Adam Sedgwick, Sir Joseph Hooker, Michael Foster, Sir Gabriel Stokes, Sir George Airy, de Morgan and Charles Darwin; he had studied under Rammelsberg, Mitscherlich, Rose and Magnus. He once mentioned to me that he and Hooker, after some preliminary discussion, walked over to see Darwin for the purpose of hastening the publication of the "Origin of the Species," which appeared in 1859.

Indeed, his life had encompassed so much scientific history, that he occasionally forgot that this was not equally true of his younger colleagues (28):

> His memory of long-past events was remarkably clear until quite recently, but he sometimes forgot that others could not reach so far back into the past. A few months ago, while still in full mental vigor, he expressed surprise that I had not noticed the splendor of Donati's comet of 1858 [Pope was born in 1870].

What was true of Liveing's memory was equally true of his physical health, which also remained intact until the end. He seems to have been one of those lucky persons who take their personal good health as an unquestioned given and who remain puzzled as to why others do not display a similar resiliency (28):

> Like many other men of robust health and great vitality, Liveing found it difficult to understand why his contemporaries dropped out and passed away. Declining health seemed to him as due to a lack of resolution. He was an enthusiastic gardener, and when well past his ninetieth birthday engaged in all the manual toil incidental to the care of a large garden.

He was also an avid walker in old age and would walk each day from his home in Maid's Causeway to his laboratory in the Goldsmith's metallurgical building, where he was working on a project related to his final publication on "The Recuperation of Energy in the Universe," which he had read to the Cambridge Philosophical Society in May of 1923 (42):

> In his old age, his tall bent figure as he made his daily journeys between his home and the College, was one of the most familiar in town.

And it was during one of these daily walks, in early October of 1924, that he was run down by a woman bicyclist—an accident which resulted in his death several months later from the resulting injuries, just five days after his 97th birthday.

Research Activities

During his extraordinarily long career Liveing published over 100 research papers and notes, although this output was not evenly distributed over time (45). For the first 25 years of his active career he published virtually nothing. Indeed, for the years prior to the date of his appointment in 1861 as Professor of Chemistry at Cambridge, the *Royal Society Catalogue of Papers* lists no publications whatsoever and, for the next 16 years, only four are given, all of them dealing with geology and all of them published in the Proceedings of the local Cambridge Philosophical Society. Here we should perhaps heed John Shorter's caution that in the 19th century (43)

> Cambridge did not seek to produce people who intended to practice chemistry ... At Cambridge, chemistry was a part of a liberal education for those who cared to include it, with the exception of its ancillary role for medicine ... The aim of a Cambridge chemical education through the Tripos was to impart a knowledge of chemistry, not to train chemists.

As a consequence, there was little incentive to acquire a Professor of Chemistry with an already established research reputation and, in any case, for his first quarter century at Cambridge Liveing's time and energy were largely consumed in establishing the very laboratory facilities necessary for such work in the first place.

A radical change in Liveing's research prospects finally occurred in 1875 with the appointment of Sir James Dewar (Figure 9) as the Jacksonian Professor of Physics at Cambridge. Though Liveing was nearly 16 years older then Dewar, the two men soon struck up a friendship that would last for nearly a half century and which would lead to the collaborative publication of more than 78 papers and notes dealing with the subject of spectroscopy. As later noted by Pope (28):

> The close and intimate friendship which existed between Dewar and Liveing was very striking. Both men were of strong personality, but no two men could have presented a greater contrast in outlook, tastes, and all essential characteristics. Yet each held the other in profound esteem, and neither ever said a word in criticism of his colleague. Without this absolute loyalty, the happy collaboration of Liveing and Dewar could not have persisted for nearly fifty years.

This collaboration would establish Liveing's reputation as a research chemist and lead to both his election to the Royal Society and his award of the Davy Medal mentioned earlier. After his retirement, he would edit much of it for inclusion in a volume of collected papers published by the Cambridge University Press in 1916 (46).

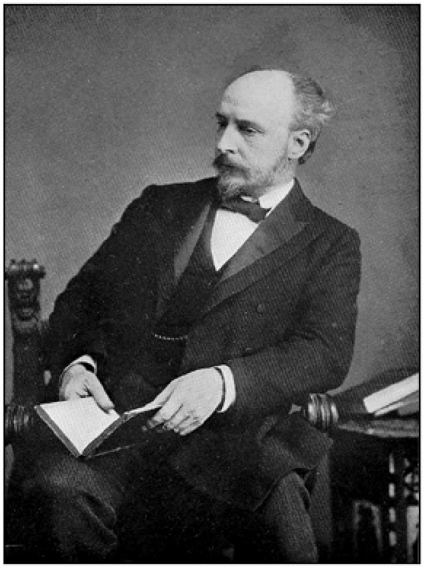


***Figure 9**. James Dewar (1842-1923).*

Most of this work belongs to what A. C. Chandler would later call the "acoustics" period of spectroscopy and consisted of the publication of raw spectral data with some qualitative classification and speculative interpretation of the results but without the empirical mathematical equations that would characterize the later "series" period of spectroscopy nor the theoretical interpretations that would characterize the even later "quantum" period (47, 48). Its most lasting contribution was the division by Liveing and Dewar of the lines in the spectra of the alkali metals into the classes of sharp, principal and diffuse—terms which, via a series of historical twists and turns, would eventually become enshrined in our current atomic orbital abbreviations of *s*, *p* and *d* (49).

Which Tradition?

With the exception of his BAAS address of 1882, five papers published in the late 1880s on the kinetic theory and some aspects of chemical reactions, solution formation and crystallization (50-54), and his final paper of 1923 on cosmology (55), little in Liveing's list of research publications would seem to be related to his small monograph on chemical thermodynamics, and it has been our assumption so far that this work evolved primarily out of his teaching duties at Cambridge and is best interpreted in light of two competing approaches to the second law. However, another interpretation is also possible.

Though at least one biographer claimed that Liveing's small booklet "attracted a great deal of attention" when first published (40), I have been able to locate only one book review, and that single review casts a very different light on the subject. Published in the *Chemical News*, it characterized the book as "evidently of a preliminary nature," dismissed its treatment of chemical equilibrium and dissipation of energy as of little interest except to the physicist and "physico-chemist," proceeded to focus solely on the final chapter containing Liveing's speculations on the nature of matter as the only part of interest to the "pure chemist," and concluded with the recommendation that (56)

> All who are not content to accept the reputed "elements" as the ultimate facts will find this book worthy of careful study.

The author of the review was not listed, but given its emphasis, it is almost certain that it was the journal's editor, William Crookes, who was well known for his own spectroscopic studies and speculations on the ultimate nature and evolution of the chemical elements—speculations that would attract widespread attention the very next year as a result of his 1886 address as President of the Chemical Section of the BAAS (57). As shown by the pioneering studies of David Knight (58) and William Brock (59) in the 1960s, both Crookes's address of 1886 and Liveing's earlier address of 1882 are part of a long-lived debate among British chemists of the 19th century over the ontological status of both the atomic theory and the ultimate nature of Lavoisier's chemical elements—a debate in which Liveing's research specialty of chemical spectroscopy played a key role in the guise of Norman Lockyer's so-called "dissociation hypothesis" (60).

Nevertheless, while the reviewer's conclusion might have been applicable to Liveing's 1882 address, it is difficult to understand how he could have extracted such a message from Liveing's booklet of 1885, which contains nothing on either Prout's hypothesis or the ultimate nature of the chemical elements. Likewise, though one might surmise that Crookes may have found the principle of energy dissipation relevant to the mechanism for the gradual cooling of the primeval *protyle* that he would postulate as the cause for the gradual evolutionary building-up of our present-day chemical elements—no mention of either Liveing or energy dissipation is to be found in Crookes's famous address of 1886. In short, the implied contention of the reviewer that Liveing's booklet is best viewed as part of a 19th-century tradition of spectroscopic speculation on the ultimate nature of the chemical elements, rather than as part of a tradition of the monographic literature devoted to the theory of chemical thermodynamics, is dubious at best, however consistent it may be with some of Liveing's other writings.

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FIFTY YEARS OF VASKA'S COMPOUND (1)

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Abstract

Textbooks in organometallic chemistry list *trans*-chlorocarbonylbis(triphenylphosphine) iridium (I) alongside the name "Vaska's compound." The year 2011 represents fifty years since the synthesis and characterization of $IrCl(CO)(PPh_3)_2$ by Prof. Lauri Vaska. From the perspective of the history of chemistry, this anniversary raises a number of questions. For example, who is Lauri Vaska? Vaska's work on group 8 and 9 transition metal compounds led to the discovery of a number of low-valent complexes during the early days of the rapidly emerging field of organometallic chemistry. How did he discover the compound that bears his name? What is the significance of $IrCl(CO)(PPh_3)_2$ and when did the term "Vaska's compound" first enter our vocabulary? We will also examine the question of whether or not Vaska really was the first to discover $IrCl(CO)(PPh_3)_2$ and his connection to the discovery of Wilkinson's catalyst.

What Is Vaska's Compound?

On April 20, 1961, the editors at the *Journal of the American Chemical Society* received a communication (2) from the Mellon Institute describing the synthesis and characterization of *trans*-chlorocarbonylbis(triphenylphosphine) iridium (I). To most organometallic chemists and in the indices of several textbooks (3), this compound is known as "Vaska's compound" after Lauri Vaska, who together with John W. DiLuzio, co-authored the aforementioned paper. At least one chemical supply house lists the compound (CAS 14871-41-1) in its catalogs under the name "Vaska's compound" as well as by its chemical name (4). Among the thousands of transition metal organometallic compounds reported over the past half-century, what makes *trans*-$IrCl(CO)(PPh_3)_2$ special enough to be known by name? Who is Lauri Vaska and what path led to the synthesis of the compound that bears his name? As we celebrate the 50th anniversary of the discovery of *trans*-$IrCl(CO)(PPh_3)_2$, this paper will explore the biography of Lauri Vaska, as well as the chemistry and history behind his compound.

Who Is Lauri Vaska? (5)

Lauri Vaska was born on May 7, 1925, in the town of Rakvere in Estonia. At the time of his birth, Estonia, the northernmost of the Baltic countries, was enjoying independence for the first time in modern history. The turmoil that followed the end of the First World War on the Eastern Front and the subsequent events of the Bolshevik Revolution in Russia opened the door to independence for the Baltic countries, Estonia, Latvia and Lithuania. His father, a decorated veteran of the war for independence, earned his living as a surveyor. The family lived in the capital of Tallinn and maintained a farm in Rakvere. Vaska received his primary and secondary education both at the Riiklik Inglise Kolledž (State English College in Tallinn) and at the Rakvere Gümnasium.

On the eve of the Second World War, Nazi Germany and the Soviet Union signed the Ribbentrop-Molotov Pact, ostensibly a non-aggression pact between the two nations (6). Included in the agreement were secret protocols that divided Eastern Europe into spheres of influence; the USSR was given the three Baltic States and half of Poland. Within a year, Soviet forces had fully occupied the Baltic countries and replaced the existing governments with Soviet-friendly regimes.

Memories of 1940-1944

The German invasion of the Soviet Union in June 1941 exchanged Soviet masters for German rule. The Baltic States were occupied by the Wehrmacht by August 1941. Estonians would live under German rule for a little over three years. The five years of global conflict (1939-1944) saw Vaska grow from a 14-year old schoolboy to a 19-year old man. As the German lines crumbled in the summer of 1944 and once again brought the Red Army to the borders of pre-war Estonia, the teenager was conscripted into an Estonian unit serving with the Wehrmacht in the final defense of Estonia. During the turbulent summer of 1944, he served as a medical orderly until the front collapsed in September 1944 (5).

In the turmoil and confusion of the German Army's retreat from Estonia, Vaska and his family joined some 100,000 of his countrymen in escaping from Estonia in September 1944. Driven by memories of the recent Soviet occupation, many followed the Germans during their evacuation of the Baltic lands to refugee camps in Germany. May 8, 1945, finally brought an end to combat in the European theater and a division of Germany into four occupation zones, one each for the four victorious Allied Powers: the United States, the United Kingdom, France and the USSR.

The Baltic University and the University of Göttingen

Life in a refugee camp in Germany in 1945 was a mixed blessing. Four years of war were over. On the one hand, the occupying authorities and the United Nations Relief and Rehabilitation Administration (UNRRA) ensured that the refugees were fed and housed (7). Conditions in the displaced persons (DP) camps were significantly better than for German citizens. On the other hand, Estonia remained occupied by the USSR. The forced deportation of the Baltic refugees from Germany back to their home countries, which the USSR demanded based on their claim that the Balts were Soviet citizens, was prevented because the United States did not recognize the 1940 occupation of the Baltic States (8). As time passed in the DP camps, Baltic intellectuals and academics sought to start a "Baltic University" that would allow the refugees to continue their education (9). Conditions at German universities at the time did not allow for sufficient seats for refugees so permission was obtained from the British Army of the Rhine and the Hamburg DP University Centre (a. k. a. Baltic University) opened its doors in March 1946. Among the four Estonians who enrolled as chemistry undergraduates in May 1946 was Lauri Vaska (10). Although the Baltic University would last another three years and see up to 1200 students enroll, Vaska's stay was limited to one semester. By the fall semester, he had transferred to the Georg-August University in Göttingen. He recalls his first meeting with Prof. Hans von Wartenberg (11), head of the Göttingen inorganic chemistry institute, whose first question was "*Sind Sie ein DP*?" (12) During his undergraduate career, Vaska studied coordination chemistry and experimental inorganic chemistry with Prof. Josef Goubeau (13) and Raman spectroscopy with Prof. Franz Feher (14). The years 1946-1949 allowed the young chemist to attend lectures by Werner Heisenberg, witness the last public presentation by Max Planck and have a beer at the same bar as Otto Hahn and his group (15).

Emigration and the University of Texas

A permanent solution to the problem of the Baltic DPs continued to elude the Allied authorities. Economic conditions in Germany were not conducive to settlement of the DPs in Germany and the escalation of the Cold War meant that the refugees refused to return to their occupied homeland. Slowly, other countries began to open their doors to these refugees. In 1949, the US Congress passed the Displaced Persons Act that allowed emigration to the United States (7c). By 1952 Vaska had emigrated to the United States and began graduate study at the University of Texas at Austin working with Prof. George W. Watt (16). His Ph.D. dissertation, "*Ammoniolysis of Potassium and Ammonium Hexabromoosmates"* focused on the use of ammonia as a solvent for transition metal chemistry. Watt's group worked with ammonia under familiar low temperature, ambient pressure conditions as well as under high pressures where reaction temperatures up to 90°C could be achieved (17). It was Watt who guided Vaska to the chemistry of the platinum group metals when he announced to his new graduate student that he would be working with osmium, handing him a 10-g vial of OsO_4

and telling him to make it last through his entire Ph.D. research (15).

Lauri Vaska's Early Career

After a brief period of post-doctoral study at Northwestern University with Prof. Pierce W. Selwood (18). Vaska began his career as an assistant professor in 1957 at the Mellon Institute for Industrial Research in Pittsburgh, a predecessor of Carnegie-Mellon University (19). It was natural that he would continue his study of coordination chemistry of the group 8 and 9 metals, submitting his first paper to the *Journal of the American Chemical Society* in March 1960 (20). The title of the paper, "Univalent Ruthenium," reported the product of a reaction between ruthenium (III) chloride and triphenylphosphine in methoxyethyl alcohol as $ClRu(PPh_3)_3$ (Figure 1). Somewhat fortunately, this paper has only been cited once, by Vaska himself, when he corrected the formulation of this compound to $HRuCl(CO)(PPh_3)_3$. (21). From the beginning of his career, Vaska's research would overlap with work from many better known inorganic chemists of the day. The recognition that the reported "univalent ruthenium" was indeed a hydrido ruthenium (II) carbonyl complex came after learning of Joseph Chatt's synthesis of hydridometal carbonyl halide complexes from metal halides and tertiary phosphines in ethanol (equation 1) in March 1960 (22).

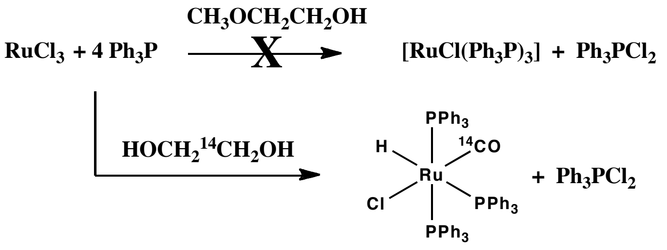


Figure 1. *Reaction between ruthenium (III) chloride and triphenylphosphine in methoxyethyl alcohol as originally interpreted by Vaska (top) and then as corrected by Vaska.*

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl + 2\ C_2H_5OH + 2\ KOH \rightarrow 2\ [HRuCl(CO)(PEt_2Ph)_3] + 2\ CH_4 + 2\ KCl + 2\ H_2O \qquad [1]$$

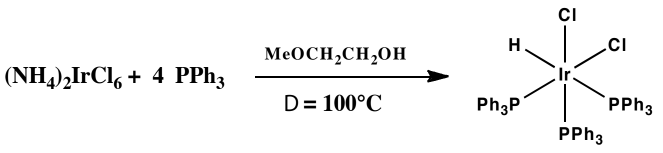
The characterization of "$ClRu(PPh_3)_3$" relied on elemental analysis, the determination of molar mass and magnetic measurements. One can only speculate as to why Vaska did not report the IR spectrum until after the initial communication was published, as it surely would have led to the identification of the CO ligand. In his defense, one notes that the elemental analyses for C, H, P, Cl and Ru for "$ClRu(PPh_3)_3$" and $HRuCl(CO)(PPh_3)_3$ are quite similar (23). The observed diamagnetism of the d^7 "univalent ruthenium" was explained by an exchange interaction between neighboring ruthenium (I) atoms, analogous to work reported the previous year by others. The dawn of the 1960s was an era where the application of NMR spectroscopy to transition metal complexes was in its infancy, so the failure to detect the Ru–H bond by ^1H NMR is excusable. In any event, both the CO and hydride ligands were identified by IR spectroscopy in Vaska's 1961 paper describing the correct composition of $HMCl(CO)(PPh_3)_3$ (M = Ru, Os). In a further significant experiment using ^{14}C labeled ethylene glycol, Vaska was able to trace the source of the carbonyl ligand to the CH_2OH group in the alcohol solvent (Figure 1).

The coordinatively saturated $HRuCl(CO)(PPh_3)_3$ has seen limited use as a hydrogenation catalyst. It is likely that Vaska was the first to discover the well known ruthenium (II) compound, $RuCl_2(PPh_3)_3$. In both his own writings (24) and in James Ibers' 1965 publication (25) of the crystal structure of $RuCl_2(PPh_3)_3$ credit for the first synthesis of this compound is assigned to Vaska. Errors in the footnotes to the Ibers paper make it difficult to track the first report of $RuCl_2(PPh_3)_3$, however, it does appear that Vaska's claim is valid. A 1961 paper in the British journal *Chemistry and Industry* (26) reports the isolation of $RuCl_2(PPh_3)_3$ as a green methanol solvate from a reaction between $RuCl_3$ and triphenylphosphine in methanol at ambient temperature (equation 2). It is only under these relatively mild conditions that formation of ruthenium carbonyl complexes is avoided. The ruthenium (II) compound isolated in this manner has proven to be an active catalyst in organic chemistry and most importantly, is a precursor to the versatile hydrogenation catalyst $HRuCl(PPh_3)_3$ (27). In light of his subsequent work on the reactivity of late-transition metal phosphine complexes with hydrogen, it is surprising that the conversion of $RuCl_2(PPh_3)_3$ to the efficient homogeneous hydrogenation catalyst $HRuCl(PPh_3)_3$ escaped his grasp.

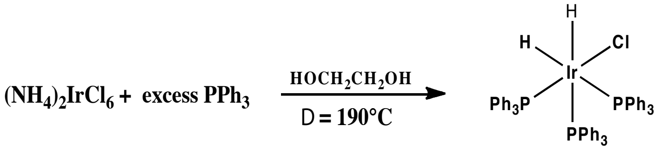
$$RuCl_3 + 4\ Ph_3P \rightarrow RuCl_2(Ph_3P)_3{\bullet}CH_3OH + \tfrac{1}{2}\ Ph_3PO + HCl \qquad [2]$$

The Discovery of Vaska's Compound

The observed reduction of late transition metal halides in the presence of phosphine in an alcohol solvent turned out to be important to Vaska's future work. In the same year that the synthesis of $RuCl_2(PPh_3)_3$•MeOH was reported, he published a short, single-author communication describing the synthesis of five iridium phosphine, arsine and stibine hydride complexes: $IrHCl_2(EPh_3)_3$ (E=P, As, Sb) and $IrH_2X(PPh_3)_3$ (X=Cl, Br, equations 3 and 4) (28). The latter compounds were all prepared by heating $[NH_4]_2[IrCl_6]$ and the corresponding group 15 ligand in alcohol solvent at temperatures ranging from ambient to 190°C. The Ir–H bond was identified by IR and no evidence is presented for the formation of iridium carbonyl complexes under these conditions. In light of his concurrent observations with ruthenium halide complexes, one concludes that indeed, Vaska did not miss a coordinated CO for a second time.



[3]



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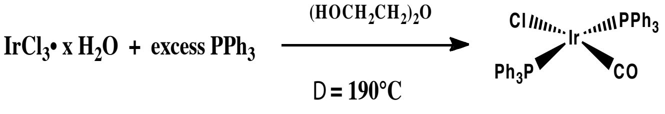

[5]

Within a few months, however, Vaska and John DiLuzio reported that when reaction conditions were altered, an entirely different product was isolated (2). Instead of six-coordinate octahedral iridium (III) complexes $IrHCl_2(PPh_3)_3$ and $IrH_2Cl(PPh_3)_3$, a square planar iridium (I) product, $IrCl(CO)(PPh_3)_2$ precipitates from solution (equation 5). A possible intermediate, $IrHCl_2(CO)(PPh_3)_2$, was isolated but could not be purified. The presence of the CO was clearly identified by IR spectroscopy and ^{14}C labeling studies. Single crystal x-ray structures were obtained in 1988 and 1991 (29) so the formulation of the compound known as "Vaska's compound" is not in doubt. It remains unclear from the scientific literature (30) precisely what modifications were made to the procedure for preparing $IrHCl_2(PPh_3)_3$ and $IrH_2Cl(PPh_3)_3$ that instead yielded $IrCl(CO)(PPh_3)_2$. The hydrido-iridium compounds and $IrCl(CO)(PPh_3)_2$ were obtained in excellent yield (87% $IrH_2Cl(PPh_3)_3$ vs 86% $IrCl(CO)(PPh_3)_2$) from both hydrated $IrCl_3$ and $[NH_4]_2[IrCl_6]$ in ethylene glycol at the same temperature (190°C). The reported yields and reaction times for the preparation of $IrCl(CO)(PPh_3)_2$ are remarkably similar for a range of solvents: 86% yield after 2 h in 2-methoxyethanol at 190°C, 75% after 7 h in ethylene glycol at 190°C, 76% after 2 h in diethylene glycol at 240°C and 83% after 4 h in triethyleneglycol at 270°C (1). In his reminiscences (24) about those days, Vaska alludes to the role of "forgetfulness" in the initial synthesis of $IrCl(CO)(PPh_3)_2$. Did he really leave a flask containing iridium chloride and triphenylphosphine in ethylene glycol accidentally at 190°C overnight? In his writings, he reveals that the synthesis of the aforementioned $RuCl_2(PPh_3)_3$ was the result of leaving a 2-methoxyethanol solution of $RuCl_3$ and PPh_3 at 20°C for "a few weeks" (24) so perhaps it is true that luck played a critical role in the discovery of both $RuCl_2(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$. (31)

How Did "Vaska's Compound" Get its Name?

Many important compounds have been discovered in the last 50 years. How did $IrCl(CO)(PPh_3)_2$ earn its place among compounds known by their discoverer's name? It seems that the term "Vaska's compound" first appeared in our lexicon in 1966 (32). Three papers submitted in 1966 (published in 1967) use some version of the name "Vaska's compound. James Collman refers to "Vaska's iridium (I) complex" in a paper submitted on March 2, 1966 (32a), while Umberto Bellucco spells out "Vaska's compound" in an article in *Inorganic Chemistry* submitted in July of the same year (32c):

> Furthermore, treating Vaska's compound with hydrogen halides, octahedral complexes of *cis*-hydrogen halide have been obtained, as confirmed by infrared spectra.

Clearly Vaska's name was already associated with $IrCl(CO)(PPh_3)_2$ in the community as James Ibers also refers to it in his 1967 paper where he compares the chemistry of $IrCl(CO)(PPh_3)_2$ to his own observations on $[PtCl(CO)(PPh_3)_2]^+$ (32d):

> The compound is now known to contain the new cation *trans*-$PtCl(CO)(PC_2H_5)_2^+$, which is isoelectronic

> with Vaska's compound $IrCl(CO)(PR_3)_2$, where R may be alkyl or aryl.

The well-known German chemist Walter Strohmeier also referred to $IrCl(CO)(PPh_3)_2$ as "Vaska's compound" in 1968 (33). Later in the same year, James Collman joined the chorus as *Inorganic Syntheses* published the preparation of $IrCl(CO)(PPh_3)_2$ writing that (34):

> The compound was first prepared by Angoletta, but was correctly formulated by Vaska, who first described its addition reactions. It is often referred to as 'Vaska's compound.'

Was Vaska First?

The reference to Angoletta in *Inorganic Syntheses* raises the question of whether or not Vaska was the first to discover $IrCl(CO)(PPh_3)_2$. Vaska admits (24) to being unaware of the work by an Italian chemist, Maria Angoletta, who reported on carbonyl derivatives of iridium in 1959 (35), two years before Vaska's report in the *Journal of the American Chemical Society*. Several reasons may account for credit for discovering $IrCl(CO)(PPh_3)_2$ being assigned to Vaska and not to Angoletta. First, the *Journal of the American Chemical Society* enjoys a wider readership than the *Gazzetta Chimica Italiana*, so perhaps Vaska is correct when he writes that he was ignorant of work published in the latter periodical. Second, Angoletta refers to compounds containing two carbonyl ligands per iridium, $Ir(CO)_2(PR_3)_2X$ and $Ir(CO)_2(AsR_3)_2X$, in her paper. As Collman mentions, it was Vaska who correctly formulated the composition of $IrCl(CO)(PR_3)_2$ as containing one CO per Ir. Finally, we can turn to the words of Walter Strohmeier in his 1968 review of homogeneous catalysis (33):

> The elucidation of the mechanism in homogeneous catalysis requires that all reactants, intermediates, and end products can be characterized and isolated. In addition, the structure, composition, and molecular weight of the catalyst in solution must be known. Another requirement is the knowledge of the composition and structure of the intermediate formed between the catalyst and one of the reaction products. Extensive research on Vaska's compound, $IrCl(CO)(PPh_3)_2$, has yielded most of the information mentioned above.

Why Is Vaska's Compound Important?

The recognition of $IrCl(CO)(PPh_3)_2$ as "Vaska's compound" and its inclusion in textbooks does not rest exclusively on his status as the discoverer of this square planar, coordinatively unsaturated iridium (I) compound. Rather, it is the reactivity of $IrCl(CO)(PPh_3)_2$ with small molecules that gives the compound its benchmark status in the field of transition metal organometallic chemistry. Even in his initial paper (2) on $IrCl(CO)(PPh_3)_2$, the important chemistry of Ir(I) is revealed; $IrCl(CO)(PPh_3)_2$ reacts with HCl to yield $IrHCl_2(CO)(PPh_3)_2$ in a process known today as oxidative addition (3). The reactivity of $IrCl(CO)(PPh_3)_2$ with HCl, Cl_2 and H_2 was investigated and discovered within a year of the original report on $IrCl(CO)(PPh_3)_2$ (36). The ability of a transition metal compound to activate H–H bonds at *ambient* temperature was fundamental to later discoveries of catalysts for the homogeneous hydrogenation of unsaturated organic substrates. The mechanisms of these reactions have been extensively studied and the results form the foundation of textbook chapters where the chemistry of $IrCl(CO)(PPh_3)_2$ is described (3). It is noteworthy that Vaska also reports (2) that reaction between $IrCl_3$, PPh_3 and 2-butenal yields small amounts of $IrCl(CO)(PPh_3)_2$. In retrospect, he may have even observed the activation of C–H bonds in aldehydes followed by decarbonylation and reductive elimination of alkane, processes that have been well documented for other coordinatively unsaturated metal complexes. Vaska's compound also reversibly coordinates small molecules such as CO, SO_2 and O_2 (37). It is the latter substrate that attracted a lot of attention as the reversible binding of oxygen to hemoglobin was one of the few other examples of this behavior among transition metal complexes.

Lauri Vaska and Sir Geoffrey Wilkinson

The connection between Vaska's compound and the advances in homogenous catalysis in the 1960s inevitably invites an exploration of the relationship between Lauri Vaska and Sir Geoffrey Wilkinson, with whom he shares proximate space in textbooks (3). Did Vaska have a hand in the discovery of $RhCl(PPh_3)_3$, known as "Wilkinson's catalyst?" If not, given his interest in H_2 activation how did he miss the reactivity of both $RuCl_2(PPh_3)_3$ and $RhCl(PPh_3)_3$ with hydrogen? The first report that $IrCl(CO)(PPh_3)_2$ oxidatively adds H_2 comes some six months after Wilkinson's report (26) of the homogeneous hydrogenation of olefins using $RhCl(PPh_3)_3$. Vaska recognized the possibility of using $IrCl(CO)(PPh_3)_2$ (1.3×10^{-3} M) as a hydrogenation catalyst in a paper received on August 9, 1965 (38), reporting 40% conversion of ethylene to ethane at 60°C after 18 hours under 290-620 mm Hg hydrogen pressure and 270-440 mm Hg ethylene pressure. Under the same conditions the rhodium analog of Vaska's compound, RhCl(CO)

$(PPh_3)_2$, is less active with only 24% conversion after 22 hours of reaction (39). In his paper, Vaska (38) cites Wilkinson's work on the catalytic activity of $ClRh(PPh_3)_3$ in homogeneous hydrogenation published earlier in the same year. Curiously, a second footnote to the chemistry of $ClRh(PPh_3)_3$ reads

> This compound, discovered by us independently several years ago, is highly dissociated in solution, and its composition and structure in solution are unknown at present.

Is there any truth to Vaska's claim? Wilkinson noted in his 1965 paper (39b) that his group probably shared the discovery of $ClRh(PPh_3)_3$ writing that the latter compound is

> Obtained as red-purple crystals by the interaction of ethanolic solutions of $RhCl_3•3H_2O$ with a ≈ 6-fold excess of triphenylphosphine acting as complexing and reducing agent and a suppressor of dissociation. This compound and the corresponding bromide and iodide have also been obtained by M. A. Bennett, University College, London (personal communication).

In fact, in Wilkinson's 1965 presentation on the catalytic activity of $ClRh(PPh_3)_3$ at a Welch Foundation Conference on Chemical Research (40), there is no mention of Wilkinson having known of Vaska's claim. Nevertheless, years later Vaska wrote (24):

> …replacing $IrCl_3$ with the corresponding isoelectronic rhodium chloride and leaving the rest of the ingredients the same, a sudden precipitation of a dark red substance occurs at ≈ 124°C. This precipitate persists but a few minutes (continued heating causes a color change to a yellow solution, from which the analogue to the iridium complex, *trans*-$RhCl(CO)(PPh_3)_2$ is isolated). After several experiments the dark red substance was isolated in chemically pure form. Analysis showed that we were dealing with a new complex $RhCl(PPh_3)_3$.

Vaska acknowledges that the same compound had been synthesized by an English and an Australian chemist before Wilkinson. Who were these unidentified chemists? In all likelihood, the "Australian" is Martin Bennett and the mystery Englishman may be Dr. Robin Coffey working at ICI. Prof. Bennett recalls that he and Coffey had also isolated $RhCl(PPh_3)_3$ but were waiting to file a patent when Wilkinson beat them to the table (41). Bennett later published his synthesis of "Wilkinson's catalyst" around the same time as Wilkinson's initial report (42). In any event, Vaska recognizes that it was Wilkinson who successfully used $ClRh(PPh_3)_3$ in homogeneous catalysis; in 1992 he wrote, "You can't win them all" (23).

Conclusions

Whether by accident or design, in Lauri Vaska's hands the reaction between iridium (III) chloride and triphenyphosphine in hot alcohol yielded a novel iridium(I) complex, $IrCl(CO)(PPh_3)_2$, known today as Vaska's compound. Its importance lies in being the first compound to undergo oxidative addition reactions with a range of small molecule substrates and yield isolable, characterizable products. The chemistry of $IrCl(CO)(PPh_3)_2$ that Vaska uncovered and published between 1961 and 1965 contributed to the explosion of research in homogeneous catalysis during this time. The fundamental reaction pathways observed for Vaska's compound contributed to the development of numerous homogeneous catalysts. His research interests intersected with those of better-known giants in the burgeoning field of organometallic chemistry, notably Geoffrey Wilkinson and Joseph Chatt.

Derivatives of Vaska's compound abound (43); there are some 62 references to "Vaska's compound" in the literature. Surprisingly, his 1961 paper on the synthesis of $IrCl(CO)(PPh_3)_2$ has been cited only about 60 times. In contrast, there are over 2000 references to $RuCl_2(PPh_3)_3$, a compound for which Vaska does not often get credit for discovering.

Between those "golden 60s" (24) and retirement from Clarkson University in 1990, Vaska continued his research into homogeneous catalysis, publishing an additional 61 papers. In retirement, Vaska has authored four books on his life growing up in Estonia, his post-war experiences as a refugee and later as an émigré in the United States. In the 50th anniversary year of the first published report of $IrCl(CO)(PPh_3)_2$, it is safe to say that "Vaska's compound" is worthy of inclusion in textbooks of organometallic chemistry and in the pantheon of historically important organometallic compounds.

References and Notes

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Prof. Vaska does not have a clear recollection of DiLuzio's career.

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4. See the catalog for Strem Chemicals, Inc. 2008-2010, *22*, 62.
5. Biographical details of Vaska's life are found in a) L. Vaska, *Neljakümnenda aasta must suvi*, AS Pakett, Tallinn, 2008. b) L. Vaska, *Sadamad ja Akadeemikud*, Tallinn, Eesti Keele Sihtasutus, 2006.
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8. The fate of most other refugees from Eastern Europe was repatriation, voluntarily or forcibly. See Ref. 6.
9. E. Järvesoo, Ed. *Balti Ülikool Saksamaal, 1945-1949*, Toronto, 1991.
10. The author's father served as an associate dean of the Baltic University for chemistry before continuing his own studies toward a doctorate in chemistry at the University of Hamburg.
11. Prof. Hans von Wartenberg (1880-1960) had served as head of the Göttingen inorganic chemistry institute from 1933 to 1937, when he was forced to retire by the Nazi administration. During the war he worked at the Göttingen physics institute. After the collapse of the Nazi regime, he was reinstalled in his previous position at the inorganic chemistry institute. See http://www.kchn.pg.gda.pl/?p=history&lng=en (accessed Nov. 5, 2012).
12. The refugees were not particularly popular among the German civilian population as they were seen as, among other things, thieves and the recipients of special treatment from the Allied Military Government.
13. Josef Goubeau (1901-1990) earned his doctorate from the University of Munich in 1926 and taught at the University of Göttingen between 1940 and 1951 when he moved to a professorship at the Technical University of Stuttgart. His research was in the synthesis and Raman spectroscopy of boron, silicon and phosphorus compounds. See http://www.uni-stuttgart.de/hkom/presseservice/pressemitteilungen/2001/32.html (accessed Nov. 5, 2012).
14. Prof. Franz Feher (1903-1991) earned his doctorate in 1927 from the Technical University of Stuttgart on the chemistry of manganese oxides. After a stint in Dresden, he moved to Göttingen in 1942 as senior assistant in the Chemical Institute. In September 1949 he took a position as Professor of Inorganic and Analytical Chemistry at the University of Cologne where he explored sulfur chemistry. See M. Baudler, "Franz Feher (1903-1991): A Personal and Professional Portrait," *Eur. J. Inorg. Chem.,* **1998**, 2089-2105.
15. L. Vaska, "Ebatäpne Aatom," *Akadeemia*, **1998**, 1453-1491.
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About the Author

Rein U. Kirss graduated from SUNY Buffalo in 1981 with a BA degree in History and a BS degree in Chemistry. A year later he completed a MS degree in Chemistry with Prof. O. T. Beachley Jr. before heading to the Midwest. He completed his Ph.D. in Inorganic Chemistry at the University of Wisconsin-Madison under the direction of Prof. Paul M. Treichel in 1986. After two years of post-doctoral study with Prof. Richard Eisenberg (University of Rochester) and a year as a research scientist at ATMI (Danbury, CT) he joined the faculty at Northeastern University in August 1989, where he has remained as an associate professor. He is co-author on three editions of *Chemistry: The Science in Context* (W. W. Norton, **2004**, **2009**, **2012**) and maintains research interests in the organometallic chemistry of iron and ruthenium.

Chemical Heritage Foundation Names Carsten Reinhardt President and CEO

Carsten Reinhardt, professor of history of science at Bielefeld University will become president and CEO of the Chemical Heritage Foundation (CHF) effective August 1, 2013. He will be the third president of CHF, succeeding Thomas R. Tritton, who is retiring.

Reinhardt was selected following a worldwide search for a leader with a great depth of experience in the history of science and technology. He has extensively researched and published on the impact of chemistry on society through topics including the history of industrial research, the emergence of instrumentation, and chemistry's links to physics, biology, medicine, and technology.

Carsten Reinhardt joined the faculty of Bielefeld University in 2007. In 2006-2007 he held a fellowship at the Max Planck Institute for the History of Science. Prior to that, he spent a decade as a professor at the University of Regensburg.

The author of three books, most recently *Shifting and Rearranging: Physical Methods and the Transformation of Modern Chemistry* (Science History Publications/USA, 2006), Reinhardt has contributed to five edited volumes and published nearly forty scholarly articles. In addition he has received many awards and fellowships, including being named a fellow at the Max Planck Institute for the History of Science and professeur invité in the Department of Philosophy, École Normale Supérieure. Reinhardt was an Edelstein Fellow at CHF in 1998-1999. He was also an Edelstein Fellow at The Hebrew University of Jerusalem in 1994.

The Chemical Heritage Foundation is a collections-based nonprofit organization in Philadelphia, Pennsylvania, USA, that preserves the history and heritage of chemistry, chemical engineering, and related sciences and technologies. The collections are used to create a body of original scholarship that illuminates chemistry's role in shaping society. In bridging science with the humanities, arts, and social sciences, CHF is committed to building a vibrant, international community of scholars; creating a rich source of traditional and emerging media; expanding the reach of our museum; and engaging the broader society through inventive public events. For more information about CHF please visit our website at www.chemheritage.org.

ANIONIC NAMES OF ACIDS—AN EXPERIMENT IN CHEMICAL NOMENCLATURE

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“*Die wahre Heimat ist eigentlich die Sprache* (The true homeland is certainly the language),” said Wilhelm von Humboldt (1769-1859). This was more than true for Germans, who in that time were not *ein Volk, ein Reich* but were dispersed in hundreds of independent kingdoms and duchies. The same holds true for the Balkan “South Slavic” peoples (“Yugoslavs”), but with a crucial difference: they share principally the same language, but neither national (Croatian, Serbian, Montenegrin, Bosnian) feelings nor religion (Catholicism, Orthodoxy, Islam). On the one hand, there were strivings to make Croatian and Serbian one standard language, and even one nation from the Croats and Serb (1, 2). On the other hand, there were effortful attempts to make the two languages as different as possible. The latter tendency went to extremes in the Nazi-controlled Independent State of Croatia (1941-1945), when all Serbian words in Croatian, as well as the Cyrillic alphabet, were prohibited. Likewise, international words (*radio*, *automobil*, *telefon*, etc.) were replaced by made-up Croatian words. It was also prohibited to start a telephone conversation by the usual *halo* (hello); it was ordered to say *spremni* (ready to do) (3).

Making One Language out of Two

It was the same with the chemical language, chemical nomenclature and terminology. Unitarily oriented, Vladimir Njegovan (1884-1971), Professor of Inorganic Chemistry at Zagreb University, Croatia, was among the first who tried to make a common nomenclature for both Croatian and Serbian chemists despite many striking differences (Croat. *dušik*, Serb. *azot* for nitrogen, Croat. *spoj*, Serb. *jedinjenje* for compound, etc.) (4). In the 19th century, however, Croatian chemists tried to use pure Croatian nomenclature, replacing international words with Croatian neologisms (*smrdik* for bromine, Croat. *smrditi* – to stink; *sumporovina*, meaning “substance obtained from sulfur,” for sulfuric acid, etc.).

In contrast to the majority of European nations, whose languages had only to be learned, Croatian, as a standard language, had yet to be created. It was especially hard to do it in chemistry, because one had to take into account not only the international rules for chemical names but also the differences between Serbian and Croatian. Many and various language experiments resulted from such a constellation of linguistic considerations.

One such experiment commenced with the proposition by Dragutin Strohal (1884-1948), Professor at the School for Education in Zagreb, who in 1942 published an idea for naming acids in a more convenient way (5). Namely he proposed to derive the names of acids from the names of their salts; therefore sulfuric acid should be “sulfatic acid” (Croat. *sulfatna kiselina*), nitric acid “nitratic acid” (Croat. *nitratna kiselina*), and hydrochloric acid “chloridic acid” (Croat. *kloridna kiselina*). The rule particularly fitted the Croatian language, because the names of acids were derived from the Croatian names of elements (H_2SO_4: *sumporna kiselina*, HNO_3: *dušična kiselina*, etc.) and the names of salts from their international (i.e., Latin) names. The first intention of Professor Strohal was to help students, because they had to learn unrelated names of acids and their salts. ("As a chemistry teacher, I find that our current names of acids often confuse the beginners in chemistry.") The other argument was a linguistic one: the adjective *sumporasta* (sulfurous) means "like sulfur" whereas *sumporna* (sulfuric) means "of sulfur," and Strohal argued, "One might conclude that there is more sulfur in sulfuric than in sulfurous acid, whereas just the opposite is true." He also claimed his system would be very useful in organic chemistry because the current names of many organic acids were derived from Croatian (e.g. *vinska kiselina* for tartaric acid; Croat. *vino*, wine). However, presumably, Mladen Deželić (1900-1989), editor of the journal *Kemijski vijestnik*, was inspired to add in a footnote: "This interesting proposition is the personal opinion of Professor D. Strohal… But we reckon it would be difficult to replace the names of common acids, which have been used for so long, with new names."

Strohal's or Ostwald's Nomenclature?

Strohal's nomenclature was well known to Croatian chemists, but nobody acknowledged it for decades. Moreover, nobody knew that "Strohal's nomenclature" was not Strohal's at all until 2005, when two authors of this contribution (V. S. and T. P.) discovered that it had been originally proposed by Wilhelm Ostwald (1853-1932) (6). In his book *Die Schule der Chemie – erste Einführung in die Chemie für Jedermann*, Ostwald introduced "*Jedermann*" into chemistry by a fictional dialogue between the teacher and his student. Among other things, they discuss the names of acids and their salts (7):

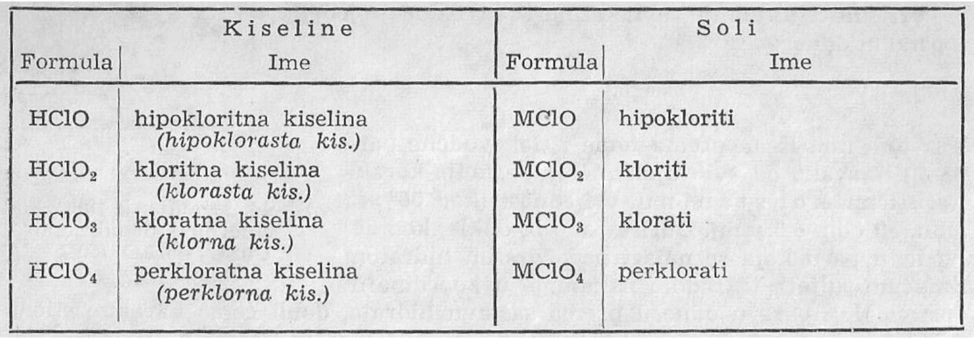
> *Schüler: Warum hat man eigentlich die doppelten Namen?*
>
> *Lehrer: Das hat geschichtliche Gründe. Anfangs waren nur die deutschen Namen üblich, dann änderte sich die wissenschaftliche Auffassung der Säuren und Salze, und das kamen für die Salze die nichtdeutschen Namen auf. Für die Säuren sind aber nicht entsprechende Namen gebildet worden, so daß hier die deutschen Namen beibehalten worden sind.*
>
> *Schüler: Aber man könnte doch ganz gut „Chloratsäure“ und „Hypochloritsäure“ sagen.*
>
> *Lehrer: Freilich. Wenn du einmal ein einflußreicher Chemiker geworden sein wirst, kannst du diese Namen in Vorschlag bringen und einführen.*
>
> *Schüler: Tue du es doch!*
>
> *Lehrer: Einstweilen mußt du die alten Namen lernen, weil sie noch in allgemeinen Gebrauch sind (…).*

There is the same problem with naming acids and their salts in German as in Croatian; in German, unlike English, the names of salts are also unrelated to the names of their respective acids (H_2SO_4: *Schwefelsäure*). But it is not entirely certain that Strohal simply accepted Ostwald's proposal without referencing it. It is very probable that Strohal read Ostwald's book, moreover, because it was translated into Croatian in 1912 (8). Accordingly, a Croatian chemical historian, Snježana Paušek-Baždar, stated that the chemist who introduced "anionic nomenclature" into Croatian was not Dragutin Strohal but the translator of Ostwald's book, Gustav Fleischer (1856-1913), one of the first Croatian chemists (9). Such claims are quite problematic; nobody introduces nomenclature by bare translation or writing the anecdotes in popular books. Strohal might or might have not been familiar with Ostwald's book and its translation, but he certainly wrote the first elaborated and argued proposal for the anionic nomenclature in a scientific journal.

Introducing Anionic Nomenclature

As already mentioned, Strohal's nomenclature was well known to Croatian chemists. Professor Njegovan found, echoing Strohal's argument, anionic nomenclature to be "very interesting and rational, but unfortunately not in use in international literature" (4). This was the major obstacle for its use until the unitary revision of chemical nomenclature and terminology took place. The translators of Wiberg's *Inorganic Chemistry* (10, 11) (Figure 1), headed by Hrvoje Iveković (1901-1991), Professor at the Faculty of Pharmacy in Zagreb, strived to coin chemical terms which should be same for both the Croatian and Serbian languages (12). As chemical terms considerably differ in the two languages, the most plausible way to unify them was to use "international," rather than Croatian or Serbian terms. Therefore Croatian *željezo* and Serbian *gvožđe*, for iron, turned into *ferum*, Croatian *kisik* and Serbian *kiseonik* turned into *oksigen*. (Clearly, if one cannot make one language out of two, one must use another language!)

Strohal's terminology best meets the needs of the new "Yugoslav" chemical nomenclature (13), because the names of acids differ in Serbian and Croatian (e.g. Croat. *dušična kiselina*, Serb. *azotna kiselina* for HNO_3), unlike the names of their salts (Croat./Serb. *nitrat*). Much



Kiseline		Soli	
Formula	Ime	Formula	Ime
HClO	hipokloritna kiselina *(hipoklorasta kis.)*	MClO	hipokloriti
$HClO_2$	kloritna kiselina *(klorasta kis.)*	$MClO_2$	kloriti
$HClO_3$	kloratna kiselina *(klorna kis.)*	$MClO_3$	klorati
$HClO_4$	perkloratna kiselina *(perklorna kis.)*	$MClO_4$	perklorati

Figure 1. *Anionic names of the oxoacids of chlorine in the Croatian translation of Wiberg's Lehrbuch der Anorganischen Chemie (Ref. 11, p 134). The traditional Croatian names of acids were printed in italics.*

was discussed at the time among chemists about which of the two nomenclatures (the old or the new Strohal's) would be easier to learn (14). However this was not the major reason for its introduction; it was rather the idea of making a unified (Serbo-Croatian) chemical nomenclature (Table 1).

Propagators and Opponents

The anionic nomenclature appeared in conversation lexicons, at first as "the new technical term for sulfuric acid" (*sulfatna kiselina*) (15), as well as in middle, high school and university textbooks. The new chemical names were preferred to the old ones, suggesting that anionic naming of acids was in accordance with the international (IUPAC) nomenclature, in contrast to the old "trivial" names. The chemists, however, were generally reluctant, seeing in the new names of acids nothing but one of many linguistic innovations, inspired by the whims and pride of their influential colleagues.

The new "Yugoslav" nomenclature found many opponents, especially among Croats. It is noteworthy that it was approved by the Union of the Yugoslav Chemical Societies, but not by its Croatian member, the Croatian Chemical Society. In spite of this, it was also used in Croatia, fortunately without political consequences to its opponents (16).

The most prominent opponent was Vladimir Simeon (b. 1939), Professor of Physical Chemistry at the Faculty of Science, Zagreb. In a round-table discussion on the feasibility of the new nomenclature (among panelists V. Njegovan, V. Simeon, and H. Iveković), Simeon pointed out that Strohal's nomenclature was "unnecessary" (17).

Table 1. Anionic names of acids

Compound	**Traditional name (Croatian)**	**Traditional name (Serbian)**	**Anionic (Strohal's) name (in both Croatian and Serbian)**
hydrobromic acid	bromovodična kiselina	bromovodonična kiselina	bromidna kiselina ("bromidic acid")
nitric acid	dušična kiselina	azotna kiselina	nitratna kiselina ("nitratic acid")
nitrous acid	dušikasta kiselina	azotasta kiselina	nitritna kiselina ("nitritic acid")
carbonic acid	ugljična kiselina	ugljena kiselina	karbonatna kiselina ("carbonatic acid")
acetic acid	octena kiselina	sirćetna kiselina	acetatna kiselina ("acetatic acid")
succinic acid	jantarna kiselina	ćilibarna kiselina	sukcinatna kiselina ("succinatic acid")

In the foreword of the Croatian translation of IUPAC nomenclature of inorganic chemistry he clearly stated: "Finally, Iveković 'resurrected' Strohal's nearly totally forgotten proposition for the local trivial nomenclature of acids (e.g. '*sulfatna kiselina*' instead of '*sumporna kiselina*'). It is not clear which reasons induced him—chemical or political—to decline the *1957 Rules*, despite the fact that IUPAC was, even in those times, against the introduction of new trivial nomenclatures. It is hard to believe that Iveković was unaware of this categorical IUPAC statement" (18). Moreover, Professor Simeon pointed out that traditional Croatian nomenclature was more in line with IUPAC rules because it was based on the "national" (i.e., Croatian) names of elements.

However, not everybody agreed with Professor Simeon. Stjepan Babić (b. 1925), a linguist, and Vladimir Grdinić (b. 1939), a pharmacist, pointed out that Strohal published his proposition in 1942, long before the unified Yugoslav nomenclature (1966), and—we should add—in a year when Yugoslavia no longer existed (19). "It has to be said that the anionic names of acids are simple, easy to learn, comprehensive, and are logically connected with the constitution of acids," they said and added that "there is more whim than linguistic arguments" in contradicting the proposition for anionic naming of acids.

But Professor Simeon's opinion, expressed in such an influential book as *Inorganic Nomenclature*, was decisive for the abandonment of anionic names of acids in Croatia. There is no trace of it left in the new textbooks, nor in lexicons. In schools its usage was judged as inappropriate and erroneous (20). However, it still persists in the commercial names of chemicals, as well as on numerous Internet sites with chemical content, and—because of the influence of Professor Grdinić—in pharmaceutical literature (21, 22, 23), which was criticized for doubling the official chemical names (one for chemists, one for pharmacists) (24).

Interestingly, anionic nomenclature is still in official use in Serbia, Bosnia and Herzegovina, and Montenegro, but the old names of acids are preferred.

Conclusions

There were many proposals worldwide for naming chemical compounds, some even without reference to any traditional nomenclature (25). But it is not enough to create new words or a new language; they necessarily have to be accepted and used by a community, however small. This was the case with the anionic nomenclature. It is very symptomatic that it was not used in Germany, the United Kingdom, the United States, France, or any country in which Ostwald's *Die Schule der Chemie* was read. Instead, it was used officially for more than 30 years in the Communist Yugoslavia, but only in the federal units in which "Serbo-Croatian" language was spoken (26). The principal reason for its use was obviously not chemical but political; as federal (Yugoslav) oriented Hrvoje Iveković was its propagator, so was nationalistically (Croatian) oriented Vladimir Simeon its principal opponent. Abandonment of anionic nomenclature in Croatia thus has to be viewed not only as an adjustment of Croatian inorganic nomenclature to the IUPAC recommendations, but also as one of many victories in the fight for the independence of the Croatian language.

References and Notes

1. "If we take his traveler diaries in our hands," Professor Fran Bubanović (1883-1956) (Ref. 2), a Croatian chemist, wrote of his colleague and friend Fran Tućan (1878-1954), Professor of mineralogy at the Zagreb University, "and also if we attend his speeches and lectures about his impressions he obtained by observing people from a viewpoint of a man of science, a man who really had the opportunity to build his own personal opinion of the world and life, we will be convinced that the mineralogist Fran Tućan in his general statements puts to the light as the most natural and the most sober thought, which stems from the nature and life of our people, that Croats and Serbs, as far as he knows them, are one nation." (F. Bubanović, *Kemijo, hvala ti!* (*Thank you, chemistry!*), Jovana i Vuića, Beograd, **1939**, p 110).
2. N. Raos, "Letters of Svante Arrhenius to his Former Croatian Student," *Bull. Hist. Chem.*, **2008**, *33*, 12-16.
3. M. Tanner, *Croatia: A Nation Forged in War*, 2nd ed., Yale Univ. Press, New Haven, 1997, pp 141-167.
4. V. N. Njegovan, *Osnovi hemije (Foundations of Chemistry)*, Naučna knjiga, Beograd, 1965, pp 110-116. Njegovan made a linguistic mishmash; for instance, a Croatian word for iron would mean iron as a chemical element, and a Serbian word for it would mean iron as a material. He also, as the first editor-in-chief (1927-1933) of the central Croatian chemical journal *Arhiv za hemiju i farmaciju* (now: *Croatica Chemica Acta*), insisted that the journal be published in the Serbian, not Croatian, language (N. Trinajstić, *Ogledi o znanosti i znanstvenicima* (*Essays on Science and Scientists*), Matica hrvatska, Zagreb, 1998, pp 125-142).
5. D. Strohal, "Prijedlog za izmjenu kemijskog nazivlja kiselina (Proposition for Revision of Chemical Nomenclature of Acids)," *Kem. Vijest.*, **1941/42**, *15/16*, 126.
6. V. Stilinović and T. Portada, "Je li 'Strohalova nonenklatura' doista Strohalova? (Is 'Strohal's Nomenclature' Really Strohal's?)," *Kem. Ind.*, **2005**, *54*, 347-350.

7. Student: Really, why are there double names?
   Teacher: This is for historical reasons. At first, German names were trivial, then the scientific opinions of acids and salts changed, and non-German names appeared. But the names of acids did not change, thus German names are still in use.
   Student: But one could also say "chloratic acid" and "hypochloritic acid."
   Teacher: Certainly. When you have become an influential chemist, you can propose and propagate these names.
   Student: Why don't you do it yourself?!
   Teacher: In the meantime you have to learn the old names, because they are in general use.
   (W. Ostwald, *Die Schule der Chemie – erste Einführung in die Chemie für Jedermann*, 3rd revised edition, Vieweg & Sohn, Baunschweing, 1914, p 232. Ostwald's book was published in English under the title *Conversations on Chemistry: First Steps in Chemistry*; however, the German title translates to *The School of Chemistry – the First Introduction to Chemistry for Everyone*.)
8. W. Ostwald, *Uputa u kemiju za svakoga* (G. Fleischer, Tr.), Bjelovar, 1912. It is interesting that Fleischer translated not only the new names of acids into Croatian, but he also "translated" *deutsch* into *hrvatski* (Croatian).
9. S. Paušek-Baždar, "Kemijski rad Gustava Fleischera (Chemical work of Gustav Fleischer)," *Radovi Zavoda za znanstvenoistraživački i umjetnički rad u Bjelovaru*, **2007**, *1*, 205-216.
10. E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 57th-70th revised edition, Walter de Gruyter & Co, Berlin, 1964.
11. E. Wiberg, *Anorganska kemija* (H. Iveković, Ed.), Školska knjiga, Zagreb, 1967.
12. In the Kingdom of Yugoslavia (1918-1941) and Communist-ruled Socialist Federal Republic of Yugoslavia (1945-1991), it was politically very dangerous to speak in the Croatian or Serbian language. The language was called Serbo-Croatian, Croato-Serbian, or Eastern (i.e. Serbian) and Western (i.e. Croatian) standard. As nobody likes to call their native language by strange names, the most popular term was "our language."
13. *Unificirana jugoslavenska nomenklatura anorganske kemije, izrađena na osnovi preporuka Internacionalne unije za čistu i primijenjenu kemiju (Unified Yugoslav Nomenclature of Inorganic Chemistry, Composed on the Basis of the Recommendations of the International Union for Pure and Applied Chemistry*), Ed. H. Iveković, Školska knjiga, Zagreb, 1966.
14. "I am irritated by the names *klorna* (chloric), *klorasta* (chlorous) and *hipoklorasta* (hypochlorous)," responded a participant to an Internet forum in 2010. "*Kloratna* (chloratic), *kloritna* (chloritic) and *hipokloritna* (hypochloritic) sound better." It is easier to learn that *sulfat* is the salt of *sulfatna kiselina* than of *sumporna kiselina*, but one has to learn that *sulfur* is a synonym for *sumpor*.
15. *Leksikon Jugoslavenskog leksikografskog zavoda (Lexicon of the Yugoslav Lexicographic Institute)*, Zagreb, 1974, p 943.
16. Another attempt to stop the unification of Croatian and Serbian languages had, however, much more serious consequences. The Declaration Concerning the Name and Position of Croatian Language, signed in 1967 by 140 of the most prominent Croatian writers and intellectuals, was judged "a counterrevolutionary act." Most of the signers were expelled from the Communist party, which practically meant that they were treated as unfit for any responsible job (Ref. 3, pp 184-202).
17. "Prijedlog Jugoslavenske nomenklature anorganske kemije (Proposition of Yugoslav Nomenclature of Inorganic Chemistry)," *Croat. Chem. Acta*, **1965**, *37*, C1-C5.
18. *Hrvatska nomenklatura anorganske kemije: izradila Komisija za nomenklaturu anorganske kemije IUPAC*, (V. Simeon, Ed.), Školska knjiga, Zagreb, 1996, p XI.
19. S. Babić, V. Grdinić "Prijedlog za rješenje nedoumica u kemijskom nazivlju (A proposition for solving the uncertainties in chemical terminology)," *Jezik*, **2002**, *49(1)*, 1-40.
20. "When I said *nitratna kiselina* to my professor, she stared at me in surprise and said: 'Which acid?' She insisted that these (*dušična kiselina* etc.) are Croatian names which sound better and are used in technical literature," said a participant of Internet forum, 2010.
21. V. Grdinić, *Hrvatsko farmaceutsko nazivlje, prinosi za hrvatsku jezičnu normu i kodifikaciju u ljetopisu, preporuke 1995 (Croatian Pharmaceutical Nomenclature, Additions to Croatian Linguistic Norm and Codification in Annales, Recommendations 1995)*, Hrvatski zavod za kontrolu lijekova, Zagreb, 1995.
22. *Hrvatska farmakopeja 2007 s komentarima (Croatian Pharmacopoeia 2007 with Comments),* Hrvatsko farmaceutsko društvo, Zagreb, 2007.
23. V. Grdinić, "Farmaceutski naslovi u Hrvatskoj farmakopeji (Pharmaceutical Titles in Croatian Pharmacopoeia)," *Farm. Glas.*, **2007**, *63(1)*, 37-55.
24. T. Portada, Letter to Editor, *Farm. Glas.,* **2006**, *62(12)*, 753-754.
25. N. Raos, "Redefining the atom," *Chem. Brit.,* **1997***, 33*, 31-32.
26. In the Slovenian federal unit, the official language was Slovenian, and in Macedonia Macedonian, similar to Bulgarian. They are also South-Slavic languages, but quite different from Serbian or Croatian. Serbian and Croatian are, however, no more different than British and American English. As Slovenian and Macedonian names of acids are also unrelated to the names of their salts (e.g. Slov. *žveplena kislina* for sulfuric acid), there is no linguistic reason against the introduction of anionic nomenclature in these languages.

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ON THE ORIGINS OF A TOOL FOR CHEMISTS, THE DEAN-STARK APPARATUS

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Summary

An utterly simple glassware tool for chemists, the Dean-Stark trap as it became known, was devised in 1920. This paper strives to elicit the multiple meanings carried by this little device, with widespread and continued use in the chemical laboratory. It also describes the milieu of American chemistry between the two World Wars in which the original paper by Drs. Dean and Stark appeared.

Introduction

During most of the twentieth century, chemistry laboratories, whether academic or industrial, contained separate enclosures: the processed material had to be protected from two main enemies, dioxygen and moisture. Hence, many shielding devices were resorted to: for the former, running reactions and separations under helium, argon or dinitrogen, and vacuum lines. For the latter, laboratories displayed ovens, conservation of solvents over sodium wire, desiccants such as Drierite® or the Fisher 4-Å molecular sieve, desiccators, dry boxes, and more.

We shall concern ourselves here with yet another laboratory tool against moisture and for its removal, the Dean-Stark apparatus (also known as the Dean-Stark trap) (1). We shall focus primarily on the early 1920s when this device was invented. Such a viewpoint, making explicit the invisible birthmarks on an artefact, is comparable to establishing the etymology of a word. Another, near orthogonal take, is comparable, in turn, to chronicle the evolution in the uses and meanings of this word, across the ages, as Jean Starobinski beautifully did for the word "reaction" (2). Both approaches, we submit, are valid historical contributions.

Birthplace

This tool for chemists was devised in 1920 at the Pittsburgh Station of the US Bureau of Mines. Its progenitors were two scientists from the chemistry section, Edward Woodward Dean (1888-1959), a Yale Ph. D. in 1912 with W. A. Druschel, and David Dewey Stark, a junior petroleum chemist (1893-1979) (3). The actual maker was the glassblower for the Station, Francis E. Donath (1874-ca. 1960).

The US Bureau of Mines concerned itself with chemistry, and with the chemistry of petroleum in this case, as a not-too-distant consequence of the breakup, in 1911, of the monopoly of Standard Oil and the so-called "independents." At the outbreak of World War I, the Federal administration and the newly-formed oil companies decided to work together, rather than in opposition, to ensure continued supply of oil-derived fuel to the military. On March 20, 1919, the American Petroleum Institute was started in New York. Its missions included collection of statistics for the oil industry and development of industry-wide standards (4).

This was indeed a period for establishment of public petroleum institutes in various countries. For example, in France, at the newly regained University of Strasbourg—the Alsace-Lorraine was returned to France from the German occupation it had undergone since 1871, after having been part of France since the seventeenth century—Henry Gault (1880-1967) a professor of chemistry, founded in 1920 the *Institut du pétrole et des moteurs*. It served as the seed for what would later become, when it departed Strasbourg after World War II, *Institut français du pétrole*.

Let us now return to the Pittsburgh Station of the US Bureau of Mines. Pittsburgh then numbered 600,000 people and it was the fifth largest metropolis in the United States (5). Fossil fuels, coal and petroleum had made it a thriving industrial center (6). The former, an abundant local mining resource, had given rise to metallurgy in the area. Pittsburgh is at the center of the northern half of the great Appalachian coal field. Beneath the so-called "Pittsburgh seam" there was another, the Freeport seam, which ensured durable coal production. In the 1920s annual coal production was in the order of 100 Mt.

As for petroleum, one will recall, underground deposits had been discovered by Titus Drake in Pennsylvania. As a consequence, Pittsburgh hosted oil refineries, no fewer than 58 in 1867 and at that time supplied over 60 % of the entire foreign export of petroleum (7). Pittsburgh in the early 1920s was a techno-city (8) that included a center of chemical research (9).

Coal, steel and oil made hefty contributions to the fortunes of the Carnegie and Mellon (10) families. As John Dos Passos wrote in *The 42nd Parallel*, published in 1930 (11),

> Andrew Carnegie believed in iron, built bridges Bessemer plants blast furnaces rolling mills;
> Andrew Carnegie believed in oil;
> Andrew Carnegie believed in steel;
> always saved his money
> whenever he had a million dollars he invested it.
> Andrew Carnegie became the richest man in the world and died.
> Bessemer Duquesne Rankin Pittsburgh Bethlehem Gary ...

A new building of the US Bureau of Mines was dedicated in 1919—construction had begun in 1915 (12) and actual occupation and use started in 1917—on Forbes Avenue in the Squirrel Hill neighborhood (13). It was a neighbor to another two laboratories also devoted largely to applied science, the Carnegie Institute of Technology, founded in 1900, and the Mellon Institute of Industrial Research, founded in 1913 by Andrew W. Mellon.

The research staff of the US Bureau of Mines in their new building immediately began working on the physicochemical properties of crude oil, such as viscosities, from various production sites in the US (14). Edward W. Dean worked there from the opening of the Station. He studied at first petroleum distillation and gasoline manufacture (15). Dr. Dean was responsible for reports on the properties of American crude oil from various locations (16). He took responsibility also for the design of laboratory instrumentation (17).

Hydrocarbon Fuels During and After World War I

In the aftermath of the Great War, two modes of transportation, aviation and the automobile, drew heavily on production by oil refineries in the United States. The Twenties roared also with automobile and airplane engines. The former is illustrated by the biography of Horatio Alger's father, an aviation pioneer in the Army Air Corps who entered the reserves in the late 1920s and then became an aviation fuel expert for Standard Oil Company. Alcock and Brown used Shell fuel to make the first trans-Atlantic flight in 1919.

The 1920s were a period of building American airports. In Chicago, for instance, originally built in 1923 as the Chicago Air Park, Midway airport was mainly used initially by airmail contractors. In 1927 it was dedicated as the Chicago Municipal Airport. 1928 marked the airport's first full year of operation with 12 hangars and four lighted runways to allow night flights.

Following Charles Lindbergh's solo and non-stop transatlantic crossing (1927), airlines began sprouting in various countries. In Europe, the French Aéropostale had opened its first route between Toulouse and Barcelona just after the end of the Great War. It was extended to Casablanca by February 1919, to Dakar by 1925, and to South America by the spring of 1930. Duration of intercontinental travel was cut down from days to hours.

As for the automobile, before the Great War, cars were a luxury reserved to the very wealthy. In the 1920s, mass-produced vehicles became common throughout North America (18). By 1927, Ford discontinued the

Model T after selling 15 million of them. Gasoline, although differing from aviation fuel, also had as a requirement the presence of an anti-knock agent, in the form of tetraethyllead: this innovation, together with the devising of the octane rating (19), also dates to the same period of the 1920s.

***Figure 1**. A Penn Oil Truck from 1920 boasts "more power" (Library of Congress Prints and Photographs Division, National Photo Company Collection).*

Hence, oil refineries in the 1920s had to supply standardized fuels with well-defined characteristics (octane 40-60), in the face of crude oil beset with highly variable parameters, not to mention its admixture with water (or rather brine) as it came out of a well—which was the origin of Dean and Stark's search for an efficient separation procedure or device.

The Devising of the Tool

In the immediate aftermath to World War I, when Dean and Stark announced their device, the presence of moisture in various commodities, such as indeed petroleum, but also quite a few others, was a nagging technological concern: how to measure its level, how to get rid of it. The same *Industrial and Engineering Chemistry*, during the year 1920 when Dean and Stark's paper appeared, carried others on that very topic (20).

The scientists, physicists and chemists, involved in petroleum studies faced the frequent occurrence of water-in-oil emulsions, which led to samples in flasks and test tubes "frothing at the mouth" so to speak. This was a problem in the field as well (21).

The two progenitors, Drs. Dean and Stark, conceived a solution. It combined the can-do mentality and the American genius for putting together a device that will do the job. Their Rube Goldberg device was, to put it in the simplest possible manner, a hybrid between a still and a funnel.

The technical problem, once analyzed, was how to separate water from a hydrocarbon solvent. The technical fix was obvious, a distillation together with removal of the offending water. Addition of a hydrocarbon solvent would make sure the mixture was removed from the azeotrope. After experimenting with a number of adjunct solvents, Dean and Stark elected either a petroleum naphta ("cleaner's naphta, of proper distilling range") or a benzene-xylene mixture. Water had the greater density, hence gravity would suffice to remove it. It was only necessary to put in an adjunct to the condenser, in the form of a small separate container for the water. The glassblower at the Station, Mr. Donath, made the all-glass contraption, henceforth to be known as the Dean-Stark adapter, apparatus, or trap. Here is their diagram of the device (Figure 2):

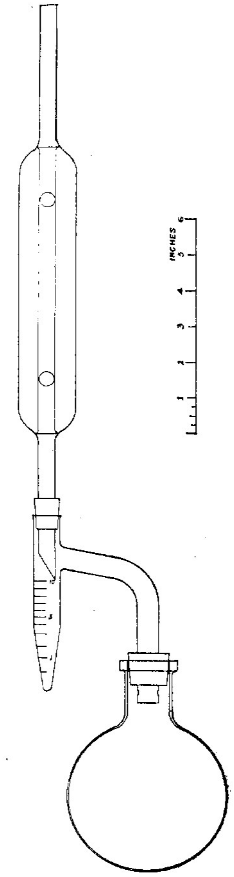

***Figure 2.** The original apparatus, as depicted in Dean and Stark's paper (Ref. 3).*

Drs. Dean and Stark chose to publish in *Industrial and Engineering Chemistry*. It was an outstanding choice. This periodical of the American Chemical Society was obviously devoted to applied science. Still, it emphasized a tight coupling with pure science as shown, for instance, by the publication the same year 1920 as Dean and Stark's report of an article by Irving Langmuir on the novel understanding of the chemical bond gained in the aftermath of G. N. Lewis's 1916 paper in *JACS* (22). It published articles on chemical education and the training of chemical engineers (23). Another sign of the breadth of the interests represented by that journal was its concern with economic geography: each issue carried reports on the chemical industry overseas or in various parts of the United States. In terms of technical problems, crude oil clearly was a major concern, as other articles published the same year 1920 attest (24). In short, a chemical engineer and many a research chemist would have been well inspired to read each monthly issue from cover to cover.

What about the writing of Dean and Stark's paper? Two qualities strike today's reader, nearly a century later. The first feature is the total absence of hype. To quote these authors, "On account of the simplicity of the modified method the authors have found it difficult to believe that their work could be new." The second feature is the detailed, exhaustive, step-by-step description of both the distillation procedure and the apparatus: this was a time when scientific reproducibility was clearly at a premium, the editors would not have tolerated any but a report which anyone could reproduce easily.

Pittsburgh Recession

About that time in the early 1920s, Pittsburgh entered a decline in attractiveness to industry and thus lost its prosperity. The City Fathers made an effort at conversion from leadership in industry to another in scientific research and in education (6).

As a memory of its heyday as a world center in oil refining, major oil companies made their headquarters in Pittsburgh. For instance, in 1922, the Penn-Okla Oil Corporation had its headquarters in Pittsburgh. Of course, Pittsburgh prided itself on the Mellon family and its fabulous wealth, which had accrued significantly from oil production and distribution. Accordingly, the headquarters for both Mellon properties, Mellon Financial and Gulf Oil, were and stayed in Pittsburgh. The most impressive Gulf Tower skyscraper was completed in 1932. In addition, Gulf Oil maintained its research and development laboratories in Pittsburgh, until its takeover by Chevron. The oil legacy was thus still alive in Pittsburgh past the 1950s (25).

The Cathedral of Learning tower, commissioned in 1921, went up in 1931-34 and it signaled the ambitions of the University of Pittsburgh. The nearby institutes for applied science, whether the Carnegie, the Mellon or the US Bureau of Mines forged on. Their part of the city underwent continued development until the Depression. To mention just one landmark from that time, the Webster Hall hotel was built in 1925. It remains to this day a monument to Pittsburgh's Golden era, that lasted for half-a-century, from the 1870s until the 1920s.

What about our three inventors, Drs. Dean and Stark, and Mr. Demuth? The first two, alert and smart scientists that they were, saw the writing on the wall. Oil prospecting and production were leaving Pennsylvania behind, electing to settle instead in places such as Oklahoma, Louisiana and Texas, and overseas locations such as the Persian Gulf. Of those two scientists, one moved East, the other moved West: in 1922 Dean moved to Standard Oil's labs in New Jersey (26) and Stark went to the Bay Area, where he worked for Associated Oil in San Francisco (27). As for Mr. Demuth, he stayed put, continuing in his work as a glassblower in the Station. In fact, he would retire in 1952, after 40 years of service to the US Bureau of Mines in its Pittsburgh Station (28).

Conclusion: the Coming of Age of American Chemistry

The devising of the Dean-Stark apparatus is not an isolated event, rather it is part and parcel of the impressive rise of American science, chemistry in particular, following the end of the First World War. The same year 1920 as Dean and Stark's publication, George Eastman started production of laboratory chemicals in Tennessee (29). Laboratory glassware started to carry a distinctly American trademark with the production of pyrex glass by the Corning company (30). Later developments, ushering in a revolution in the tools of chemistry completing the switch from a craft to a profession, if they came later, during the 1930s, were also American: the building of X-ray diffractometers, of electron diffractometers, of mass spectrometers (with their first appearance within petroleum chemistry as well), of infrared spectrometers (31), of the microelectrode by Ida H. Hyde (1857-1945) (32), … All were signs of the times. Among other laboratory tools devised by Americans between the two world wars, pride of place might go to the pH meter, invented around 1936 by Arnold Beckman. A trickle-down from academia (Caltech), it shared with the Dean-Stark trap being a device for solving practical problems of field work (33).

Let me briefly list some of the factors for the rise of American chemistry to the fore: the boost of the economy due to the war in Europe (34); the World War I defeat of Germany, of course, and the new role of the US as the world economic leader; the passing of the baton from Germany to the US in dyes manufacturing (35); other technological transfers (36); electrification of the country (37); industrialization of the West Coast (38) and the setting-up on its campuses of large chemistry institutes on the German model (whereas on the East Coast, at least in the Ivy League, the British tradition continued to rule); somewhat earlier on, during the period prior to the Great War, the start in the US of professional institutions of lasting value such as, to mention but a few, in addition to *Industrial and Engineering Chemistry*, the Chemical Abstracts Service (1907), annual meetings of the American Institute of Chemical Engineers (1908); enrollment of women among engineers and scientists (39); and last but not least, great American scientists (40). Other assets, belonging to mentalities, were more than a taste: a yearning and a need for innovation; a well-educated elite; the size and diversity of the country; and, last but not least, sharing with the British not only their language, also an ambition of scientific excellence.

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About the Author

Pierre Laszlo, who was born in Algiers in 1938, is a French physical organic chemist. After obtaining his Ph.D. with Edgar Lederer, he was a postdoc at Princeton University with Paul von Ragué Schleyer (1962-63). After his D. Sc. (1965), he returned to Princeton as an assistant professor (1966), accepting in 1970 a call from the University of Liège, Belgium, as a full professor. He taught there until 1999 while, from 1986 on he also held a professorial appointment at the *École polytechnique*, near Paris. Modifying clays into catalysts for organic reactions, his research group made extensive use of the Dean-Stark trap (41). After retirement in 1999, he became a science writer and chemical historian.

BOOK REVIEWS

The Chemical History of Color, Mary Virginia Orna, Springer, Heidelberg and New York, 2013, xv + 153 pp, ISBN 978-3-642-32641-7, $49.95, softcover (978-3-642-32642-4, $39.95, eBook).

The subject of color encompasses a broad range of disciplines, including physics, chemistry, biology, physiology, psychology, geography, geology and the arts, and there are many intersections. The topic is also steeped in a rich history, from prehistoric times, through the industrial revolution and up to the present day. There have been many books written over the years on various aspects of color, with a large proportion devoted to the chemistry of dyes and pigments which provide the range of synthetic colors that enrich our lives. It is thus a delight to find this new book with such a unique take on the historical development of our understanding of the phenomenon that is color. The book illustrates not only in the way that advances in science, notably chemistry, have impacted on our understanding of color, but also, conversely, the immense contributions towards developments in science that have taken place in the quest to understand color.

It is not a long book, in keeping with the philosophy of the series, Springer Briefs in Molecular Science: History of Chemistry. The stated series aim is "to present concise summaries of historical topics covering all aspects of chemistry, alchemy, and chemical technology." This book meets this aim admirably and the author's style ensures that it is an easy and captivating read. Since acquiring my copy, I have read it a few times. It is a delightful combination of historical accounts and anecdotes surrounding the subject of color, while at the same time dealing properly with the science. The book may be read not only as entertainment, but also as an excellent way to acquire a broad introduction to the essential chemical and physical principles of color. For such a short book, it is packed full of useful and remarkably detailed information. The author achieves this throughout the chapters by liberal use of tables which provide details of timelines, technical milestones and landmarks. It also makes good use of illustrations, many in color. A notable feature of the text is way in which the author deals with those scientists who have made the most important discoveries or have developed the most important theories, by relating the stories of their scientific contributions as influenced by their individual personality and character traits. The stories are also enhanced by relevant use of quotations. Although some stories may already be well-known to the reader, the author has a knack of finding a new twist to a familiar story.

The book is logically structured into eight chapters, organized into specific themes and in terms of the chronology. In chapter 1, the colors used by ancient civilizations are introduced. Color has indeed fascinated mankind for centuries. A commonly overlooked feature of the history of color is that in ancient times not only natural but also synthetic colors were used. The ancient Egyptians manufactured colors from rudimentary applications of inorganic chemistry, the most notable product being Egyptian blue. Chapter 2 deals with the evolution of our knowledge of the physics of color, in the context of the nature of light, its interaction with matter and the operation of the human eye. It is in this chapter that the greatness of the individuals who were involved in this experimental and theoretical development of the subject comes to the fore. The early contribution of the ancient Greek philosopher, Aristotle is acknowledged and, rather later, the physics of light was one of the many interests of Leonardo da Vinci. Other relatively more recent historical figures of note include Robert Hooke, Albert Einstein, Max Planck, Michael Faraday and James Maxwell. However, the chapter rightly gives particular prominence to the immense contribution of Isaac Newton. In chapter 3, the chemical causes of color are outlined in a historical context, dealing with the development of current theories of bonding in organic and inorganic compounds and the mechanisms by which they can give rise to color. Chapter 4, labeled as "from antiquity to the Perkin era," relates the historical development of the materials and processes used in coloration of a range of substrates, such as human skin and hair, glass and artists' colors. There is, of course, special mention of the development of dyes for textiles, from the Tyrian purple of antiquity through to Perkin's mauveine, the first synthetic textile dye produced on an industrial scale. This link illustrates how the color purple and its association with wealth and opulence played such a pivotal role. Chapter 5 takes up the next phase of the story when the Western European textile dye industry blossomed, with the processes involved in the search for new dyes evolving from a semi-empirical to a theoretical approach, as knowledge of structural chemistry advanced. The notable contributions from such as Hoffman, Kekulé and von Baeyer are discussed. The chapter concludes with a summary of the legacy of the dye industry, its recognition of research as such an essential sustaining feature, and its broad influence on political, educational and social structure within society. The final three chapters deal with some selected specific color-related themes, bringing the story through to modern times. Chapter 6 discusses the role of color in analytical techniques, for example those using the human eye as a detector of color change, and also in chromatography, spectroscopy and color measurement. Chapter 7 deals with some applications of color in biology and biochemistry, including staining techniques and chemotherapy. The book concludes, in chapter 8, with a series of miscellaneous topics, related by alliteration—foods, photochemistry, pharmaceuticals, fireworks, fun and the future.

This little book is not expensive and I would recommend it as essential reading for anyone with an interest in color. That probably includes most of us. The book will be of interest not only to those seeking a readable introduction to the fundamental principles of the science of color, in the context of its historical development, but also to individuals already familiar with the subject who will find gems of new or clarifying knowledge. I have reviewed many books on color over the years, generally positively, but I can honestly give this one my most enthusiastic recommendation. The author quotes Benjamin Franklin as saying "About light, I am in the dark." After reading this book, no one will be making such a statement.

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King of Poisons: A History of Arsenic, John Parascandola, Potomac Books, Washington, DC, 2012, ix + 197 pp, ISBN 978-1-59797-703-6, $27.50.

John Parascandola, a distinguished historian of chemistry, pharmacy and medicine, has produced a learned and accessible volume on perhaps the most notorious of the elements—arsenic, the king of poisons. The book begins with two chapters on the source of arsenic's fascination for many, its role as an intentional poison in fact and fiction. The next two chapters can also be considered as a pair, discussing hazards posed by arsenic exposure to those who work with it and to the larger public. The book closes with a chapter on the possibly beneficial side of arsenic's toxicity: its applications in medicine, broadly construed.

Chapter 1, "King of Poisons: *Arsenic and Murder*," begins with some of the chemical basics of arsenic as an instrument of homicide. The arsenic compound of choice for deliberate surreptitious poisoning is arsenic trioxide (As_2O_3), which is white, easily soluble, odorless, tasteless, and fairly readily available for much of the past few centuries. The more common naturally occurring sulfides of arsenic, realgar and orpiment, on the other hand, would be difficult to get victims to ingest, since they are highly colored and insoluble. The effects of ingesting arsenic are unpleasant and often lethal. A victim is likely to experience vomiting and diarrhea, and possibly burning in the mouth or gut. These symptoms could be confused with those of common diseases, such as cholera, making homicide difficult to diagnose, particularly before the availability of forensic tests for arsenic. The chapter mentions the tests devised by James Marsh in 1832, then a quicker and simpler test a decade later by Hugo Reinsch.

The bulk of the first chapter treats specific famous and notorious instances of proved and suspected arsenic poisoning, from Renaissance Italy through twenty-first century America. The chapter closes with a brief overview of arsenic in chemical warfare, particularly the work of the US Chemical Warfare Service during the first World War. Several chlorinated arsines were developed and tested at the time, of which the best known came to be called Lewisite, after Winfred Lee Lewis, head of one of the units of the Chemical Warfare Service.

The second chapter, "Poison in the Plot: *Arsenic in Fiction*," treats arsenic in fictional rather than actual homicides. I found the descriptions of fictional poisonings much more interesting than those of actual or suspected ones in the previous chapter. The fictional cases often involve imagination, clever or convoluted plots, exotic characters or artifacts, and of course no actual victims. The real or suspected cases, on the other hand, usually struck me as sordid and banal.

Parascandola points to the 1875 Wilkie Collins novel, *The Law and the Lady*, as possibly the first work of detective fiction to feature arsenic. Another relatively early appearance of arsenic in detective fiction was in R. Austin Freeman's story, "The Moabite Cipher." Dr. John Evelyn Thorndyke, Freeman's physician-detective, finds his way through the thicket of mysteries, including a sample of arrowroot in which he finds lots of arsenic by the Marsh test. The prolific mystery writer Agatha Christie was apparently fond of poison—as a plot device. Someone is poisoned in over half of her novels, and arsenic is mentioned in nearly a quarter of them. Her first use of arsenic as the murder weapon was in the 1932 story, "The Tuesday Night Club." Christie's famous detectives Miss Marple and Hercule Poirot both deal with cases of arsenic poisoning. Outside the detective genre, arsenic figures prominently in the plot of Gustave Flaubert's masterpiece *Madame Bovary*. And the comedic possibilities of the poison are explored in Joseph Kesselring's play *Arsenic and Old Lace*. In addition to the relatively well known works listed above, Parascandola describes several more obscure and more recent examples of arsenic in fiction.

Arsenic and its compounds are toxic, whether or not they are administered with malevolence. Chapters three and four treat the hazards of occupational and environmental exposure. The oldest of these hazards are associated with mining and smelting. Because arsenic is often found in copper deposits, mining and smelting copper frequently exposed its workers to arsenic. Bernardino Ramazzini mentioned arsenic in mining and pharmacy in *De Morbis Artificium Diatriba* (*Of Diseases of Tradesmen*), which is generally considered the first general work in occupational medicine (1700). In the 19th century, however, arsenic itself became more frequently mined for a variety of applications, and not surprisingly, those who extracted and processed it were also at risk of exposure. So were those who made and used arsenic-containing products. Among the most widely diffused such products were pigments, including Scheele's green (copper arsenite) and Paris green (copper (II) acetoarsenite). Among the workers exposed to these pigments were those who made artificial flowers or who decorated hats and clothing with them—not to mention those who made such pigments or made or used paints or wallpaper containing them. Arsenic's toxic properties were deliberately used in products intended to kill pests or to preserve objects prone to putrefaction. Thus makers and users of pesticides could be exposed to arsenic, as could taxidermists and enbalmers.

Some of the hazards of arsenic-containing products were more widely diffused, affecting not only those who made or used such products for their livelihood. Arsenic released by smelting often went directly into the atmosphere, spreading beyond the workplace the possibility of exposure to the toxic element. Arsenical pigments were used in garments and wallpapers widely used by the public. Similarly, arsenical pesticides could find their way into the food supply. Wood impregnated with chromated copper arsenate to inhibit rot was widely used in the 20th century in telephone poles, railroad ties, and even in playground equipment. Although the US Environmental Protection Agency does not believe that the arsenic in such wood poses an unreasonable risk, some local authorities are choosing to replace it in playgrounds.

Some arsenic in the environment is natural, including arsenic released by volcanoes into the atmosphere. Of far greater impact to human health, however, is arsenic from naturally occurring minerals turning up in drinking water. This phenomenon has become evident most tragically in Bangladesh in the late 20th century. There, the government and international aid agencies constructed millions of tube wells in order to provide rural Bangladeshis with drinking water free from disease-carrying microorganisms. The wells were indeed effective in dramatically cutting rates of infant and child mortality from water-borne diseases, but they introduced a new problem because many of the wells delivered water high in arsenic.

Parascandola's final chapter turns to the area for which he is best known, history of pharmacy and medicine. Thomas Fowler, an 18th-century Englishman and Edinburgh-trained physician attempted to duplicate and then modify a patent medicine of the day. He called the resulting potion Solutio Mineralis. Under the name Fowler's solution, it found its way into many pharmacopoeias in the 19th century, and it became a widely used remedy for a variety of ailments. Paul Ehrlich's research into chemotherapeutic agents, including some containing arsenic, is also described. Ehrlich's "compound 606," patented under the name of Salversan, was an effective treatment against syphilis and trypanosomal diseases. A section of this chapter is devoted to the arsenic-eaters of Styria (a region now part of Austria). Reports of rural inhabitants of the area who deliberately consumed and tolerated arsenic in quantities that are generally harmful circulated widely in the middle of the 19th century. Such reports caused considerable debate in medical circles about their accuracy and plausibility—debate that continued into the 20th century. Meanwhile, the reports were so widely diffused that they appear to have influenced the use of arsenic in 19th-century cosmetics and inspired a key plot point in Dorothy Sayers's 1930 novel *Strong Poison*. Arsenic in homeopathy is also mentioned in this chapter. Arsenicum album is a homeopathic remedy based on arsenic trioxide (albeit diluted to submolecular concentrations).

Parascandola refers rather frequently to two other recent books in which arsenic figures prominently. John Emsley devotes one of the five major sections of *The Elements of Murder* (Oxford, 2005) to arsenic. As one might gather from Emsley's title, perhaps the greatest overlap of his material is with the first chapter of Parascandola's book, but Emsley treats a great variety of other applications of arsenic as well, at least in overview. James Whorton's, *The Arsenic Century* (Oxford, 2010) touches on the toxicity of the element as both a deliberate and inadvertent poison. Its subtitle, "How Victorian Britain was Poisoned at Home, Work, and Play" suggests the breadth of the applications of arsenic it considers and the limitations to its geographic and temporal scope. A reader of more than one of these volumes should not be surprised to find quite a bit of material in common.

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Early Russian Organic Chemists and their Legacy, David E. Lewis, Springer, Heidelberg and New York, xii + 136 pp, ISBN 978-3-642-28218-8, $49.95, softcover (978-3-642-28219-5, $39.95, eBook).

When one considers the history of organic chemistry in the nineteenth century, the names that most quickly come to mind are those of German chemists like Liebig, Wöhler, and Hofmann. In this excellent book, Professor Lewis (University of Wisconsin-Eau Claire) makes a strong case for the inclusion of the significant and sometimes overlooked contributions of Russian chemists. As an example the rules of Markovnikov and Zaitsev are introduced in most organic chemistry courses during the study of alkenes. Professor Lewis is well known to readers of the Bulletin. This book is based in part on a series of thoroughly researched and well written articles that have appeared in its pages.

The initial chapters cover concisely the evolution of higher education in Russia particularly after the reforms introduced by Peter the Great. In 1725 he established the Russian Academy of Sciences and his work of modernization and secularization of Russian higher education was continued by the rulers who immediately followed him. New universities were established in Moscow, and at the start of the nineteenth century at Dorpat, Vilna, Khar'kov, Kazan, Warsaw (at that time part of the Russian empire) and St. Petersburg. Later universities were opened in Kiev, Odessa, and Tomsk. All these universities were charged with developing advanced studies and research.

The first great figure in Russian science, including chemistry, was Lomonosov (1727-1797), a founder of Moscow University, and an anti-phlogistonist before Lavoisier. Many Russian university posts were initially occupied by German scientists but by 1830 there was a nationalist movement towards Russification of the universities, and more and more Russian professors were appointed during the nineteenth century. The principal loci of Russian organic chemistry in that period were the universities of Kazan and St. Petersburg. Zinin was an important early figure in the Kazan school of chemistry. Trained initially in physics and mathematics he was instructed, for such was the autocratic nature of Russian universities at that period, to become a teacher of chemistry. He was given three years to study in Western Europe, and attended courses in Germany, France, and England. He spent a year doing research with Liebig, and then returned to take up his duties in Kazan. Major contributions made by Zinin to organic chemistry included the discovery of the benzoin condensation and the preparation of aniline from nitrobenzene.

Lewis writes in similar depth about the lives and careers of many other Russian organic chemists including Butlerov, Menshutkin, Borodin, Beilstein, Markovnikov, Zaitsev, Zelinskii, and Favorskii, bringing his story up to the early twentieth century.

Spinger Verlag has made an admirable choice in starting its series "Springer Briefs in Molecular Science: History of Chemistry" with David Lewis's book. It is nicely illustrated and has a full index and bibliography. This important work sheds light on a relatively little studied area of the history of organic chemistry in an easily read and authoritative manner.

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Inventing Chemistry. Herman Boerhaave and the Reform of the Chemical Arts, John C. Powers, The University of Chicago Press, Chicago and London, 2012, viii + 260 pp, ISBN 978-0-226-67760-6, $40.

Herman Boerhaave (1668-1738) received his degree in Philosophy at the University of Leiden (1689) and a degree in Medicine at Haderwijk (1693). He was appointed lecturer at Leiden in 1701 and Professor of Botany and Medicine in 1709. In 1714 he became Rector and introduced a system of clinical medicine to advance the experiential education of medical students. In 1718 Boerhaave was appointed Chair in Chemistry. In 1729, in ill health, he resigned the Chairs of Botany and Chemistry and suffered declining health until his death.

The impact of Herman Boerhaave (1668-1738) on the history of chemistry is all too commonly considered to derive solely from his masterwork, *Elementa Chemiae*, the first authorized edition appearing in 1732. In a very limited sense that book can be considered the bridge between the important series of seventeenth-century chemistry textbooks, especially those published by the French chemists beginning with Jean Beguin, then Nicaise le Fèvre, Chistolphe Glaser and Nicolas Lemery and textbooks in the middle-to-late eighteenth century that provided more discussion of theory. Indeed while the first edition of Lemery's *Cours de Chimie* appeared in 1675, the final printing of the final edition was published in 1757. Still, Lemery's text book was in a classical tradition that discussed chemical operations (e.g. distillations, crystallizations) before providing specific preparations of reagents, useful substances and medications.

The author of the present monograph, John Powers, is a faculty member in the Department of History and Assistant Director of the Science, Technology and Society Program at Virginia Commonwealth University. He assesses Boerhaave's pioneering work in formulating a powerful didactic approach in his teaching, providing standing for chemistry in the university curriculum and contributing to the application of experimentation to test chemical theory.

Chapter one ("Medicine as a Calling") provides background relevant to appreciating medical education in late seventeenth century Europe and young Boerhaave's early intellectual development. The section "Path to Professorship" in this chapter has a familiar ring to it for twenty-first century university faculty: a university's appointments swayed by powerful public officials; a university suffering financial distress and failing in attempts to hire academic "stars," filling diminishing ranks with part-time lecturers and facing diminishing matriculations. Boerhaave barely held onto his lecturer's appointment at this time but was kept on because he had a three-year contract. Jacob Le Mort, Boerhaave's predecessor to the Chair of Chemistry at Leiden, had earlier campaigned hard for the chemistry chair and would have been appointed in 1697, except that William of Orange, King of England and Dutch stadholder, objected because of Le Mort's acceptance of Cartesian Philosophy. However, when William died in 1702, Le Mort's appointment was accomplished in short order.

Chapter Two describes Boerhaave's contributions to "didactic chemistry" in the historical context. The first chemistry textbook, one that really developed the foundation for performing chemical operations (building ("chemical house"), furniture, apparatus, chemicals) was the *Alchemia*, published by Andreas Libavius in 1597 (expanded illustrated folio edition, 1606). Nonetheless, the chemistry taught in the medical schools of the seventeenth and early eighteenth centuries did not recognize chemistry (or perhaps "chymistry" as Lawrence Principe and William Newman describe it) as sufficiently "philosophical" to be a rigorous academic subject. Typically, the expectations of the chemistry course were limited to useful descriptions of techniques and specific recipes for medications. During the first half of the seventeenth century a very small number of medical schools provided professorships and specific courses in chemistry. Two of these early professors were Johannes Hartmann (Marburg) and Werner Rolfinck (Jena). Le Mort's appointment to the Chair of Chemistry at Leiden was an early recognition of the growing importance of chemistry in the medical school curriculum.

Chapters Two ("Didactic Chemistry in Leiden") and Three ("The Institutes of Chemistry") focus on the development of the didactic chemistry and Boerhaave's advancement in chemistry at the University. Boerhaave taught his first chemistry course in 1702 as lecture only but began to include demonstrations in fall 1703. Le Mort's course, part of the Leiden curriculum, could be attended without extra fees, since the price was included in the matriculation fees that covered Le Mort's salary. In contrast, Boerhaave was given permission by the University to offer his course for a separate fee, from which he could derive some salary. Despite this extra expense, students favored the more dynamic Boerhaave's course. Upon Le Mort's passing in 1718, Boerhaave ascended to the Chair in Chemistry and Chapter Four ("Chemistry in the Medical Faculty") describes modifications in the curriculum and in the perception of the role of chemistry in medicine that followed. Powers notes that "Boerhaave's appointment to the chair of chemistry represented the success of a new type of chemical medicine, derived from the empirical and experimental practices of his medical mentors, Anton Nuck and Charles Drélincourt" (the latter used the pseudonym "Le Vasseur").

Boerhaave's contribution to didactic chemistry was to adopt what is termed the "instrument theory," which had its origins with Daniel Sennert (at Wittenberg) in 1629 (second edition of his *De Chymicorum…*) and was transmitted to Boerhaave by Johannes Bohn. A very "heterogeneous group" of instruments ("fire, air, water, earth, menstrua and chemical vessels") would be applied to "shift the focus of chemical theory to the latent properties of chemical species, which were seen as inherent to individual species, and were revealed only through action with instruments."One of these instruments, fire, was the subject of some of Boerhaave's most important work (Chapter Five "Instruments and the Experimental Method"). In attempting to quantitate fire, Boerhaave remarked how subjective human perceptions of heat are. A damp cave feels colder than a dry cave even as the temperatures of the two, via the newly-designed Fahrenheit thermometer might be equal. As noted by Powers: "The instruments course instilled in students a methodology and philosophical perspective that supported Boerhaave's vision for a chemistry based on experimentally determined principles." Curiously, the word "phlogiston" does not appear in this chapter or in the book's index. However, it is widely agreed that Boerhaave had reservations about phlogiston theory since this "substance of fire" could not be quantitated using thermometry. Boerhaave's advocacy of thermometry as an objective measure of the ability of fire to "rarify" matter was a very important contribution both to the teaching and the practice of chemistry.

Chapter Six (Philosophical Chemistry) is largely devoted to Boerhaave's magnum opus, the *Elementa Chemiae* (1732). The "pre-history" of this book is well known to chemical historians (and book collectors). Leiden students had assembled Boerhaave's lectures into a textbook, not authorized by the professor, published in 1724 and, indeed, this unauthorized work was translated into English in 1727. (In 1684, students published the *Collectanea Chymica Leydensia*, liberally mixing the lectures of Carel De Maets, the Leiden predecessor of Le Mort, Le Mort himself- at the time "merely" a lecturer, and Christiaan Marggraf, another competing chemistry lecturer in this academic "free market." All three despised the book, particularly De Maets, the one with highest standing and having the most to lose). Boerhaave was quite upset with the unauthorized publication of his lectures. He signed an attestation page for every copy of his sumptuous, illustrated first Leiden edition of 1732. In this chapter, Powers does briefly discuss the fact that Boerhaave does not mention Stahl's phlogiston theory anywhere in his *Elementa Chemiae*. He notes that Boerhaave's *pabulum ignis*, compared by some modern day scholars to phlogiston, was presented as "the material cause of inflammability… needed to interact with instrumental fire… for combustion to occur." Stahl's phlogiston, by contrast, was considered to be the very substance of fire "fixed" in an inflammable body. The final chapter ("From Alchemy to Chemistry") describes Boerhaave's investigations and teachings over three decades of the mercurialist theory of chemistry. Essentially the concept that all metals shared a rarified form of mercury gave some theoretical support to the possibility of transmuting metals. However, Boerhaave's devotion to experimental testing of theory led him to discredit this notion. In considering the credulity to the notion of transmutation by outstanding minds of the period (Boerhaave and, earlier, Boyle and Newton), it is well to remember that it was only near the end of the eighteenth century that Lavoisier provided a useful definition of the term "chemical element."

Professor Powers' book is a concise work, dense with information, yet highly accessible for historians and non-historians alike. In each of seven chapters, followed by a section titled CONCLUSION ("Boerhaave's Legacy"), the author provides an outline at the start and a brief, helpful wrap up at the conclusion. There are 30 pages of Notes, nicely indexed both to chapter and also in the running header to pages. This is followed by a 21-page bibliography and an adequate index that occasionally misses important specifics- for example, le Fèvre and Glaser are important chemists, discussed in the body of the book, but missing in the index.

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Sir James Dewar, 1842-1923: A Ruthless Chemist, J. S. Rowlinson, Ashgate, Farnham, 2012, xviii + 236 pp, ISBN 978-1-4094-0613-6, $124.95.

The dictionary defines a clerihew as a "whimsical, four-line biographical poem" invented by the British humorist, Edmund Clerihew Bentley (1875-1956), while still a 16-year old schoolboy. One of his earliest attempts is an example well-known to historians of chemistry:

Sir Humphry Davy
Abominated gravy.
He lived in the odium
Of having discovered sodium.

Recently I had occasion to examine Bentley's first published collection of clerihews, *Biography for Beginners* (London, 1905), and was delighted to discover that, in addition to Davy, yet another chemist was embedded among the many satirized literary figures, politicians, philosophers and theologians:

Professor Dewar
Is a better man than you are,
None of you asses
Can condense gases.

Aside from the rather exaggerated pronunciation of Dewar required to make the rhyme work, this little ditty is of interest for two reasons. First, it focuses on Dewar's later work on the liquefaction of gases at low temperatures, which led in turn to his development of the vacuum flask or thermos bottle—probably the only aspect of his career known to most present-day chemists. In recognition of this accomplishment, the vacuum flask—at least among American chemists—is often referred to simply as a "Dewar."

Second, there is a suggestion of intellectual arrogance on the part of Dewar—an aspect of his personality also reflected in the subtitle of the book under review: *A Ruthless Chemist*. Though short biographical summaries of Dewar's life and career have long been available, this is the first book-length study of this talented, albeit irascible, Scottish chemist. Its author, Sir John Rowlinson, is well-known among physical chemists for his work on the theory of liquids and liquid mixtures, and is increasingly known among historians of science as well for such works as his reprinting with commentary of the English translation of J. D. van der Waals' classic 1873 thesis, *On the Continuity of the Gaseous and Liquid States*

(Amsterdam, 1988); his coauthoring (with A. Y. Kipnis and B. E. Yavalov) of the biography, *Van der Waals and Molecular Science* (Oxford, 1996); his magisterial study, *Cohesion: A Scientific History of Intermolecular Forces* (Cambridge, 2002); and, most recently, his coediting of the volume, *Chemistry at Oxford: A History from 1600 to 2005* (Cambridge, 2009).

Rowlinson's path from the work and life of van der Waals and the history of the study of molecular cohesion to the life of Sir James Dewar is perhaps a natural one, given Dewar's experimental contributions to the study of the liquefaction of gases mentioned above. But, of course, a reading of his book quickly reveals that this was but one aspect of Dewar's long and fruitful career. Trained in chemistry at the University of Edinburgh under Lyon Playfair and Alexander Crum Brown, Dewar's first publications were in the field of organic chemistry, including the invention of a flexible two-dimensional mechanical model to illustrate the application of Crum Brown's topological bonding symbolism to the problem of the structure of benzene, and his proposal that pyridine had an analogous aromatic ring structure. This led to postgraduate work in the laboratory of Kekulé at Ghent, after which he held a series of short-term appointments at Dick College and the Highland and Agricultural Society of Scotland. Finally, in 1875, at age 33, Dewar was appointed Jacksonian Professor of Natural Philosophy at Cambridge University, followed two years later by a concurrent appointment as the Fullerian Professor of Chemistry at the Royal Institution in London. These events were accompanied by an increasing preference for work in the field of physical chemistry and experimental physics. Thus, while at Cambridge, he initiated a long series of researches in the area of atomic spectroscopy in collaboration with the Cambridge Professor of Chemistry, George Liveing, and it is largely in connection with his appointment at the Royal Institution that he began his best-known work in the field of cryogenics, including both gas liquefaction and the measurement of physical properties at low temperatures. In between he found time to do work on the metal carbonyls and to invent, in collaboration with Frederich Abel, the explosive known as cordite—a commercial venture that led to a long and acrimonious dispute with Alfred Nobel over patent rights. Nor was Dewar's combative behavior reserved for commercial competitors, as throughout his career he also managed to become entangled in personal disputes with both his scientific competitors and with many of his colleagues and assistants—whence Rowlinson's choice of subtitle.

Unlike many biographies of scientists by professional historians and science journalists in which little is said of the scientist's actual laboratory work for fear it will turn off the lay reader, Rowlinson takes great pains to explain the nature of Dewar's work and has included many diagrams illustrating the apparatus used. About the only criticism I would have is the absence of a similar series of photos illustrating Dewar's personal life (i.e., his appearance at various ages, his family, his close friends and associates, etc.)—the only photo of him in the entire book being the frontispiece, which shows the famous portrait taken by his assistant, Alexander Scott, in which Dewar is examining a vacuum flask in his laboratory at the Royal Institution. But this is a purely personal bias and should not deflect the interested reader from acquiring and enjoying this informative biography.

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Progresive Enlightenment: The Origins of the Gaslight Industry, 1780-1820, Leslie Tomory, MIT Press, London; Cambridge, MA, 2012, 368 pp, ISBN 978-0-262-01675-9, $28.

Gas lighting was a ubiquitous western technology of the nineteenth century, yet one which has been given relatively little importance by historians in comparison to, say, the railways or electricity networks. In *Progressive Enlightenment*, Leslie Tomory successfully argues that there should be a more prominent place for gas lighting in discussions of large-scale "network" technologies of that era. In this detailed study, Tomory traces the origins and development of the gas lighting industry from experiments in the pneumatic chemistry of inflammable airs in the eighteenth century to the widespread distribution and utilization of coal gas for lighting streets, homes, and factories in the first decades of the nineteenth century.

In the process, Tomory engages with broader historiographical issues relating to the history of technology and economic history. The first involves locating gas lighting in different stages of invention and innovation that are identified as characterizing the Industrial Revolution. A "first wave" of technologies had little use for science and entailed invention by individuals and small partnerships. Gas lighting belonged to a "second wave" of technologies which demanded large-scale capital investments and had their foundation in recent or current scientific research. Tomory also situates gas lighting in broader debates about the nature of Joel Mokyr's notion of the "Industrial Enlightenment" concerning the place of scientific knowledge in the development of industrial enterprises in Europe. With qualification, Tomory supports Mokyr's interpretation by proposing that gas lighting represents a fairly clear-cut example of chemical know-how obtained from the laboratory being applied to the creation of a successful industrial product. Gas lighting was "a major first step" in the fulfillment of the "Enlightenment dream of science at the service of industry" (pp 3-4, 239).

Progressive Enlightenment is divided into two parts. The first part proposes a "two traditions" explanation of the emergence of gas lighting as an industrial enterprise in the early nineteenth century. Tomory claims that gas lighting only emerged when a natural philosophical tradition of pneumatic chemistry and an industrial tradition of destructive distillation came together around 1800 (discussed respectively in chapters 1 and 2). Tomory contrasts this account with internalist histories which root gas lighting in various discoveries of the inflammability of coal gas in the seventeenth century, and histories which see more continuity between the nineteenth-century industry and various projects using inflammable air to generate light in the late eighteenth century. While the former account cannot explain why gas lighting did not emerge as soon as the discovery of its inflammability was made, the projects of the latter account cannot be true precedents because they were not "transformed into a commercial technology" (p 9). To make this argument depends, of course, on how one defines "commercial," and if one's definition of gas lighting is that it was an industry, then inevitably an enterprise which was not industrial cannot be equated with the full fruition of gas lighting as a technology.

Part two explores in fine detail the scaling-up of gas lighting from small and scattered projects to an expansive network in the first decades of the nineteenth century. First came the development of stand-alone gas lighting plants manufactured by Boulton and Watt with the help of William Murdoch between 1802 and 1810 (chapter 3). Then came the creation of a fully-fledged gas lighting network by about 1820 (chapters 4 and 5). In Britain this was the work of the Gas Light and Coke Company which emerged from the efforts of German immigrant Frederick Winsor to found a "National Light and Heat Company" in the first years of the nineteenth century. The book ends rather abruptly in 1820, as British gas lighting was about to gain widespread use across continental Europe (a story which itself would be deserving of a monograph).

In concluding, Tomory qualifies traditional views that gas lighting succeeded in Britain while it failed on the continent by pointing to the distinctive place of coal in the British economy. Continental manufacturers did not fail to produce what Britons achieved with gas but instead went down a different path to the production of wood distillates. Hence local conditions shaped technological paths and "there was no failure of technical imagination on the Continent" (p 241). Tomory also highlights the importance of display in the history of gas lighting, its links to old traditions of fireworks and illuminations, and its frequent exploitation of garish advertising and provocative publicity. There is also valuable discussion of the historiography of entrepreneurship and why users matter in the history of technology. In relation to the history of chemistry, Tomory's study is valuable for broaching common boundaries drawn between the era before and after Lavoisier, and for investigating the links between chemistry and industry. Some might dispute the boundaries erected from the outset between science, technology, commerce, industry, and invention, and Mokyr's interpretation of the period has not been without its critics. But this is an important contribution to the history of gas lighting and is successful in staking a place for gas lighting in the economic and technological history of the era.

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