

BULLETIN FOR THE HISTORY OF CHEMISTRY

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Mendeleev

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DEXTER AWARD 2001

The 2001 Dexter Award for Outstanding Achievement in the History of Chemistry was awarded posthumously to William A. Smeaton at the Dexter Award Symposium held at the Chicago ACS Meeting, August 28, 2001. Speakers at the symposium, organized by Martin D. Saltzman, were Robert Siegfried, Elsa Gonzalez, Mi Guyng Kim, and Allen G. Debus.



We are most grateful that Dr. Smeaton's wife Jacqueline and son John were in attendance to accept the award on his behalf. Recognized primarily for scholarly research in 18th-century French chemistry, Dr. Smeaton held appointments in the Department of History and Philosophy of Science at University College, London, from 1959 until his retirement in 1982.

CUTTING-EDGE CHEMISTRY: SOME 19TH-CENTURY RUSSIAN CONTRIBUTIONS

Introduction

Richard E. Rice, James Madison University

The four papers and commentary on 19th-century Russian chemistry in this issue of the *Bulletin for the History of Chemistry* constituted the session "Cutting-Edge Chemistry: Some 19th-Century Russian Contributions" at the Semisesquicentennial Anniversary Meeting of the History of Science Society (HSS) in November 1999 in Pittsburgh. This was the first session officially sponsored by the Mendeleev Interest Group, which developed as a result of another recent HSS session devoted to the great Russian chemist.

At the 1996 HSS Meeting in Atlanta, the session "Dmitrii Mendeleev: New Perspectives" was chaired by Loren Graham, the dean of Russian science studies (1). Besides Nathan Brooks and me, the other two speakers were the only American historians who had at that time written doctoral dissertations specifically on Mendeleev: Beverly Almgren (2) and Francis Stackenwalt (3). Also present were Masanori Kaji, author of a book on Mendeleev and his law of periodicity (4), and Michael Gordin, a graduate student in Harvard's Department of History of Science, who was planning to write his dissertation on Mendeleev (5). Thus, most of the world's non-Russian scholars with an interest in Mendeleev were assembled at that session.

Following the formal portion of the session, we all participated in an informal roundtable discussion of Mendeleev and the state of historical studies of Russian science in general. Graham suggested that the timing of the session was propitious in that he believed Mendeleev studies would soon experience the same kind of surge in popularity that Newton and Lavoisier studies, for example, had in recent years. We all agreed,

however, that a blossoming of Mendeleev studies would face the additional problems of an unfamiliar language that English and French do not pose for most historians of science in the West. Even for those who know Russian, there are still obvious difficulties in visiting the archives with material on Mendeleev and other Russian scientists.

The papers from that 1996 session, along with an additional paper by Michael Gordin, were subsequently published in a special issue of *Ambix* in July 1998 (6). That session was also the impetus for organizing the Mendeleev Interest Group (MIG) under the aegis of HSS. We wanted this group to serve as a focal point not just for Mendeleev studies, but for the history of Russian science, particularly chemistry, more broadly. Thus, this first HSS session under MIG sponsorship focused on some important Russian contributions at the forefront of 19th-century chemical knowledge.

The first two papers examine particular aspects of the work of several chemists at Kazan' University, including Zinin, Zaitsev, Vagner, and Reformatskii. Kazan' was the incubator for a number of great 19th-century Russian organic chemists. This may be surprising in view of the fact that the provincial city of Kazan' is located some 500 miles east of Moscow, virtually the easternmost outpost of European civilization in early 19th-century Russia. The third paper examines the interplay of Mendeleev's famous textbook, *The Principles of Chemistry*, and his development of the periodic law in the late 1860s. The final paper of the session looks at two young Russian chemists, attracted to the "new" physical chemistry in Leipzig in the late 1880s, in spite

of the opposition of chemists in St. Petersburg, particularly Mendeleev.

These four papers are ordered chronologically by their topics, from the 1840s to the 1890s, but they also represent two other important trends, one in Russian chemistry specifically and the other in chemistry more broadly. Although Kazan' was an important center of Russian chemistry—perhaps the most important—in the 1840s and 1850s (7), this center moved west as the century progressed, eventually reaching St. Petersburg. Many of the major chemists of Kazan' eventually moved to other universities. Zaitsev moved to St. Petersburg in 1848, and Butlerov, the most eminent chemist from Kazan', went there in 1868. Markovnikov left for Odessa in 1871 and then moved to Moscow in 1873. In addition, these papers mirror the global shift in focus from organic chemistry in mid century to the inorganic and theoretical chemistry of the time of Mendeleev and finally to the new physical chemistry of Ostwald and his disciples in the late 1880s.

Our hope is that readers of the *Bulletin* will find this an interesting and thought-provoking set of papers, along with the commentary by Seymour Mauskopf that generated discussion at the session and should provide a counterpoint for readers' responses to these papers as well. We also hope that this issue will spark further interest in the chemical heritage and history of a fascinating country, which are still not well known (8).

Finally, I want to point out that all of us involved with the two HSS sessions and subsequent publications in both *Ambix* and the *Bulletin* are especially proud of the fact that these endeavors have all along been collaborative efforts between professional historians and professional chemists with similar interests. Our work together has been harmonious and mutually beneficial. We hope that we are a model for other collaborations.

REFERENCES AND NOTES

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3. F. M. Stackenwalt, The Economic Thought and Work of Dmitrii Ivanovich Mendeleev, Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1976.
4. M. Kaji, *Mendeleev's Discovery of the Periodic Law of the Chemical Elements—The Scientific and Social Context of His Discovery* [in Japanese], Hokkaido University Press, Sapporo, Japan, 1997.
5. He has since done so. M. D. Gordin, The Ordered Society and its Enemies: D. I. Mendeleev and the Russian Empire, 1861-1905, Ph.D. Thesis, Harvard University, 2001.
6. N. M. Brooks, (Guest) Ed., "Mendeleev: Beyond the Periodic Table," *Ambix*, **1998**, *45*, 49-128. This special issue (No. 2, July 1998) includes the four papers from the 1996 Atlanta HSS Meeting by B. S. Almgren, "D. I. Mendeleev and Siberia," pp 50-66, F. M. Stackenwalt, "Dmitrii Ivanovich Mendeleev and the Emergence of the Modern Russian Petroleum Industry, 1863-1877," pp 67-84; R. E. Rice, "Mendeleev's Public Opposition to Spiritualism," pp 85-95; and N. M. Brooks, "Mendeleev and Metrology," pp 116-128; along with one paper not presented at that meeting, M. D. Gordin, "Making Newtons: Mendeleev, Metrology, and the Chemical Ether," pp 96-115.
7. D. E. Lewis, "The University of Kazan—Provincial Cradle of Russian Organic Chemistry: Part I. Nikolai Zinin and the Butlerov School," *J. Chem. Educ.*, **1994**, *71*, 39-42; "Part II. Alexandr Zaitsev and His Students," *J. Chem. Educ.*, **1994**, *71*, 93-97.
8. N. M. Brooks, "The Evolution of Chemistry in Russia During the Eighteenth and Nineteenth Centuries," in D. Knight and H. Kragh, Ed., *The Making of the Chemist: The Social History of Chemistry in Europe, 1789-1914*, Cambridge University Press, Cambridge, 1998, 163-176.

HISTORY OF CHEMISTRY DIVISION

<http://www.scs.uiuc.edu/~maintzvHIST/>

D. I. MENDELEEV'S CONCEPT OF CHEMICAL ELEMENTS AND *THE PRINCIPLES OF CHEMISTRY*

Masanori Kaji, Tokyo Institute of Technology

Introduction: Mendeleev's Textbook, *The Principles of Chemistry*

Dmitrii Ivanovich Mendeleev (1834-1907) was primarily a chemist even though he later worked in many other fields. One of his most important contributions to chemistry was the discovery in 1869 of the periodic law of the chemical elements, which is still a fundamental concept in modern chemistry. In 1905, shortly before his death, he listed what he considered his four main contributions to science (1): the periodic law, the elasticity of gas, the understanding of solutions as associations, and *The Principles of Chemistry* (hereafter referred to as *Principles*). Mendeleev himself stated the close relationship between the first and fourth contributions in his first paper on the discovery of the periodic law, written in early March of 1869 (2,3):

In undertaking to prepare a textbook called 'Osnovy khimii' [*Principles*], and to reflect on some sort of system of simple bodies in which their distribution is guided not by chance, as might be thought instinctively, but by some sort of definite and exact principle.

Few outside Russia, however, have pointed to the direct relationship between *Principles* and the periodic law (4). In Russia B. M. Kedrov (1903-1984), who made a very detailed analysis of Mendeleev's discovery of the periodic law, has discussed this close relationship. In the late 1940s he found new archival material related to Mendeleev's first periodic table, and in the 1950s he published reliable source books on Mendeleev's discovery. His work culminated in his book *The Day of a Great Discovery* (5) in 1958, a very

detailed analysis of Mendeleev's process of compiling his first periodic table. All subsequent works on this topic have begun from this work (6). From a critical examination of Kedrov's works, the author has also published a book on Mendeleev's discovery, considering social, as well as scientific, factors (7). All recent studies have included a consideration of this direct relationship between *Principles* and the periodic law (8). However, there are no studies that consider the background of Mendeleev's writing of *Principles* and the changes made in subsequent editions (9). The purpose of this paper is to analyze the text of the first and later editions of *Principles* with its background and show the role played by Mendeleev's concept of the chemical elements in the discovery of the periodic law and its later development.

Origin of Mendeleev's Concept of the Chemical Elements and So-called Indefinite Compounds

Mendeleev entered the Main Pedagogical Institute at St. Petersburg in 1850 after graduating from the gymnasium in the Siberian city of Tobol'sk, where he was born in 1834. While a student, he published his first scientific papers on the chemical analysis of minerals from Finland (10). His undergraduate thesis was on isomorphism and was concerned with the development of mineral analysis (11). Even this thesis foreshadows Mendeleev's future line of research: first, it shows his talent for compiling and systematizing large amounts of data; second, it mentions Auguste Laurent (1808-

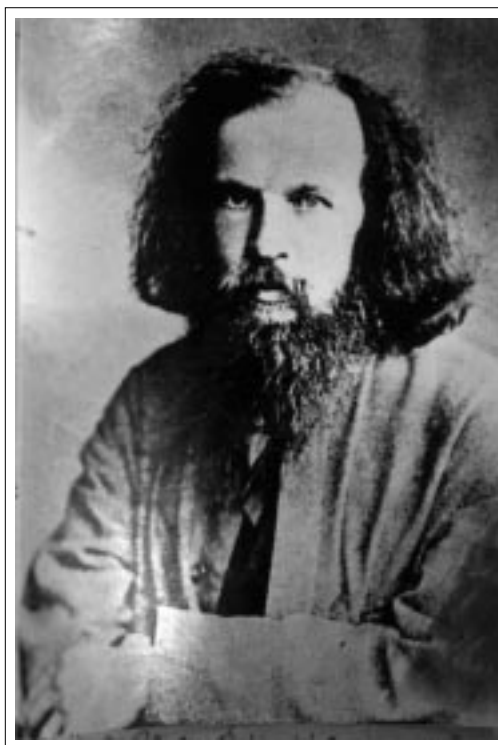
1853) and Charles Gerhardt (1816-1856), the reformers of chemistry in the 1840s and 1850s (12); and third, its theme, the relationship between similarities of crystal form and composition, made Mendeleev seriously consider the problem of the similarity of substances. I think this was the beginning of his involvement with the problem of classifying substances.

Mendeleev taught briefly at gymnasiums in southern Russia before returning to the capital to receive a master's degree and become a lecturer at St. Petersburg University. His master's thesis on specific volumes illustrates his later line of thought even more clearly (13). He adopted the atomic weight system of Gerhardt and Laurent and Avogadro's hypothesis (which Mendeleev called Gerhardt's law). This thesis also shows Mendeleev's interest in the natural classification of substances based on their specific volume.

In April 1859 Mendeleev went to Western Europe to study. During his two-year stay in Europe he studied the "cohesion" of various substances (the forces holding their molecules together), especially of organic compounds, through capillary phenomena. He tried to find a universal formula to explain the relationship of cohesion expressed in terms of surface tension with composition, density, or molecular weight. The instruments that Mendeleev purchased in Heidelberg, Bonn, and Paris enabled him to measure the properties of substances with very good precision. In September 1860 he attended the International Congress of Chemists in Karlsruhe, which considered significant contemporary issues in chemistry, especially atomic weights. Along with everyone else in attendance, Mendeleev received a copy of the famous paper on the new atomic-weight system by Stanislao Cannizzaro (1826-1910), who distributed it at the meeting (14). Immediately after reading the paper, Mendeleev wrote to his teacher A. A. Voskresenskii (1808-1883) in St. Petersburg with an informative report on both the Congress and the content of Cannizzaro's paper. His letter was published in a St. Petersburg newspaper and in a Moscow journal that same year (15). In pointing out

the inconsistency of Gerhardt's atomic weights of metals and arguing that Cannizzaro corrected them with the "multiatomicity of metals," Mendeleev clearly recognized Cannizzaro's successful system of atomic weights. In his letter to Voskresenskii, Mendeleev showed that, for various substances, the atomic heat (i.e., the product of specific heat and atomic weight) divided by the substance's number of atoms results in a constant (about 6-7). Thus, Cannizzaro's atomic weights were found to be in accord with the law of Dulong and Petit.

Early in 1861 Mendeleev returned to Russia. That same year, while teaching at various schools, he completed his first chemistry textbook, *Organic Chemistry*.



Mendeleev, 1878

In this he was already seeking "some sort of definite and exact principle" as a guide, like that later in *Principles*, finding it in what he called "the theory of limits" (16). This was the classification of organic compounds on the basis of their degree of saturation and their substitution reactions. Although this theory would soon be forgotten because of the advent of the structural theory of organic compounds, Mendeleev's textbook was well received in Russia. In 1862 the St. Petersburg Academy of Sciences awarded him the Demidov Prize for the outstanding book written in Russian during the previous year. In this textbook Mendeleev followed Cannizzaro's principle for determining atomic weights and defined them as "the minimum quantity of an element in the compound molecules of the element" (17). He also explicitly distinguished between "bodies" and "radicals," terming the former "something divisible (molecule)" and the latter "the theoretical notion" and "indivisible whole (atom)" (18).

After completing his textbook of organic chemistry, Mendeleev intended to write a textbook on inorganic and theoretical chemistry. He tried to extend the idea of saturation (his "theory of limits") to inorganic compounds, but with little success (19). He also left an 1864 lecture notebook on theoretical chemistry (20).

I believe that Mendeleev made one more change in his line of thought on atomic weights during 1860s. Even before his acquaintance with Cannizzaro's paper, Mendeleev had been especially concerned with deviations from the law of definite proportions. In his 1856 habilitation dissertation, he discussed the structure of silicate compounds (21), arguing that such compounds must be a kind of "alloy" of oxides, because, like alloys, "to some extent they can vary their composition (and formula) without changing their forms and main properties" (22). He developed this line of research, calling substances that had constant physical properties, but varied composition—such as solutions, alloys, isomorphous mixtures, and silicate compounds—"indefinite compounds." Such compounds had been studied very little, and Mendeleev himself could not explain their formation in any proper way. However, he emphasized the following points: they are not simply physical mixtures; some chemical power must be involved in their formation; and they show some properties that are similar to those of definite compounds (23). His doctoral thesis "On Compounds of Alcohol with Water," submitted in 1865, can be regarded as a study of solutions that arose from his interest in so-called indefinite compounds (24).

Underlying this interest was Mendeleev's concern that the formation or composition of indefinite compounds was difficult to explain in terms of the atomic theory, which was based on the concept of definite proportions. Even though no previous writers have emphasized the idea that Mendeleev was moving away from a belief in the atomic theory in this period (1864-1868), Mendeleev himself made this point clear in a lecture on theoretical chemistry published in 1864 (25):

In fact, although on the one hand, the law of definite chemical compounds has persuasively proven the atomic theory, on the other hand, a whole group of com-

pounds, the so-called indefinite compounds, have shown evidence, which is directly against the theory.

Almost the same passage appears in the first part of the first edition of *Principles* (26):

[C]ompounds with indefinite compositions . . . speak against the atomic doctrine as much as definite chemical compounds speak in its support.



Russian Chemists in Heidelberg in 1859-1860: (left to right) N. Yitinskii, A. P. Borodin, Mendeleev, V. I. Olevinskii

It is important to note that Mendeleev paid very little attention to atomic weights in the first part of this new textbook. He mentioned the atomic weights of only some 22 of the most familiar elements (27). It is true that a table of the 63 elements then known appears in the second chapter of the first part, but the elements are arranged alphabetically with no mention of their atomic weights (28). It seems likely that the existence of indefinite compounds made Mendeleev accept the limitation of the atomic theory and the narrow scope of atomic weights (29).

Even as Mendeleev regarded atomic theory with caution because of exceptions to the law of definite proportions, he insisted on the existence of distinct chemical elements, which were clearly distinguished from simple bodies. He argued this point in his first series of lectures at St. Petersburg University in the fall of 1867 (30):

[I]t is necessary to distinguish the concept of a simple body from that of an element. A simple body substance, as we already know, is a substance, which taken individually, cannot be altered chemically by any means produced up until now or be formed through the transformation of any other kinds of bodies. An element, on the other hand, is an abstract concept; it is the material that is contained in a simple body and that can, without any change in weight, be converted into all the bodies that can be obtained from this simple body.

A similar definition of element and the same argument for the need to distinguish clearly between element and simple body were later presented in the first part of *Principles* (31).

Thus, this distinction between “simple bodies” and “elements” is essentially the same as that between “bodies” and “radicals” in Mendeleev’s 1861 organic chemistry textbook, but without any mention of atoms or molecules. Paradoxically, then, it appears that Mendeleev was led to the weight of elements as an invariable characteristic and hence to his periodic system, not by adherence to the concept of chemical atoms, but by seeking freedom from it, as the failures of the law of definite proportions seemed to demand. It is reasonable to suppose that he refined the concept of the elements to bear an attribute of an individual chemical entity without employing the notion of atoms because of the supposed limitations of the atomic theory.

During the 1860s the theory of valence enjoyed great success, helping in the development of a new theory of organic chemistry, i.e., a structural theory of organic compounds. After Mendeleev wrote his textbook of organic chemistry based on a pre-structural theory, his “theory of limits,” it seems that he tentatively took the valences of the elements as a basic principle in writing

The Social Background of Mendeleev’s Writing of *The Principles of Chemistry*

Before analyzing the relationship between *Principles* and the discovery of the periodic law, let us briefly examine the social background of the writing of *Principles*. Published between 1868 and 1871, *Principles* grew out of Mendeleev’s need for a suitable textbook on chemistry in Russian, which was lacking when he began teaching at St. Petersburg University in the fall of 1867 as the Professor of General Chemistry (32):

I began to write [*Principles*] when I started to lecture on inorganic chemistry at the university after [the departure of] Voskresenskii and when, having looked through all the books, I did not find anything to recommend to students.

Mendeleev had obtained the position of a permanent lecturer at St. Petersburg University in 1864. He became an extraordinary professor of technical chemistry the following year and was promoted to full professor at the end of the same year. In the fall of 1867 Mendeleev was transferred to the professorship of general chemistry to succeed Voskresenskii, his own teacher, who left the university that year.

Mendeleev’s research career in chemistry, which began in 1854, reached its first zenith with the discov-

Table 1. BOOKS PUBLISHED WITH MENDELEEV AS AUTHOR OR EDITOR

1861	<i>Organic Chemistry</i> , 1st edition
1862	<i>Cahours’ Textbook for Elementary General Chemistry</i> , second pt. (translation) <i>Wagner’s Technology</i> (1862-1869), 8 Vol. (translation and compilation)
1863	<i>Organic Chemistry</i> , 2nd edition
1864	<i>Gerhardt and Chancel’s Analytical Chemistry, Qualitative Analysis</i> (translation)
1866	<i>Analytical Chemistry</i> , second pt., Vol. 1-3 (1866-1869)
1867	<i>Today’s Development of Some Chemical Productions—From the Point of View for the Application to Russia</i> (Report of International Exposition at Paris in 1867)
1868	<i>The Principles of Chemistry</i> , first pt., first vol.

his inorganic chemistry textbook, *Principles*, at the end of the 1860s, because of the success of valence theory in organic chemistry. But without the assumption of atoms, valence was incomprehensible. Hence Mendeleev had to look further for “some sort of definite and exact principle.” He had to find a fundamental property of the elements. Out of this exigency, weight—which we think of as “atomic,” but Mendeleev thought of as “elementary”—took on a new and increased importance.

ery of the periodic law in 1869. This discovery can also be considered the culmination of his social activity during this period. Those years, beginning in the middle of the 1850s after the Crimean War and running their course by the 1860s with the emancipation of the serfs in 1861, constituted a period of great change and reform in Russia. This was the second attempt at social and economic change after the social and political reforms of Peter the Great in the early 18th century; it has been called by

Table 2. CHRONOLOGY OF THE PUBLICATION OF THE FIRST EDITION OF *PRINCIPLES* AND DISCOVERY OF THE PERIODIC

DATE	PUBLICATION
May-June 1868	<i>Principles</i> , first volume (part 1, chapters 1-11)
February 17, 1869	“An Attempt at a System of the Elements Based on Their Atomic Weight and Chemical Affinity” (the first periodic table)
March 6, 1869	“The Correlation of the Properties and Atomic Weights of the elements” (the first paper on the periodic law, Paper I)
March 1869	<i>Principles</i> , second volume (part 1, chapters 12-22).
February-March 1870	<i>Principles</i> , 3rd volume (part 2, chapters 1-8).
February 1871	<i>Principles</i> , 4th & 5th volumes (part 2, chapters 9-23).
July 1871	“The Periodic Law of the Chemical Elements” (in <i>Annalen der Chemie und Pharmacie</i> , Paper II)

some historians “the Great Reforms Era.” It was also a time of change in chemistry: the dispute over the merits of different atomic weight systems had finally been settled after the Karlsruhe Congress; and classical organic structural theory had appeared.

The emergence of a new generation of chemists in Russia, eager to engage in original laboratory work and pursue a European trend in chemistry, was the important background to Mendeleev’s activities in this period. The educational system, especially at the higher levels, was also reorganized during this time. Because of the large numbers of Russian chemists moving into posts at academic institutions, the Russian Chemical Society was organized in 1868, Mendeleev being one of the founding members.

Let us consider the objectives that Russian chemists, including Mendeleev, were expected to achieve during this period. They consisted of the practical and the theoretical. The practical objective was to educate qualified professionals for the new capitalistic production that Russia required. The theoretical objective was to deal with current theoretical and experimental problems in chemistry to meet the needs of the time, as the classical foundations of chemistry were being established. Mendeleev was aware of these objectives. In his *Principles* he answered not only the theoretical requirements, but also the practical ones.

This point is illustrated by a listing of the books Mendeleev published during the 1860s after his return

from Europe (Table 1). The contents of these books indicate that they all met the practical demands of Russian society. *Wagner’s Technology*, for example, was initially the translation of German encyclopedic manuals on technology. As the editor, Mendeleev proposed to translate the pertinent sections needed in Russia, i.e., the parts on agricultural products and processing. Later on, he added the translations from other related books and also asked appropriate specialists to write original texts. They were all issued by the same publisher, “Obschestvennaia pol’za” [“Social Benefit”], a company that produced books and pamphlets on science and technology for the “social benefit and enlightenment of the people” (33). *Principles*, offering an advanced method for systematizing inorganic chemistry, was the new textbook for higher education urgently needed by Russian society. Mendeleev’s famous textbook was the culmination of his work to help satisfy his country’s needs during that period.

The Principles of Chemistry and the Discovery of the Periodic Law

First, let us consider the chronology of the publications of the first edition of *Principles* and the discovery of the periodic law (Table 2). In May or June 1868, Mendeleev published the first volume (Chapters 1-11). On February 17, 1869 (34), he compiled the first periodic table, titled “An Attempt at a System of the Elements Based on Their Atomic Weight and Chemical Affinity” (35).

On March 6, N. A. Menshutkin (1842-1907), the secretary of the recently established Russian Chemical Society, read Mendeleev's first paper on his discovery, "The Correlation of the Properties and Atomic Weights of the Elements" (Paper I) (36) at a meeting of the society. At almost the same time, Mendeleev published the second volume of *Principles*, Chapters 12-22. At the end of February or early in March 1870, the third volume, which comprises Chapters 1-8 of Part 2, appeared. Finally, the last volumes (the fourth and fifth),

Pharmacie (Paper II) (37). This chronology (Table 2) makes it clear that Mendeleev discovered the periodic law in the middle of writing *Principles*. As Kedrov has pointed out, a careful reading of this text reveals exactly when he discovered that law (38).

Let us examine Mendeleev's first paper on the periodic law (Paper I) and the early chapters of the second part of his textbook, which must have been written around the same time. He organized the first part of *Principles* on the basis of the principle of valence: first

Table 3. DIFFERENCES BETWEEN THE THIRD/FOURTH AND FIFTH EDITIONS OF *PRINCIPLES*

Third/Fourth Editions	Fifth Edition
chapters	chapters and elements [group number]
1 & 2	Introduction
3 & 4	1: H ₂ O
5	2: H ₂ O, H [I]
6 & 7	3: O [II]
9 & 10	4: O ₃ , H ₂ O ₂
11	5: N [III]
12 & 13	6: N with H & O
14	7: Molecules and Atoms
15 & 16 & 19	8: C & Hydrocarbons [IV]
17 & 18	9: C with O & N
20	10: NaCl, HCl [VII]
21 & 22	11: Cl, Br, I, F [VII]
23	12: Na [I]
24	13: K, Rb, Cs, Li [I]
25 & 26	14: Mg, Ca, Sr, Ba, Be [II]
27	15: "The Similarity of the Elements and the Periodic Law"
28	16: Zn, Cd, Hg [II]
29 & 30 & 31	17: B, Al, Ga, In, Tl [III], the rare earths
32 & 33	18: Si, Ge, Sn, Pb [IV]
34 & 35	19: P, As, Sb, Bi, V, Nb, Ta [V]
36 & 37 & 38	20: S, Se, Te [VI]
39	21: Cr, Mo, W, U [VI], Mn [VII]
40 & 41	22 Fe, Co, Ni [VIII]
43	23 Or, Ir, Pt, Pd, Rh, Ru [VIII]
42 & 44	24: Cu, Ag, Au [I]

which include Chapters 9-23, were published in February 1871. In July of that year, his most comprehensive paper on the periodic law, "The Periodic Law of the Chemical Elements," was published in a supplemental volume of the *Annalen der Chemie und*

he discussed univalent hydrogen, then divalent oxygen, trivalent nitrogen, and tetravalent carbon (39). After his treatment of the univalent halogens, which concludes the first part of the textbook, Mendeleev began the second part with a description of the univalent alkali met-

als. At the end of the chapter on heat capacity, which follows the alkali metals, he explained that he would next treat the alkaline-earth metals, which are divalent and not analogs of copper, which awkwardly exhibits both univalence and divalence (40). Although he had followed the principle of valence to this point in the textbook, he abruptly began the next chapter from a different perspective: a comparison of the alkaline-earth metals with the alkali metals on the basis of their atomic weights. In this connection, it should be noted that toward the end of Paper I, Mendeleev stressed that (41):

[T]he purpose of my paper would be entirely attained if I succeed in turning the attention of investigators to the relationships in the size of the atomic weights of *nonsimilar* elements, which have, as far as I know, been almost entirely neglected until now.

He emphasized the word “nonsimilar” with italics. Alkali metals and alkaline-earth metals were obviously such nonsimilar groups of elements.

If Kedrov’s analysis in *The Day of a Great Discovery* (42) of Mendeleev’s process is followed, then Mendeleev noticed this comparison of nonsimilar groups of elements in the middle of February 1869; and he first compiled the central part of the table on the basis of this principle. With the help of cards of the chemical elements, which he made for this occasion, Mendeleev finally succeeded in organizing a table of all the known elements on the basis of their atomic weights. He completed this on February 17, 1869 (43). Clearly, at that moment, Mendeleev had conceived the idea that atomic weight might be the fundamental numerical property of the elements.

In Paper I Mendeleev wrote (44): No matter how properties of simple bodies may change in the free state, *something* remains constant, and when the element forms compounds, this *something* is material existence and establishes the characteristics of the compounds, which include the given element. In this respect we know only one constant peculiar to an element, namely the atomic weight. The size of the

atomic weight, by the very essence of matter, is common to the simple body and all its compounds. Atomic weight belongs not to coal or diamond, but to carbon.

This “something,” italicized in the quotation above, corresponds exactly to Mendeleev’s definition of element. In other words, atomic weights belong to elements!



Mendeleev in St. Petersburg, Nov. 19, 1861

As a result of this reconceptualization or discovery, Mendeleev realized that he should use atomic weights, not valence, as the guiding principle for the remainder of his textbook. This was the moment when he started to write the chapter on alkaline-earth metals. However, since he defined the concept of element without the notion of atoms, he considered atomic weights to be the fundamental property of the elements. They were not necessarily based on atomic theory, which was still somewhat speculative. Thus, the scope of atomic weights would have to be broader than that of definite proportions on which the atomic theory was thought to be based. Mendeleev even once suggested the use of the word “elementary weight” instead of “atomic

weight” (45).

Changes in Later Editions of *The Principles of Chemistry*

Contrary to many statements in the existing literature on the periodic law—that Mendeleev kept the original version of *Principles* unchanged through subsequent edition—(46), he actually revised the structure of the textbook significantly with each new edition. Much confusion has resulted from this misunderstanding. In all, eight editions were published during Mendeleev’s lifetime. Let us look briefly at some of the changes in ensuing editions of *Principles*.

There were two type fonts in the text of the first four editions: sections in a larger font for beginning students and those in a smaller font for advanced learners. In the second edition, published in 1872-1873, just

one year after the completion of the first, there were only minor changes in the text. Mendeleev moved indium and uranium to the appropriate chapters because of the improved values of their atomic weights. He also changed the positions of the rare earths, which remained problematic throughout his life (Fig. 1).

The third edition, which appeared in 1877, underwent substantial change; and the chapters were completely reorganized in accord with the periodic law. The

The fourth edition in 1881-1882 was the same as the third in organization but slightly larger, increasing in size from 18 x 11 cm to 20 x 12 cm. Mendeleev first mentioned the discovery of scandium in this edition.

The fifth edition of 1889 underwent the second major change after the third edition. It was considerably larger, and for the first time the text was printed in double columns rather than in single columns. Therefore, the whole work became much shorter, reduced from

Table 4. MENDELEEV'S AND BRAUNER'S ARRANGEMENTS OF THE ELEMENTS (both from the 7TH Russian Edition, 1902)

Mendeleev's arrangement [copy from the 7th Russian edition]

Mendeleev's arrangement, 1902

Rows	Groups of Elements								
	0	I	II	III	IV	V	VI	VII	VIII
8	Xe	Cs	Ba	La	Ce	---	---	---	---
9		---	---	---	---	---	---	---	
10	---	---	---	Yb	---	Ta	W	---	Os Ir Pt

Brauner's arrangement, 1902 [copy from the 7th Russian edition]

Brauner's arrangement, 1902

Groups:	0	I	II	III	IV	V	VI	VII	VIII
8th-Row	Xe	Cs	Ba	La	Ce etc.	Ta	W	---	Os Ir Pt
where		Ce etc. = Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho Er Tu Yb

textbook was divided into two parts, as were the first two editions, but the chapters were now numbered successively throughout. Only small changes were needed in the first part, which was introductory and devoted to the elements frequently encountered in daily life. Mendeleev placed the chapter on the periodic law, entitled "Similarity of Elements and Their System," in the second part, immediately after the description of the alkali and alkaline-earth metals. After these chapters he described the elements in order of their position in the periodic table: from the second group to the sixth group, ending with the eighth group, iron and platinum analogs. The final chapters were devoted to the noble metals. The third edition also included gallium, the first of the elements to be discovered after Mendeleev had predicted their existence.

1176 pages in the fourth edition to 789 pages in the fifth. Some of the material from previous editions was moved into the footnotes in smaller font. There were no longer two parts, only one, bound as a single volume, a format retained in all subsequent editions. The chapters were also completely reordered. Many of them were combined, and the 44 chapters in the fourth edition became only 24 chapters in the fifth (see Table 3). The chapter on the periodic law was expanded to include the history of its discovery and the problem of priority (47). This fifth edition was translated into English, German, and French (48).

The sixth edition of 1895 was essentially unchanged in format from the fifth, but Mendeleev revised many of the footnotes. He added notes on argon, the newly

discovered gas from the air, at the end of the textbook, and he argued for the possibility that argon might be N_3 .

By the seventh edition of 1902-1903 Mendeleev had abandoned N_3 and fully accepted the noble gases, which he incorporated into the chapter on nitrogen and air. Mendeleev asked the Czech chemist Bohuslav Brauner (1855-1935) to write the section on the rare earths for the seventh and eighth editions, even though they had somewhat different opinions on the positions of these elements within the periodic system. They agreed to place scandium, yttrium, and lanthanum in the third group and tantalum in the fifth.

However, while Mendeleev believed that future research would reveal sufficient numbers of rare earth elements with different properties, so they could be placed in different groups to fit neatly into his periodic table, Brauner proposed that the rare earths should be all placed together in group IV, which was formerly occupied by cerium alone (Table 4). Effectively, this demon-

strates Mendeleev's admission of the difficulties in placement of the rare earths, so many in number and so similar in properties, within his periodic system. He also mentioned the discovery of radium in this edition, but denied the possibility of the transformation of the elements. He suggested other possible explanations of radioactivity, such as a "state" like a magnetic property or an absorbency and the projection of the "ether" in the vicinity of the radioactive atom.

The eighth edition in 1906 was the last published before Mendeleev's death. All the notes were separated from the main text and placed in the second half of the book. He argued for the possibility of a "chemical ether" as an extremely light element in the noble gas group, which he thought could explain radioactivity (49).

As shown in his textbook, Mendeleev's concept of the chemical elements demonstrates his firm and persistent belief in their conceptual priority. His clear understanding of the elements is evident from the very first edition. In his concept of an element, Mendeleev clearly departed from Lavoisier, who had offered a negative definition of an element as an undecomposed substance. For Mendeleev, the concept was defined positively as something abstracted from the diverse properties of simple bodies and their compounds. Therefore, elements were strictly distinguished from simple bodies.



Members of the Chemistry Section of the First Congress of Russian Naturalists (front row, 5th from left, A. A. Voskresenskii; back row, 2nd from right, Mendeleev; 6th from right, N. A. Menshutkin)

Beginning with the first edition of *Principles*, Mendeleev carefully denied the speculative connotations of the atomic hypothesis. Although it is tempting to say that his "element" is a substitute for "a t o m," Mendeleev resisted the use of the hypothetical atom. He was also opposed to any suggestion that served to reduce simple substances to a single sub-

stance or a few substances called "primary matter" (50). This attitude was in sharp contrast to those of other individuals who also sought a system of the elements during the 1860s (51).

Lothar Meyer's Approach to the Classification of the Elements

Let us briefly consider the case of Lothar Meyer (1830-1895) as an example of the "reductionist" tendency (52). His paper, "The Nature of the Chemical Elements as a Function of their Atomic Weights," appeared early in 1870 (53). He began with speculation related to Prout's hypothesis (54). On some points he went further than Mendeleev did in 1869 in his Paper I. Meyer succeeded in vividly conveying the periodic dependence of the

properties of the elements on their atomic weights by plotting the solid-state atomic volumes of the elements (simple bodies) against their atomic weights (55). Although he admitted in the paper that his table was essentially the same as Mendeleev's, his table of elements was more refined than Mendeleev's first attempt, especially in clearly showing the so-called transition metals. Meyer also had the correct weight of indium, to which Mendeleev had attributed an incorrect weight in his first paper. However, the conclusion of Meyer's paper was very tentative, even timid (56):

It would be hasty to undertake to alter on such uncertain bases the previously accepted atomic weights. On the whole, one may not attribute any very great weight to arguments of the sort here given, nor expect from them so certain a decision [regarding atomic weight] as is given by determination of the specific heat or the vapor density. They may however serve even now to turn our attention upon doubtful and uncertain assumptions and to challenge us to a renewed testing of them. And again, conversely, this testing will help to clarify and extend the meager beginnings of our knowledge of atoms.

Meyer's conclusion lacks the confidence expressed by Mendeleev in his first paper. In 1869 there was a noticeable difference between these two men in their attitudes toward the concept of the atom. Whereas Mendeleev discarded the atom and relied solely on the refined concept of a chemical element, Meyer embraced the atom and even supported the speculation of Prout's hypothesis of a primordial matter (hydrogen) as the building block of the elements. This prompted Meyer to underestimate his findings and prevented his having full confidence in his discovery of 1869. In 1873, however, Meyer published another paper (57), in which he fully applied the periodic law, citing Mendeleev's comprehensive 1872 paper on the subject (Paper II in Table 2) as the evidence for the validity of his own work.

Conclusion: Mendeleev's Concept of the Chemical Elements and 19th-Century Chemistry

Mendeleev's concept of the chemical elements as a stable, intermediate level of matter, not necessarily based on the speculative concept of the atom, corresponded to the state of chemistry in the mid-19th century. Ironically, it helped him discover the periodic law. This deep insight, which assured him of the validity of his discovery, allowed him to apply it fully to the chemistry of his time, without being bothered by a seeming regularity in

numbers on the one hand, or being misled by a speculative primordial matter on the other. As a result of his discovery, the concept of an element gained another positive characteristic in its definition: an element occupies a specific place in the periodic system (58). Later Mendeleev's concept of chemical elements developed into "chemical individuals," his further attempt to avoid the speculative connotations of the atomic theory (59). Even though the formats of Mendeleev's textbook changed substantially with each edition, his firm belief in the validity of the concept of the chemical elements remained unchanged from the 1860s.

In the course of revising his textbook, Mendeleev developed his concepts further. Eventually, however, he encountered insurmountable difficulties, including the placement of the rare earths in his system (60), abnormalities in the order of atomic weights, and new phenomena, such as radioactivity. These were the predicaments that could be solved only by a new concept of the elements, which was beyond Mendeleev's understanding and that of 19th-century chemistry in general.

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2. This date is in the Julian calendar, used in Russia until January 1918. The Julian calendar lagged 12 days behind the Gregorian calendar in the 19th century and 13 days in the 20th century. In this paper I am using the Julian calendar for events in Russia and the Gregorian dates for events outside Russia.
3. D. Mendeleev, "Sootnoshenie svoystv s atomnym vesom elementov" ["The Correlation of the Properties and Atomic Weights of the Elements"], *Zh. Russ. Khim. Obshch.*, **1869**, 1, No. 2/3, 60-77 (65). I have used the English translation of this paper, with some modification, from H. M. Leicester and H. S. Klickstein,

- Sourcebook in Chemistry 1400-1900*, Harvard University Press, Cambridge, MA, 1952, 439-444.
4. Leicester was one of the few historians in the West who clearly pointed out this connection before Kedrov. See, e.g., H. M. Leicester, "Factors which Led Mendeleev to the Periodic Law," *Chymia*, **1948**, *1*, 67-74 (71); also H. M. Leicester, *The Historical Background of Chemistry*, 1956, reprinted Dover Publications, New York, 1971, 193.
 5. B. M. Kedrov, *Den' odnogo velikogo otkrytiia* [*The Day of a Great Discovery*], Izd. Sotsial'no-ekonomicheskoi Literatry, Moscow, 1958. His main points are also available in English: B. M. Kedrov, "Dmitry Ivanovich Mendeleev," *Dictionary of Scientific Biography*, C. C. Gillispie, Ed., Charles Scribner's Sons, New York, 1974, Vol. 9, 286-295 (288).
 6. For example, I. S. Dmitriev's recent paper in Russian on the discovery of the periodic law starts from criticism of Kedrov's analysis and tries to present an alternative version: I. S. Dmitriev, "Nauchnoe otkrytie *in statu nascendi*: periodicheskii zakon D. I. Mendeleeva" ["Scientific Discovery *in statu nascendi*: The Periodic Law of D. I. Mendeleev"], *Vopr. Istor. Estestvozn. Tekh.*, **2001**, No.1, 31-82.
 7. M. Kaji, *Mendeleev's Discovery of the Periodic Law of the Chemical Elements—The Scientific and Social Context of His Discovery* [in Japanese], Hokkaido University Press, Sapporo, Japan, 1997.
 8. For example B. Bensaude-Vincent, "Mendeleev's Periodic System of Chemical Elements," *Br. J. Hist. Sci.*, **1986**, *19*, 3-17.
 9. Loren R. Graham has emphasized the need to study the evolution of Mendeleev's views in later editions of *Principles* more thoroughly. See L. R. Graham, *Science in Russia and the Soviet Union: A Short History*, Cambridge University Press, Cambridge, 1993, 266, note 34. There is a recent study of these aspects by N. M. Brooks, "Dmitrii Mendeleev's *Principles of Chemistry* and the Periodic Law of the Elements," in A. Lundgren and B. Bensaude-Vincent, Ed., *Communicating Chemistry: Textbooks and Their Audiences, 1789-1939*, Science History Publications, Canton, MA, 2000, 295-309. However, Brooks' conclusions are different from mine, especially on the organization of later editions of *Principles*.
 10. Reprinted in D. Mendeleev, *Sochineniia* [*Collected Works*], Izd. Akademii Nauk SSSR, Leningrad, 1949, Vol. 15, 16-19, 20-23. Hereafter referred to as *Works*.
 11. "Izomorfizm v sviazi s otnosheniami kristallicheskoj formy k sostavu" ["Isomorphism in the Relationship Between Crystal Form and Composition"], reprinted in *Works*, Vol. 1, 7-137.
 12. On the role of Laurent and Gerhardt in the reform of the atomic weight-molecular formula problem, see A. J. Roche, *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*, Ohio State University Press, Columbus, OH, 1984, 192-214. For their influence in Russia, including that on Mendeleev, see M. G. Faershtein, *Istoriia ucheniia o molekule v khimii (do 1860 g.)* [*The History of Molecular Theory in Chemistry (up to 1860)*], Izd. Akademii Nauk SSSR, Moscow, 1961, 290-321.
 13. "Udel'nye ob'emy" ["Specific Volumes"], reprinted in *Works*, Vol. 1, 139-323; Vol.25, 112-228.
 14. S. Cannizzaro, "Sunto di un corso di filosofia chimica," *Nuovo Cim.*, **1858**, *7*, 321-366 (1858). For an English translation, see *Sketch of a Course of Chemical Philosophy by Stanislao Cannizzaro (1858)*, Alembic Club Reprint No. 18, Alembic Club, Edinburgh, 1910. This translation is also reprinted in M. J. Nye, *The Question of the Atom: From the Karlsruhe Congress to the First Solvay Conference, 1860-1911*, Tomash Publishers, Los Angeles, CA, 1984, 31-87.
 15. Mendeleev's letter to Voskresenskii is reprinted in D. I. Mendeleev, *Periodicheskii zakon* [*The Periodic Law*], B. M. Kedrov, Ed., Izd. Akademii Nauk SSSR, Moscow, 1958, 660-669, and also in N. A. Figurovskii, *Dmitrii Ivanovich Mendeleev, 1834-1907*, 2nd ed., Nauka, Moscow, 1983, 274-280.
 16. D. Mendeleev, "Essai d'une théorie sur les limites des combinaisons organiques," *Bull. Acad. Imp. Sci. St.-Petersbourg*, **1862**, *4*, 245-250; reprinted in *Works*, Vol. 8, 22-27.
 17. D. Mendeleev, *Organicheskaiia khimiia* [*Organic Chemistry*], 1st ed., St. Petersburg, 1861, v.
 18. Ref. 17, note on p 36.
 19. A. A. Makarenia, *D. I. Mendeleev i fiziko-khimicheskie nauki—Opyt nauchnoi biografii D. I. Mendeleeva* [*D. I. Mendeleev and the Physico-Chemical Sciences—An Attempt at a Scientific Biography of D.I. Mendeleev*], 2nd ed., Energiizdat, Moscow, 1982, 92-100.
 20. "Fragmenty iz lektsii D. I. Mendeleeva po teoreticheskoi khimii" ["Fragments from D. I. Mendeleev's Lectures on Theoretical Chemistry"], in D. I. Mendeleev, *Izbrannye lektsii po khimii* [*Selected Lectures on Chemistry*], Izd. Vysshiaia Shkola, Moscow, 1968.
 21. "O stroenii kremnezemistykh soedinenii" ["On the Structure of Silicate Compounds"], a dissertation pro venia legendi, 1856, reprinted in *Works*, Vol. 25, 108-228.
 22. Ref. 21, p 220.
 23. For his arguments during the 1860s, see Ref. 20, pp 9-69, especially pp 11-14, 26-59.
 24. "O soedinenii spirta s vodoi" ["On Compounds of Alcohol with Water"], St. Petersburg, 1865, reprinted in *Works*, Vol. 4, 1-52.
 25. Ref. 24, p 24.
 26. D. Mendeleev, *Osnovy Khimii* [*The Principles of Chemistry*], 1st ed., Part 1, Ch.10, reprinted in *Works*, Vol. 13, 337.
 27. Ref. 26, 1st ed., Part 1, Ch. 10, reprinted in *Works*, Vol. 13, 342.
 28. Ref. 26, 1st ed., Part 1, Ch. 2, reprinted in *Works*, Vol.

- 13, 77-82. The third edition has the same table, but with atomic weights.
29. Ref. 26, 1st ed., Part 1, Ch. 10, reprinted in *Works*, Vol. 13, 340-341.
30. *Lektsii po obshchei khimii 1867/68 g.* [*Lectures on General Chemistry in 1867/68*], Lecture V, St. Petersburg, reprinted in *Works*, Vol. 15, 381-382. A lithographic edition of these lecture notes was found in the library of the former Bestuzhev women's courses, one of the most important institutions of higher education for women in pre-revolutionary Russia. Consisting of sixteen lectures, these notes are similar to the first half of part 1 of *Principles* written in 1868. In the fifth lecture, there is a table of 63 elements, ordered alphabetically by their Latin names. The atomic weights of 12 of these elements were incorrect, which could not have been the case after the discovery of the periodic law. All this evidence shows that these notes are a record of Mendeleev's lectures on general chemistry given at St. Petersburg University in the fall of 1867.
31. Ref. 26, 1st ed., Part 1, Ch. 2, reprinted in *Works*, Vol. 13, 73-74 and also Ch. 15, reprinted in *Works*, Vol. 13, 488-490.
32. Ref. 1, pp 52-53.
33. *Tridtsatipiatiletie vysochaishe utverzhdennogo Tovarishchestva "Obshchestvennaia pol'za"* [*The Thirty-Fifth Anniversary of the Founding of the "Social Benefit" Company*], Obshchestvennaia Pol'za, St. Petersburg, 1895, 5.
34. See the clarification of dates in Ref. 2.
35. D. Mendeleev, "Opyt sistemy elementov, osnovannoi na ikh atomnom vese i khimicheskom skhodstve," ["An Attempt at a System of the Elements Based on Their Atomic Weight and Chemical Affinity"], in Ref. 15, p 9.
36. Ref. 3. Mendeleev was not present for this meeting because he had left St. Petersburg on March 1 for a consulting trip with farmers in cheese-making communities. He was sent by the Free Economic Society (Vol'noe ekonomicheskoe obshchestvo), one of the oldest scientific societies in Russia.
37. D. Mendelejeff, "Die periodische Gesetzmässigkeit der chemischen Elemente," *Ann. Chem. Pharm.*, **1871**, Supplementband, 8, 133-229. Mendeleev's manuscript was translated into German by Felix Wreden, a friend of Mendeleev in St. Petersburg. The original Russian text was first published in D. I. Mendeleev, *Novye materialy po istorii otkrytiia periodicheskogo zakona* [*New Materials on the History of the Discovery of the Periodic Law*], Izd. Akademii Nauk SSSR, Moscow, 1950, 19-82; reprinted in Ref. 15, pp 102-176. The Russian versions published earlier were translations from the German, the first by B. N. Menshutkin in D. I. Mendeleev, *Periodicheskii zakon* [*The Periodic Law*], Leningrad, 1926, 70-133; and the second by V. Ia. Kurbatov in *Works*, Vol. 25, 239-305.
38. Ref. 5, Kedrov, 1958, pp 32, 138-145.
39. Ref. 26, 1st ed., Part 1, Ch.19, reprinted in *Works*, Vol. 13, 650-652. Mendeleev argued that their compounds could be types for all the other compounds. Obviously, Gerhardt's "type theory" could be seen as influential here since Mendeleev was familiar from his student days. However, he did not mention Gerhardt and went directly to the concept of valence, for which he used the word atomnost' (atomicity).
40. Ref. 26, 1st ed., Part 2, Ch.3, reprinted in *Works*, Vol. 14, 120-121.
41. Ref. 3, p 77.
42. Ref. 5, pp 39-91. Also see my recent analysis of the process of the discovery, Ref. 7, pp 183-199.
43. D. N. Trifonov has criticized Kedrov's version on several minor points: "Versiya-2 (K istorii otkrytiia periodicheskogo zakona D. I. Mendeleevym)" ["Version 2 (Toward a History of the Discovery of the Periodic Law by D. I. Mendeleev)"], *Vopr. Istor. Estestvozn. Tekh.*, **1990**, No.2, 25-36; No. 3, 20-32. I. S. Dmitriev has recently offered an alternative version of Mendeleev's discovery; see Ref. 6.
44. Ref. 3, p 66.
45. Ref. 37, D. Mendelejeff, p 136, note. This is Paper II in Table 2.
46. It is often said that Mendeleev kept the text of *Principles* unchanged through all the subsequent editions, but with the addition of footnotes that became longer and longer. As I show in this paper, this interpretation is a misunderstanding or at least inaccurate. This may originate partly from the fact that most Western literature refers to the translations of later editions of *Principles* and partly from the rather vague description of the textbook by Leicester, Ref. 4, 1948, p 71. See, for example, Bensaude-Vincent, Ref. 8, p 8. Brooks has also written recently that Mendeleev made no substantial change in the organization of the book for these eight editions (Ref. 9, Brooks, p 307).
47. D. Mendeleev, *Osnovy Khimii* [*The Principles of Chemistry*], 5th ed., Ch. 15, 448-472.
48. The format of the fifth and subsequent editions was completely different from that of the preceding editions; i.e., this and subsequent editions were bound as a single volume, but English and French translations were issued in multiple volumes. This has given rise to the incorrect ideas about the formats of Mendeleev's textbook. The English translation appeared in two volumes: *The Principles of Chemistry* by D. Mendeléeff. Translated from the Russian (fifth edition) by George Kamensky, edited by A. J. Greenway in two volumes, Longmans, Green & Co., London and New York, 1891; Vol. I, xvi + 611 pp. & Vol. II, vi + 487 pp. Later, the sixth and seventh Russian editions were also translated into English and published in 1901 and 1905, respectively, as the second and third English editions. Each of these English editions also appeared in two volumes. The German translation was issued in one volume like the Russian edition:

- Grundlagen der Chemie*. Aus dem russischen übersetzt von L. Jawein und A. Thillot, Verlag von C. Ricker, St.-Petersburg, [1890]-1891, [4], 1127 S. Both the fifth and the sixth editions were used for the French translation since the sixth edition appeared while the French edition was being prepared. The French translation should have been published in three volumes, but the third volume never appeared for some unknown reason: *Principes de chimie* par M. Dimitri Mendéléeff le professeur de chimie à l'Université impériale de Saint-Pétersbourg. Traduit du russe par E. Achkinasi [et] H. Carrion, avec préface de M. le professeur Armand Gautier. Vol. 1-2, Éditeur B. Tignol, Paris, 1895-1896; Vol. I, [4], iv + 585 pp. & Vol. II, [4], 499 pp.
49. D. Mendeleev, *Popytka khimicheskogo ponimaniia mirovogo efira* [An Attempt at a Chemical Understanding of the Universal Ether], St. Petersburg, 1903. An English translation appeared as D. Mendéléeff, *An Attempt Toward a Chemical Conception of the Ether*, trans. G. Kamensky, Longmans, Green & Co., New York, 1904. See B. Bensaude-Vincent, "L'éther, élément chimique: un essai malheureux de Mendéléev?" *Br. J. Hist. Sci.*, **1982**, *15*, 183-188.
 50. Ref. 26, 1st ed., Part 2, Ch.6, reprinted in *Works*, Vol. 14, 247.
 51. Bensaude-Vincent has pointed out that the logical consequence of Lavoisier's definition is the hypothesis of a primordial matter. See Ref. 8, p 12.
 52. In 1969 van Spronsen claimed that there were six independent discoverers of the periodic law: A. E. B. de Chancourtois, J. A. R. Newlands, W. Odling, G. D. Hinrichs, J. L. Meyer, and D. I. Mendeleev. J. W. van Spronsen, *The Periodic System of Chemical Elements: A History of the First Hundred Years*, Elsevier, Amsterdam, 1969. On the other hand, in the 1860s, these six individuals had classified almost all the elements already discovered on the basis of the atomic weights proposed by Cannizzaro and on some relationships between different groups of elements. However, as I have argued elsewhere, there were significant differences in their scientific contents, as well as the social contexts, for the acceptance of their discoveries. See Ref. 7, pp 101-141, 239-260.
 53. L. Meyer, "Die Natur der chemischen Elemente als Function ihrer Atomgewichte," *Ann. Chem. Pharm.*, **1870**, Supplementband, 7, 354-364. Also reprinted in K. Seubert, Ed., *Das natürliche System der chemischen Elemente*, Ostwald's Klassiker No. 68, W. Engelmann, Leipzig, 1895, 9-17. For a partial translation of this paper into English, see Ref. 3, Leicester and Klickstein, pp 434-438.
 54. Ref. 53, Meyer, pp 354-355.
 55. Note that Meyer did not strictly and explicitly distinguish elements from simple bodies.
 56. Ref. 53, Meyer, p 364.
 57. L. Meyer, "Zur Systematik der anorganischen Chemie," *Ber. Dtsch. Chem. Ges.*, **1873**, *6*, 101-106.
 58. See J. R. Smith, Persistence and Periodicity: A Study of Mendeleev's Contribution to the Foundation of Chemistry, Ph.D. Thesis, University of London, 1976, 516; also Ref. 8, Bensaude-Vincent, p 15.
 59. "Referat soobshcheniia 'O edinstve veshchestva v sviazi s periodicheskim zakonom'" ["Abstract of the Report 'On the Unity of Substance in Connection with the Periodic Law'"], *Zh. Russ. Khim. Obshch.*, **1886**, *18*, No. 1, sect. 1, 66-67, reprinted in Ref. 15, Kedrov, pp 438-439; D. Mendéléeff, "The Periodic Law of the Chemical Elements" (Faraday Lecture Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution on Tuesday, June 4, 1889), *J. Chem. Soc.*, **1889**, *55*, 634-656, also in Appendix II of D. Mendéléeff, *Principles*, 3rd English ed., 1905, reprinted 1969, 494.
 60. Ref. 52, van Spronsen, p 260. Van Spronsen has made the point that the rare earths were such an insurmountable difficulty for the periodic system that it could have been constructed only during the 1860s when few of them were known.

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HYDRATING IONS IN ST. PETERSBURG AND MOSCOW; IGNORING THEM IN LEIPZIG AND BALTIMORE

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Debates over the “New” Physical Chemistry

The debates that swirled around the early development of modern physical chemistry in the late 19th century played themselves out in several different arenas: free ions vs. hydrates, dissociation vs. association, and, more broadly, physics vs. chemistry (1). But regardless of how any particular aspect of these debates was framed, the two sides were almost always seen as incompatible with each other. On one side were the “Three Musketeers of Physical Chemistry(2)” — Arrhenius, van’t Hoff, and Ostwald — and their numerous converts, many of whom were initiated into the physical theory of solutions, including dissociation and ions, in Ostwald’s lab in Leipzig (3). On the other side were the “three irreconcilables(4)” — Henry Armstrong, Louis Kahlenberg, and Isidor Traube — along with a few other holdouts, who could not bring themselves to believe that substances simply “fell apart” in solution and preferred a chemical view of association instead.

Because of the centrality of aqueous solutions in these debates, the role of water was crucial. The ionists regarded water as nothing more than an inert medium throughout which the dissociated ions of a dissolved electrolyte distribute themselves. Until the end of the 19th century, the ionists in Western Europe and America remained steadfast in their conviction that water and ions do not interact with each other, even with the increase in experimental results that seemed incompatible with a model of the solvent as an uninvolved bystander. The anti-ionists, though fewer in number, believed just as ardently that association, rather than dissociation, is the

process occurring in solution. Hydrate formation was seen as one way in which water and the dissolved substance could interact with each other, and Mendeleev’s hydrate theory (5) provided a rallying point for the anti-ionists, at least for a while.

This standoff over hydrates continued until after the turn of the century even though they had been mentioned nearly forty years earlier as a possible explanation for the anomalous results of freezing-point measurements on electrolyte solutions, first by Friedrich Rüdorff [1832-1902] in 1861 (6) and then by Louis de Coppet [1841-1911] ten years later (7). Although hydrates, as well as more general questions about the nature of solution, generated considerable discussion and debate throughout the latter part of the 19th century (8), the ionists’ unified front on this issue remained intact until the early years of the 20th century.

Beginning in 1900, Harry Clary Jones [1865-1916], Professor of Physical Chemistry at Johns Hopkins University, developed a solvate theory, which he regarded as compatible with dissociation theory. After a Ph.D. degree from Hopkins in 1892, he traveled to Europe as a postdoctoral student for two years, working with Ostwald, as well as with Arrhenius in Stockholm and van’t Hoff in Amsterdam. Probably the most ardent American ionist of his time, Jones proselytized vigorously on behalf of dissociation theory, with Ostwald describing him (9) as “one of my most loyal and devoted pupils.”

After returning to Baltimore in 1894, Jones continued his research on electrolytes and solution theory,

but he and his students could not explain certain freezing-point data (10):

...in terms of any relation that was then known. . . . Yet it seemed impossible to interpret the results obtained in terms of any other assumption than that a part of the water present was combined with the dissolved substance, and was therefore removed from playing the rôle of solvent. Accordingly, in 1900, the suggestion was ventured, for want of any better, that hydration in solution would explain these results.

Admittedly “antagonistic to any hydrate theory” (11) prior to his “suggestion . . . ventured, for want of any better,” Jones then spent more than a decade in developing his solvate theory of solutions. He reviewed the work by himself and his students in two long papers (12), as well as in several shorter summaries (13). While he still ignored previous work by Rüdorff and most others on the topic of hydration, Jones (14) specifically dismissed the earlier hydrate theory of Mendeleev as having no relevance or connection to his own. Referring to experiments that he had carried out in Arrhenius’ laboratory in Stockholm in 1893, Jones stated categorically that they showed “not the slightest evidence in favor of Mendeléeff’s theory of the existence of very complex hydrates in dilute solutions(15)”.

Jones characterized his theory as “radically different” from Mendeleev’s, which predicted the formation of “a few definite compounds with water,” such as $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 25 \text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4 \cdot 100 \text{H}_2\text{O}$. Jones believed that his own evidence for sulfuric acid and other electrolytes suggested the formation of “a complete series of hydrates with water, having all compositions ranging from one molecule of water up to at least thirty or forty molecules” (16), with “the amount of combined water for any given substance being a function of the concentration of the solution and of the temperature” (17). His theory encompassed all solvents, not just water, and he wrote (18):

Indeed, enough evidence has already been obtained to make it highly probable that solvation is not limited to aqueous solutions but is a general property of solutions. Solvents in general have more or less power to combine with substances dissolved in

them—in a word, *we have the solvate instead of simply a hydrate theory.*

However, a full decade before Jones reluctantly stopped ignoring the possibility of hydrated ions and embraced the concept of solvation, two Russian chemists, Ivan Alekseevich Kablukov [1857-1942] and Vladimir Aleksandrovich Kistiakovskii [1865-1952], independently suggested that hydration could—and *should*—be regarded as complementary, rather than contradictory, to dissociation. Both had been students of Mendeleev in St. Petersburg and also in Ostwald’s laboratory in Leipzig, where they studied with the original ionists. Neither of them assembled the extensive experimental basis for hydration that Jones did (19), but they certainly deserve recognition for their roles in the early improvements to Arrhenius’ original dissociation hypothesis (20). Kablukov and Kistiakovskii promoted the concept of hydrated ions long before Jones began his flirtation with them in 1900.

Ivan Alekseevich Kablukov

Kablukov was born into the family of an emancipated serf in a small village near Moscow. At the age of eleven he began formal schooling at the Second Moscow Classical Gymnasium, from which he graduated in 1876. Later that year he entered Moscow University as a student in the Natural Science Section of the Physics and Mathematics Department. Kablukov recalled his university matriculation (21):

I remember that year when I became a student at Moscow University for the first time. I was very poor and wore an overcoat loaned to me by my brother, but it seemed to me that all of Moscow envied me. With pride, I repeated to myself: “I am a student at the university established by the great Lomonosov.”

It was not chemistry, however, that initially attracted Kablukov to science. He spent more than a year in the Zoological Museum until he “happened upon the chemistry laboratory at Moscow University at a time of enthusiasm for organic chemistry” (22). V. V. Markovnikov [1838-1904], who occupied the chair of organic chemistry at that time, must have seen the young student’s potential since he set him to work almost immediately on the synthesis of a glycerine derivative. Kablukov received his candidate’s de-



I. A. Kablukov as a student at Moscow University. Photo courtesy of LAFOKI, Russian Academy of Sciences.

gree from Moscow University in 1880, and the following year he was awarded a gold medal for his thesis, "Polyatomic Alcohols and Their Immediate Derivatives" (23).



An undated photograph of I. A. Kablukov. Photo courtesy of LAFOKI, Russian Academy of Sciences.

Markovnikov arranged for Kablukov to study with his own teacher, A.

M. Butlerov [1828-1886], at St. Petersburg University during 1881-1882. Besides attending Butlerov's lectures on organic chemistry, Kablukov also heard Mendeleev [1834-1907] lecture on inorganic chemistry and N. A. Menshutkin [1842-1907] on analytical chemistry and the history of chemistry. Kablukov later recalled that Mendeleev had awakened his interest in inorganic and (pre-Ostwaldian) physical chemistry. Although he again performed research under the direction of Markovnikov after his return to Moscow, he was also branching out beyond the boundaries of organic chemistry by teaching a practical course in quantitative analysis (24).

By 1887 when he defended his master's thesis, "Glycerines or Triatomic Alcohols and Their Derivatives," Kablukov had become a privat-docent and was teaching courses on physical and inorganic, as well as organic, chemistry. With the appearance of the new physical chemistry in 1887, Kablukov began offering a course entitled "On the Phenomena of Dissociation" (25). His increasing interest in applying physical methods of investigation to chemical problems led him to undertake research in the Physics Laboratory at Moscow University while still teaching chemistry.

In 1889 Kablukov arranged to spend three months in Ostwald's laboratory, where he worked under the direction of Arrhenius. His results on the electrical conductivity of HCl and H₂SO₄ in various nonaqueous solvents showed—perhaps for the first time—that the relationship between the electrical conductivity and concentration of these electrolytes in alcohol solutions is the opposite of that in aqueous solutions (26). Kablukov

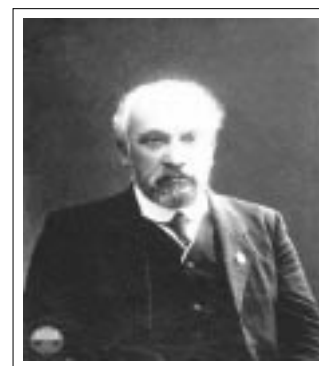
interpreted these results as suggesting some kind of solvent effect on the solute, though he apparently did not speculate on the exact nature of the effect.

Back in Moscow Kablukov continued this work on electrolyte solutions in the laboratory of A. P. Sabaneev [1843-1923], professor of analytical chemistry. Two years later he defended his doctoral dissertation (27), which was the first systematic discussion of the new physical chemistry in Russian. After presenting Arrhenius' picture of the breakup of an electrolyte into separate ions in aqueous solution, Kablukov wrote (28): "In our opinion, water does indeed decompose the molecules of the dissolved substance into separate ions, but in addition, these ions that are formed can combine with water into more complex groups .." He returned to this idea later in his dissertation (29):

[I]t is impossible to look at the solvent as a medium that is indifferent to the dissolved substance, and it is necessary to accept some kind of chemical interaction between the dissolved substance and the solvent.

In recalling this work many years later, Kablukov said that as a student of Mendeleev, he was unable to accept Arrhenius' idea that ions in solution do not interact in any way with the solvent (30). His dissertation concludes with the following observation (31):

Our investigations once more confirm that the solution of one substance in another should be regarded as a medium containing a mixture of different products from the chemical interaction between solute and solvent. Such a solution changes the physical and chemical properties of the solute, and all the properties of the solution depend on the strength of the interaction between solute and solvent. Our investigations into the "avidity" of acids show that this property is not a constant property of each acid, but depends on the nature of the solvent in which the acid is dissolved. And it depends not only on the nature of the solvent, but also on the relative amount of solvent, in other words, on the concentration of the solution. Referring to the viewpoint of Arrhenius, we can say that the "avidity" or "relative affinity" of an acid depends on its degree



An undated photograph of I. A. Kablukov. Photo courtesy of LAFOKI, Russian Academy of Sciences.

of dissociation, which can serve as a measure of the chemical interaction between the solute and solvent.

Thus, Kablukov contended that there is no inherent contradiction between ionic dissociation and ionic hydration, and in the 1902 edition of his *Basic Principles of Physical Chemistry*, he wrote that “in the forthcoming and more complete theory of solutions, both theories will merge” (32). This was exactly what Harry Jones was beginning to work toward about that time (33).

Amid the generally hostile reception of the new solution theory in Russia—though somewhat less in Moscow than in St. Petersburg—Kablukov voiced his ardent support in the debates among his university colleagues and members of the various scientific societies, as well as in the popular press (34). However, he never elaborated any specific merger of dissociation and hydration himself as his teaching positions and research interests led him to other areas of physical and inorganic chemistry, as well as to practical problems in industry and agriculture (35).

Vladimir Aleksandrovich Kistiakovskii

Kistiakovskii's immediate family origins (36) were very different from those of Kablukov. He was born in Kiev in 1865, the son of a prominent academic and expert in criminal law, and he grew up in a household of intense intellectual activity. This also included science as a paternal uncle, a physician, had defended his doctoral dissertation in medical chemistry (37).

After graduating from the Second Kiev Gymnasium in 1883, Kistiakovskii entered the Physics and Mathematics Department at Kiev University, which celebrated the fiftieth anniversary of its founding the following year. During these celebrations student protests erupted against restrictive regulations and the low level of instruction. In response, officials closed the university and expelled the entire student body. Although students were readmitted the next fall, Kistiakovskii chose not to return. A year later he entered St. Petersburg University, where instruction in the physical and mathematical sciences was far superior to that in Kiev at the time.

In his first experimental work at St. Petersburg, Kistiakovskii studied the action of the acids of arsenic on alkenes under the supervision of M. D. L'vov [1848-1899], a former student of Butlerov. At the same time, however, Kistiakovskii was falling under the spell of the new physical chemistry emanating from Leipzig, and in December 1888 he gave Menshutkin an essay entitled

“The Planck-Arrhenius Hypothesis,” for which he received the candidate's degree the following year. This unpublished thesis was discovered only in the mid-1950s in the archives of the Academy of Sciences of the USSR (38).

Despite the general hostility of the St. Petersburg chemists toward dissociation theory, Menshutkin was sufficiently curious about the new physical chemistry from Leipzig to have a student examine it in detail (39). Kistiakovskii's thesis consists of three parts: a description of the theory of electrolytic solution, a critical analysis of the theory, and a detailed attempt to merge the concept of ions with Mendeleev's hydrate theory (40). Although this project began as a literature study, it became a vehicle for serious speculation by the 23-year-old Kistiakovskii. The young student did not regard the discrepancies between the theory and experimental data on strong electrolytes and concentrated solutions as the most serious flaw in Arrhenius' theory; rather, it was the refusal of the Ostwaldian camp to admit any kind of interaction between solute and solvent particles. To Kistiakovskii's way of thinking, such interaction was the only possible source of the energy needed for dissociation to occur (41).

Early in 1889 Kistiakovskii received the candidate's degree from the Physics and Mathematics Department at St. Petersburg University, and that spring he traveled to Leipzig for a year-long stay in Ostwald's laboratory. Kablukov was there at the time, and L'vov wrote to him (42):

His name is Kistiakovskii. . . . Please become acquainted with him. I am certain you will not regret it. In spite of the fact that he has been doing serious study for only about a year or less, you will find in him good stuff and a continual tendency to independent speculation, sometimes very original and ingenious. Frankly speaking, I will be sad if he gets bogged down with ions.

These must have been heady days for Kistiakovskii, as they were for many young chemistry students from Europe and America, toiling on the Mt. Olympus of the Leipzig laboratory with the gods themselves of the new physical chemistry. Kistiakovskii worked on an experimental problem concerning the ionic nature of double salts, but the young Russian also engaged in theoretical discussions with Arrhenius, Ostwald, Nernst, and others. He argued that ions must interact with the surrounding solvent molecules. Kistiakovskii recalled one such debate in which he said that “it was difficult to understand the existence of free (unhydrated) ions in water.”

Ostwald replied, “You will agree that if it is difficult to understand, then it was even more difficult to discover” (43).

The 1890 paper (44) describing Kistiakovskii’s investigation of double salts concludes with a section entitled “Specific Attractions in Salt Solutions.” In it he undertakes a theoretical analysis of solute-solvent interactions in terms of van der Waals forces between an ion and the water molecules within its sphere of influence. Kistiakovskii specifically examines the freezing of an electrolyte solution—the very anomaly that later drove Jones to embrace hydrates—on the basis of the principle of least work. His results suggested that salt solutions contain complexes of ions and water molecules. Writing about this period in his life, Kistiakovskii remarked that although it was extremely gratifying to have been heading in the right direction in connection with ionic hydration, it grieved him that he had never been able to convince his friend Arrhenius of the relevance of Mendeleev’s hydrate theory to ions (45). But curiously, even when Jones, who had worked with Arrhenius, became convinced of the relevance of solvates to electrolytes in solution, he never referred to this paper by Kistiakovskii. While it would be understandable that Jones was unaware of Kablukov’s dissertation, which was not translated from Russian into any other language, it seems implausible that he could have been unaware of a paper written in German and appearing in *Zeitschrift für physikalische Chemie*.

Kistiakovskii returned to St. Petersburg in November, 1890. Even though the attitude toward the new physical chemistry was far more conservative and critical there than it was for Kablukov in Moscow, Menshutkin formally requested the chemistry faculty to admit Kistiakovskii to prepare for the examination for the master’s degree. After a year without financial support, Kistiakovskii requested a stipend, which was denied in spite of a faculty report of his “excellent accomplishments.” He worked a second year with no financial support and passed his master’s examination in 1892. After a third such year Kistiakovskii took a position in the government’s Department of Trade and Manufacture, became a regular contributor to several popular science magazines, and began teaching physics at the St. Petersburg Women’s Gymnasium (46).

In 1896 Kistiakovskii became a privat-docent at St. Petersburg University, offering the courses “Chemical Transformations” and “Nernst’s Theory of Diffusion.” Also that year he presented his master’s thesis, “Chemical Transformation in a Homogeneous Medium at Constant Temperature,” a kinetic study of ether formation, but he was not given the opportunity to defend it. The committee of three chemists and a mathematician (47) rejected the thesis as unsuitable for a degree in chemistry. They objected to the focus on mathematical equations and the calculation of rate constants. While admitting that the thesis did “touch on the very interesting and much discussed problem of the reasons for the specific influence of an acid on the formation and decomposition of complex ethers,” the committee concluded that Kistiakovskii had not only failed to advance a solution to this problem, but had actually pushed the problem aside. Their decision stated that the thesis contained nothing new, original, or worthy of their attention (48).



An undated photograph of V. A. Kistiakovskii. Photo courtesy of LAFOKI, Russian Academy of Sciences.

In spite of this setback, Kistiakovskii continued his experimental investigations in the physics laboratory at the university. In January, 1898 he accepted a temporary appointment as laboratory assistant in chemistry, while still offering courses, including new ones in physical chemistry and electrochemistry. Over the next several years he gave up his other positions in order to spend more time on his research, apparently still with the hope of receiving a permanent place at the university. At the same time, however, he continued as an active proponent of the new physical chemistry (49). In 1901 he was invited to deliver the paper “An Analysis of the Objections to the Theory of Electrolytic Dissociation” to the Eleventh Congress of the Russian Chemical Society (50). While Kistiakovskii managed to find some allies in this area, particularly outside St. Petersburg, his advocacy of the new physical chemistry effectively excluded him from a permanent position at the university (51).

This difficult and uncertain period in his life finally came to an end in 1902 when he became laboratory assistant in chemistry at the newly created Polytechnic Institute in St. Petersburg. The following year Kistiakovskii wrote a second master’s thesis, “Physicochemical Investigations”—which contained his earlier work on ethers, as well as additional work on the elec-

trochemistry of double salts and the determination of molecular weights of liquids—and submitted it, not in St. Petersburg, but to Moscow University (52). After receiving the degree, he became Professor of Chemistry at the Polytechnic Institute, where he set up the first independent laboratory of physical chemistry and electrochemistry in Russia (53).

Because of the applied nature of the education offered at the Polytechnic Institute, Kistiakovskii's research became more directed toward practical problems in electrochemistry and metallurgy. In 1910 he successfully defended his dissertation "Electrochemical Reactions and Electrode Potentials of Various Metals" for the degree of Doctor of Chemical Sciences, also at Moscow University (54). Kistiakovskii became an important figure in the development of the Russian and Soviet physical chemistry and electrochemistry. He was a member of the Academy of Sciences of the USSR, and in 1930 he organized a laboratory of colloid electrochemistry, which became an institute of the Academy of Sciences of the USSR in 1934 (55).

Conclusion

As students in Leipzig, Kablukov and Kistiakovskii came from a scientific culture that was still moving to catch up with that of Western Europe. Original research was not a significant part of the professional life of Russian chemists before the 1860s (56). In 1861, for example, a letter from Academician C. J. Fritzsche [1808-1871] to the young Mendeleev demonstrates the attitude of at least one older Russian chemist (57):

I received a shallow education—not the sort you received. . . . I do not have the strength to catch up with you. . . . I respect, with my whole soul I respect your views, your direction. Your theoretical frame of mind sometimes is incomprehensible to me.

This transformation of Russian science to the Western research model was still incomplete in the 1870s and 1880s when Kablukov and Kistiakovskii were students.

In their student days at St. Petersburg, Kablukov and Kistiakovskii were immersed in a scientific culture in which there already was a "physical" chemistry predating the new physical chemistry that originated in Leipzig in the latter 1880s. Among Mendeleev's many interests was the application of physical methods to the study of chemical systems, and it was his density measurements on solutions over wide concentration ranges that lent support to his hydrate theory (58). Interestingly, the students from Russia brought definite ideas

about the nature of solutions with them to Leipzig, but the ideas that Kablukov and Kistiakovskii brought were not ones that appealed to the ionists. The physical theory of solution was sufficiently successful in the limited domain of dilute aqueous solutions that its proponents felt little need to re-examine their rejection of solute-solvent interactions.

In spite of their background—or because of it—students from the Russian chemical tradition would undoubtedly be seen as having inferior training in comparison to students from the West. This attitude about Russians undoubtedly extended even to Kablukov, who had spent nearly twelve years as a student of chemistry at Moscow and St. Petersburg universities before going to Ostwald's laboratory. Kablukov had considerably more experience in the study and teaching of chemistry than the typical student from the West, and he was actually two years older than Arrhenius [1859-1927] and only 4-5 years younger than Ostwald [1853-1932] and van't Hoff [1852-1911]. Nor was returning to Russia from Leipzig necessarily the end of their status as outsiders, though the ease of their reintegration into the Russian chemical community seems to have been directly proportional to their distance from St. Petersburg, the epicenter of Mendeleev's influence. In Moscow Kablukov fared rather well—he was also older and more experienced than Kistiakovskii—and he was able to use the new physical chemistry as the basis of his successful doctoral dissertation (59). Kistiakovskii was far less successful in St. Petersburg. Not only was he unable to obtain any further degrees there, but his continued advocacy of the new physical chemistry ultimately kept him from an academic appointment at the university.

As students, Kablukov and Kistiakovskii were caught between the new physical chemistry of Leipzig, which intrigued them, and the older physical chemistry of St. Petersburg, which helped mold them, but then hindered them—though to different degrees—in their subsequent careers in Russia. In Leipzig there were ions, but no hydrates; in St. Petersburg there were hydrates, but few ions. The academic niches they were able to find beyond the direct influence of St. Petersburg University enabled them to work in areas of research that capitalized on the new ideas about electrolyte solutions, but did not directly involve the fundamental issues that still needed to be resolved in order to bring dissociation theory into better agreement with experimental observations. While Harry Jones was apparently unable to accept the limited role of solvate theory in explaining the anomalies of electrolyte behavior (57), Kablukov

and Kistiakovskii spent many productive years in solving more applied problems in physical chemistry and electrochemistry and making important contributions to the development of these fields of research in Russia and the Soviet Union.

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 24. Ref. 23, pp 28-34.
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 26. I. Kablukoff, "Über die elektrische Leitfähigkeit von Chlorwasserstoff in verschiedenen Lösungsmitteln," *Z. Phys. Chem.*, **1889**, *4*, 429-434.
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 28. Ref. 27, pp 85-86.
 29. Ref. 27, p 134.
 30. I. A. Kablukov, "Istoricheskii Obzor Razvitiia Ucheniia o Nevodnykh Rastvorakh" ["Historical Survey of the Development of the Study of Nonaqueous Solutions"], in *Sbornik Trudov Pervoi Vsesoiuznoi Konferentsii po Nevodnym Rastvoram [Proceedings of the First All-Union Conference on Nonaqueous Solutions]*, Izd. Ukrainskoi Akademii Nauk, Kiev, 1935, 13-28 (17). Quoted in English by K. M. Gorbunova, L. J. Antropov, Iu. I. Solov'ev, and J. P. Stradins, "Early Electrochemistry in the USSR," in G. Dubpernell and J. H. Westbrook, Ed., *Selected Topics in the History of Electrochemistry*, Electrochemical Society, Princeton, NJ, 1977, 226-256 (235).
 31. Ref. 27, p 215.
 32. Ref. 30, Gorbunova *et al.*, p 237.
 33. Jones eventually reached the same conclusion as Kablukov. "The solvate theory of solution has been regarded in some cases as a rival of the electrolytic dissociation theory of solution, if not directly antagonistic to it. Such is not the case at all. The solvate theory begins where the theory of electrolytic dissociation ends. . . . The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution." See Ref. 13, *Chem. News*, p 126.
 34. I. Kablukov, "Sovremennaiia Teoriia Rastvorov" ["The Modern Theory of Solutions"], *Russkaia Mysl'*, **1891**, bk. 2, 208-228.
 35. Ref. 21, p 183.
 36. In anticipation of the inevitable question—yes, Vladimir Aleksandrovich Kistiakovskii and George Kistiakowsky [1900-1982] were, in fact, related. They were uncle and nephew. Vladimir Aleksandrovich's brother, Bogdan Aleksandrovich Kistiakovskii [1868-1920], was George Kistiakowsky's father. Trained in philosophy, Bogdan Aleksandrovich devoted his life to the law and sociology of the law and was a passionate advocate of "individual rights and democratic political institutions." See S. Heuman, *Kistiakovskii: The Struggle for National and Constitutional Rights in the Last Years of Tsarism*, Harvard University Press, Cambridge, MA, 1998, 1-38.
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 38. Ref. 37, pp 17-20; K. M. Gorbunova, "Akademik Vladimir Aleksandrovich Kistiakovskii, Nekrolog" ["Academician Vladimir Aleksandrovich Kistiakovskii, Obituary"], *Zh. Fiz. Khim.*, **1952**, *26*, 1717-1720 (1717); and Iu. I. Solov'ev, "O Neopublikovannoi Robote V. A. Kistiakovskogo 'Gipoteza Planka-Arreniusa'" ["On V. A. Kistiakovskii's Unpublished Work 'The Planck-Arrhenius Hypothesis'"], *Zh. Fiz. Khim.*, **1956**, *30*, 1910-1915. Kistiakovskii's dissertation is in the Archives of the Russian Academy of Sciences, fond 610, opis' 5, No. 1.
 39. Ref. 38, Solov'ev, p 1910.
 40. Ref. 37, pp 20-23.
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46. Ref. 37, pp 34-36.
47. The committee consisted of the chemists D. P. Konovalov, N. A. Menshutkin, and A. E. Favorskii and the mathematician K. A. Posse. See Ref. 37, pp 37-38.
48. Ref. 37, pp 36-40.
49. V. A. Kistiakovskii, "K Teorii Rastvorov Vant-Goffa-Arreniusa" ["On the van't Hoff-Arrhenius Theory of Solutions"], *Zh. Russ. Fiz.-Khim. Obshch., Chast' Khim.*, **1897**, 29, sect. 1, pt. 4, 286-287; V. A. Kistiakovskii, "Desiatiletie Teorii Elektroliticheskoi Dissotsiatsii" ["Tenth Anniversary of the Theory of Electrolytic Dissociation"], *Elektrotekh. Vestn.*, **1898**, _ 55, 313-316, _ 56, 349-354; V. A. Kistiakovskii, "K Ucheniiu o Rastvorakh" ["On the Study of Solutions"], *Zh. Russ. Fiz.-Khim., Chast' Fiz.*, **1898**, 30, sect. 1, pt. 6, 576-585. See A. F. Kapustinskii, *Ocherki po Istorii Neorganicheskoi i Fizicheskoi Khimii v Rossii ot Lomonosova do Velikoi Oktiabrskoi Sotsialisticheskoi Revoliutsii [Essays in the History of Inorganic and Physical Chemistry in Russia from Lomonosov to the Great October Socialist Revolution]*, Izd. Akademii Nauk SSSR, Moscow/Leningrad, 1949, 140.
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60. Ref. 9, Goldsmith, p 199.

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NIKOLAI ZININ AND SYNTHETIC DYES: THE ROAD NOT TAKEN

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During the nineteenth century and up to 1917, Russian chemists produced a significant number of “cutting-edge” advances in all branches of chemistry. Indeed, one could plausibly argue that—considering the size of the chemical community—Russian chemists were among the most productive chemists at that time. Some of these advances in chemical theory and practice produced by Russian chemists were quickly acknowledged by the international community of chemists, while others were not. In still other cases, the Russian chemists themselves did not follow up their discoveries with additional investigations. Many different factors—such as being on the scientific periphery—influenced these decisions and the reception of these discoveries.

In this paper, I will examine the scientific and cultural contexts of one of the earliest and most important discoveries by a Russian chemist during the nineteenth century: Nikolai Zinin’s reduction of nitrobenzene to produce aniline in 1842. This work done by Zinin is particularly interesting because it later became the key step in the synthesis of many coal tar dyes and was the basis for the explosion of the German chemical industry during the second half of the nineteenth century.

Zinin was well positioned to take the lead in the development of coal tar dyes. He was trained in Liebig’s laboratory and closely allied himself with Liebig’s vision of chemistry. His research interests centered on reactions of various aromatic compounds, which became important building blocks in the production of synthetic dyes. Yet Zinin did not follow up his initial discovery of 1842 with additional investigations of this reaction and he seemed oblivious to the rapid development of the synthetic dye industry during the late 1850s and

1860s. In 1867 at the Paris International Exhibition, D.I. Mendeleev reported that Zinin was astonished by the exhibitions of synthetic dyes. Why did Zinin not see the potential usefulness of his reaction and why did he not participate in the development of synthetic dyes?

Instead of Zinin, it was August Wilhelm von Hofmann, who took the lead in developing the theoretical and practical basis for the coal tar dye industry. Hofmann had also studied with Liebig during the same years that Zinin was in Giessen. Immediately after Zinin published his work, Hofmann realized the value of Zinin’s reaction and devoted much attention to understanding and developing it as a practical tool. Other chemists also studied aniline, as well as Zinin’s reaction. What was it in Zinin’s environment or background that conditioned his actions?

Nikolai Nikolaevich Zinin was born in 1812 in Shusha, a small town in the Caucasus region, where his father was serving as an officer in the Russian army (1). Shortly after Zinin’s birth, however, both of his parents died in some sort of epidemic, and he went to live with his uncle in Saratov, on the Volga River. Zinin received a good education at the local gymnasium and excelled at ancient languages, as well as mathematics and physics. Although he initially planned to attend a technical institute in St. Petersburg after graduation from the gymnasium, the death of his uncle induced him to attend Kazan’ University, which was considerably less expensive than an institution in the northern capital. Kazan’ is located on the Volga River, about 500 miles east of Moscow, and for years it was the easternmost university in Europe.

Zinin enrolled at Kazan' University in 1830, when it was slowly recovering from the deleterious effects of M.L. Magnitskii's seven-year rule as curator of the Kazan' Educational District during 1819-1826 (2). In the years before he went to Kazan', Magnitskii served as a provincial governor and had gained recognition for his attempts to cleanse the province of "atheistic influences." Upon appointment as curator, Magnitskii at first attempted to close down Kazan' University because of its atheism and immorality but grudgingly settled for dismissing those professors whose teaching Magnitskii found to be insufficiently Christian, as well as many of the foreigners who taught at the university. In 1820, Magnitskii drew up instructions that specified how professors should teach their subjects from a religious point of view. For example, professors of astronomy were to demonstrate "how the omniscience of the Creator is written in fiery letters in the heavenly bodies, and how the beautiful laws of the celestial universe were revealed to mankind in the most distant past" (3). Magnitskii's instructions were copied by other universities and led to mass dismissals at these institutions as well. However, Magnitskii and the other officials in both the central and provincial administrations who held similar values became increasingly mystical in their pronouncements of this new conservatism and finally drew opposition from the Russian Orthodox Church. In 1826, Magnitskii was dismissed and replaced as curator by M. N. Musin-Pushkin, a wealthy nobleman, whose family lived near Kazan'.

Although the traditional view claims that it took 25 years for Kazan' University to recover fully from the effects of Magnitskii, in reality, Curator Musin-Pushkin quickly acted to improve the teaching and research at the university (4). With the assistance of the mathematician Nikolai Ivanovich Lobachevskii, who was the University Rector—essentially, the university president—

the new curator secured funds to build new classrooms, laboratories, and other facilities and worked to build up the faculty ranks, which had been decimated by Magnitskii's actions (5). Zinin was a direct beneficiary of Musin-Pushkin's actions.



Zinin entered the physics-mathematics faculty as a "state student," who would receive a free education in return for agreeing to work for the Russian government for a specified period of time following graduation. This type of arrangement was vital for the state at this time because relatively few nobles, who could afford to pay tuition, entered the universities, and few of them remained until graduation. Thus when the state wanted to reduce its reliance on foreign-born professors, as it did in the 1810s and 1820s, it needed to provide support for students such as Zinin, who was not a member of the nobility. Kazan' University was in particular need of Russian profes-

sors as many of the foreign-born professors at the university had been purged during the Magnitskii years (6).

In his studies, Zinin primarily concentrated on astronomy, taught by Professor Ivan Matveevich Simonov, and mathematics, taught by Lobachevskii. As part of the requirements for students in the physics-mathematics faculty, he also took courses in chemistry from Professor Ivan Ivanovich Dunaev, who had been teaching chemistry at Kazan' University since 1811 (7). The available evidence indicates that Dunaev conducted little or no laboratory work himself and that he likely had an outdated knowledge of chemical theory. Dunaev's lectures in chemistry were presented without lecture demonstrations until 1832 when he was compelled by the university administration to introduce some demonstrations, as well as some minimal laboratory training for the students. While the premises of the chemistry laboratory were quite substandard, Professor Adol'f Iakovlevich Kupfer (who had taught at Kazan' University during the 1820s) had managed to supply it with adequate supplies and equipment (8).

Zinin graduated from Kazan' University in 1833 with a gold medal as the most outstanding student in the physics-mathematics faculty. The title of his *kandidat* [candidate's] dissertation—"Perturbations of the Elliptical Movement of the Planets"—suggests his close relationship with Simonov, the astronomy professor. Zinin's accomplishments had attracted the attention not only of his professors, but also the administration of Kazan' University, including Curator Musin-Pushkin. Following graduation, Zinin was kept on at the university for advanced training in order to prepare him for a teaching position. In 1833, Zinin was appointed "repetitor" in physics, assisting Professor Knorr, while the following year he also taught astronomy in the absence of Professor Simonov, who was conducting research away from Kazan'. Later in 1834, Zinin assisted Simonov in this research by collecting data on magnetic phenomena. Also in 1834, after the move of Professor Brashman to Moscow, Zinin also took over the teaching of hydrostatics and hydrodynamics as well as an introductory chemistry course. Thus it seems clear that Zinin was being groomed to teach physics or astronomy at Kazan' University.

However, at this time the direction of Zinin's career changed dramatically. Apparently, in 1835, the administration of Kazan' University—likely Curator Musin-Pushkin—decided that Dunaev, the professor of chemistry, needed to be replaced, and he settled on Zinin to be Dunaev's replacement (9). Zinin was relieved of his other teaching duties and was ordered to teach only chemistry "in support of Dunaev" (10). Meanwhile Zinin prepared for the extensive series of examinations for the *magistr* [master's] degree, which he passed in April 1835. The *Sovet* [Council] of the physics-mathematics faculty then gave Zinin the topic for his *magistr* dissertation: "The phenomena of Chemical Affinity and the Superiority of Berzelius's Theory about Constant Chemical Proportions over the Chemical Statics of Berthollet." Upon defending this dissertation—purely a literature investigation, with no laboratory work involved—in October 1836, Zinin received the degree *magistr* of physical-mathematical sciences. The university quickly appointed Zinin as adjunct, and in early 1837 the curator requested permission from the Ministry of Education to send Zinin abroad for two years for advanced training in chemistry.

The plan for Zinin's training abroad was drawn up by Curator Musin-Pushkin, presumably with Zinin's assistance (11). The plan called for him to attend lectures by Jöns Jacob Berzelius and Eilhard Mitscherlich,

both important chemists, but also nearing the end of their influence. Numerous other chemists were mentioned, including Liebig, but the plan indicated that Zinin would visit these chemists only for brief periods of time. Based on the information contained in this plan of study, it is likely that Zinin's conception of chemistry at this time was formed by the ideas of Berzelius, probably derived from his work on his *magistr* dissertation. It is also possible that Zinin and the university administration relied on Dunaev for information in order to draft the plan of study. The plans for Zinin's study abroad did not include any provisions for conducting original research or even any laboratory training whatsoever. This was not unusual, however, as few Russians conducted original laboratory research for a *magistr* degree until the 1850s and 1860s. The curator was mainly concerned with having Zinin learn enough while abroad to be able to teach chemistry upon his return to Kazan', and it is evident that work in the laboratory was not part of the original plan.

Zinin traveled to Berlin in September 1837 and spent the first year of his study trip there attending lectures in mathematics, physics, chemistry, and mineralogy with Heinrich Rose, Eilhard Mitscherlich, and Rudolph Fittig. Zinin was not satisfied with these lectures, though, believing them to be too elementary for him to learn much of interest (12). In addition to attending lectures, he also visited mines, factories, and various manufacturing plants near Berlin. During the spring of 1838, he traveled with some Berlin friends to various cities in Germany, intending eventually to go to Switzerland, France, and England. However, while visiting Giessen, Zinin was captivated by Liebig's lectures, and he decided to remain there until January 1839 to work with Liebig. It appears that Zinin did little laboratory research at this time since there was no room for him in Liebig's laboratory (13).

In the meantime, circumstances in Kazan' changed, which altered the objectives of Zinin's study abroad. Curator Musin-Pushkin had originally intended for Zinin to take over the teaching of chemistry from Dunaev, but in 1837—while Zinin was studying abroad—Karl Karlovich Klaus (aka. Carl Ernst Claus) moved to Kazan' (14). Klaus had worked for many years as a pharmacist in Kazan' but had given up his business in order to obtain a degree in chemistry at Dorpat University, with the goal of becoming a professor of chemistry at a Russian university. Curator Musin-Pushkin quickly recognized that Klaus could easily fill the position of chemistry professor, while Zinin could then become professor

of technology, a position that was also vacant. The curator thus arranged for Zinin to remain abroad for an additional year in order to study technology and to visit sites of industrial importance (15). Zinin did not object to this change in plans. Indeed, he submitted a detailed description of his intended activities—mainly concerning technology—if granted an extension by the Ministry of Education, perhaps because it would afford him extra time abroad and thus would enable him to spend more time in Giessen with Liebig (16).

Technology had been taught at Russian universities from the creation of the university system in the early nineteenth century. The original educational statute in 1804, which provided a blueprint for many educational developments up to 1917, included the teaching of technology at all educational levels and was greatly influenced by Marquis de Condorcet's essay on public instruction (17). For the universities, a *kafedra* (chair) of "Technology with Application to Trade and Industry" was to be included in the physics-mathematics faculty (18). This utilitarian impulse received greater emphasis during the reign of Nicholas I (1825-1855), particularly during the years when Count Sergei Semenovich Uvarov was the Minister of Education (1833-1848). Uvarov hoped to stimulate the development of agriculture and industry throughout Russia by means of instruction and public lectures, and he greatly increased the number of teaching positions and resources for technology (19). Thus Curator Musin-Pushkin was responding to this increased emphasis on technology when he decided that Zinin should occupy the *kafedra* of technology at Kazan' University instead of that of chemistry.

Ending his first stay in Giessen in January 1839, Zinin returned to Berlin to continue his studies there. However, he soon fell in with a group of Russian students, who were in Berlin studying medicine. Zinin was so influenced by these fellow Russians that he began studying medical subjects and almost decided to become a physician himself (20). This incident has drawn fleeting attention from Zinin's biographers, but they do not note its implications. It is possible that Zinin was not happy with the idea of concentrating on teaching "technology and analytical chemistry" as he was beginning to center his chemical interests on organic chemistry under Liebig's influence. Becoming a physician may have been a way for Zinin to avoid the concentration on technology. It is also possible that Zinin's attachment to any one particular field of study was not yet settled. Remember, at this time it was less than a scant four years

since Zinin had switched from astronomy and mathematics into chemistry, a move that also was not of his own choosing. Contacts with enthusiastic disciples of another field of science might have swayed Zinin's ideas about his future.

Whatever the case, Zinin did not continue with the study of medicine and instead returned to Giessen in the summer of 1839, at which time he was finally able to work in Liebig's laboratory. He focused on experiments concerning the benzoyl radical, which was one of the primary topics of interest in Liebig's laboratory at the time (21). Liebig gave Zinin the problem of obtaining benzoin, benzil, and their products, using oil of bitter almonds, which contained benzaldehyde, as the starting material. This research formed the basis for two articles published by Zinin in Liebig's *Annalen* in 1839 and 1840 (22). The first article briefly describes a new method of preparing benzoin from oil of bitter almonds with potassium cyanide as a catalyst. Zinin treated amygdalin, a glucoside of bitter almonds, with emulsin in the presence of potassium cyanide to produce a mixture of products, including benzaldehyde and benzoin. The second article gave a detailed description of this new method as well as methods for producing benzil from benzoin with nitric acid, benzoic acid from benzil, and several other products. Zinin demonstrated that one of these compounds was identical with "Benzamid" produced by Laurent. The two articles are straightforward descriptions of Zinin's methods and contain no discussion of any possible theoretical significance of the reactions.

In September 1839, Zinin left Giessen and went to Paris, where he attended lectures of Joseph Louis Gay-Lussac and Jean Baptiste André Dumas on organic chemistry and of Theophile Jules Pelouze on analytical chemistry. He was able to work in the laboratory of Pelouze, continuing his investigations of the benzoyl radical. In addition, he visited mines, factories, and other sites of interest for chemical technology. Finally, in June 1840, Zinin went to England for three weeks and then returned to Russia.

Zinin arrived in St. Petersburg in September 1840. However, instead of returning immediately to Kazan', as would be expected, he sent a letter to the Ministry of Education requesting permission "to undertake the examinations for the doctoral degree at St. Petersburg University" (23). In this petition Zinin stated that he was an adjunct of chemistry, had been sent abroad for advanced training in chemistry, had spent three years

abroad studying chemistry, had attended lectures by famous chemists, had worked in chemistry laboratories, and had published two chemistry articles. Note that this petition mentions only the field of chemistry and includes nothing about technology. The Ministry quickly gave him its approval to remain in St. Petersburg while completing the requirements for the doctoral degree, but also requested that he “hurry” in order to minimize the amount of time spent there (24). Zinin then requested permission from St. Petersburg University to begin the examinations for the doctoral degree (25).

At the same time, Curator Musin-Pushkin wrote from Kazan' to the Ministry of Education, stating that he approved Zinin's request, believing that “through an examination in the capital Mr. Zinin can prove that he satisfactorily made use of the time he spent abroad.” However, the curator also requested that Zinin remain in St. Petersburg only for the short amount of time necessary to pass the examinations for the doctoral degree: “The writing of the dissertation . . . the review of it, and, finally, the defense may better be conducted here [Kazan'], where meanwhile he would be very useful for presenting lectures in the *kafedra* of technology, which has remained unfilled for such a long time” (26).

Zinin successfully completed both oral and written examinations in chemistry and several other subjects by early November and then quickly turned to writing his dissertation (27). This dissertation, “About the Benzoyl Series and about the Discoveries of New Bodies Relating to This Series,” was completed by the end of November; but he was not able to defend it until the end of January 1841 because of a delay in the readers' reports (28). The first part of the dissertation is a theoretical discussion of organic compounds based on ideas about complex radicals and the theory of types. Next, Zinin examined the production of oil of bitter almonds from amygdalin. By analogy, he asserted that the formation of bitter almond oil occurred through the same type of process as in the formation of oil from the seeds of black mustard, thus supporting Liebig's idea of “metamorphosis” rather than Berzelius' idea of catalysis (29). The final part of the dissertation is a reworking of Zinin's two earlier papers.

In letters sent to Zinin and the Ministry of Education during the months Zinin was in St. Petersburg, Curator Musin-Pushkin urged Zinin to return to Kazan' as soon as possible. However, Zinin was not eager to return. While finishing his doctoral dissertation, he learned that the *kafedra* of chemistry at Khar'kov University

was vacant, and he wrote a petition to the Ministry of Education, asking for an appointment to that position instead of returning to Kazan' University as professor of technology. Zinin requested the move to Khar'kov because he did not want to teach technology, as is clearly shown in a letter from Curator Musin-Pushkin to the Minister of Education on December 12, 1840 (30). Musin-Pushkin noted that he was “astonished” to receive a letter from Zinin requesting permission to enter the competition for the *kafedra* of chemistry at Khar'kov University. The curator stated that, in this letter, Zinin wrote that he “does not see any use in occupying the *kafedra* of technology at Kazan' University that was intended for him.” In a letter to the Ministry, the curator strongly opposed losing Zinin to Khar'kov University (31). He argued that Zinin was sent abroad by Kazan' University for advanced training in both chemistry and technology, and he noted that the one-year extension was designed so that Zinin could concentrate exclusively on technology. The curator emphasized how much money Kazan' University had spent on Zinin's education, in addition to the cost of his time abroad. The Ministry supported the curator, and, thus, Zinin was forced to return to Kazan' in early 1841 following the defense of his dissertation in St. Petersburg.

Zinin remained at Kazan' University until 1847 when he was appointed to the *kafedra* of chemistry and physics at the Medical-Surgical Academy in St. Petersburg. Shortly after his return to Kazan' University in 1841, Zinin was elected extraordinary professor (similar to associate professor) and in 1845 ordinary professor (similar to full professor) of technology. Despite his official position as professor of technology, he spent less time teaching technology than he did other areas of chemistry although he was not able to teach organic chemistry, the subject of his research. For example, during the 1843-1844 academic year Zinin taught analytical chemistry for two hours per week and the “chemistry of living things” for two hours per week, while teaching only two courses in technology for one hour each per week. Klaus taught inorganic chemistry for three hours per week and organic chemistry (“according to Liebig”) also for three hours per week (32).

Perhaps more revealing about Zinin's attitude toward technology is his evident neglect of the technology laboratory (33). As noted above, a new chemistry laboratory had been built in the mid-1830s, and space in this new building was provided for the technology laboratory. However, Zinin did not devote much attention to equipping it. In 1844, the technology laboratory

contained only six items, valued at 310 rubles, 57 kopecks. At the same time, the chemistry laboratory contained 4,730 items valued at 6,106 rubles, 7 kopecks. Moreover, it was noted that the technology laboratory was “combined with the chemistry laboratory, due to a lack of space” (34). The items in the technology laboratory were intended not only for research in technology but mainly for demonstrations during lectures in technology. In 1845, the chemistry laboratory added equipment and glassware worth 444 rubles, 28 kopecks, while there is no record of any additions to the technology laboratory (35).

Thus it appears that Zinin had little interest in fostering the growth of technology as a subject at the university. He did not personally conduct research in technology and did not promote the subject of technology outside his lecture courses. This is in stark contrast to his successor in the *kafedra* of technology, Modest Iakovlevich Kittary, who actively worked to stimulate interest in technology by offering public lectures on various topics in technology, resuscitating the moribund Kazan’ Economic Society and making it an effective organ for publications and information, founding the Society of Young Technologists, as well as developing contacts with local factory owners and entrepreneurs. In addition, Kittary served as a consultant for several factories in Kazan’ and attended many exhibitions both in Russia and abroad (36).

While Zinin did not have much interest in technology, he did continue his research in organic chemistry. This was fairly unusual for chemistry professors in Russia during the first half of the nineteenth century, even for those who studied with Liebig. Most conducted some research for their doctoral dissertations but little or no research after that. They were mainly concerned with building a “local” reputation as this would help gain them promotions and other types of honors, such as bureaucratic awards, which were coveted in Russia (37). Most chemists during these years were active in the affairs of their university and also served on committees for various government agencies or, much more rarely, acted as consultants for private companies. Zinin, however, did not pursue such committee assignments or consulting work while he was in Kazan’. The archival record indicates only one instance of his doing such a “local” activity during his years in Kazan’; he performed a chemical analysis of an ore sample at the request of a government agency (38). While it is possible that Zinin did not have the opportunity to undertake many such activities during his years in Kazan’, I believe it is more likely

that he chose not to pursue them. Instead, he concentrated on his research in organic chemistry, perhaps in hopes of building a scientific reputation that would allow him eventually to move to a different institution where he could concentrate on teaching chemistry and not technology. Even though his scientific output was modest during these years, it was sufficiently unusual and impressive to help him win the position of professor of chemistry and physics at the Medical-Surgical Academy in St. Petersburg in a competition with other chemists, including another student of Liebig.

It was during Zinin’s few years in Kazan’ that he completed his most famous work, the reduction of nitrobenzene to aniline. When Zinin returned to Kazan’ following his study trip abroad, he was faced with the problem of selecting a new research problem. His work in Liebig’s laboratory had utilized oil of bitter almonds as a starting material, as had a considerable amount of the work in Liebig’s laboratory during the late 1830s. However, Zinin was not able to continue using this substance upon his return because its import into Russia was prohibited since it contained small amounts of hydrogen cyanide and, thus, was potentially very toxic. Instead, he decided to investigate the action of hydrogen sulfide on a series of organic compounds closely related to oil of bitter almonds, first studying nitrobenzene and nitronaphthalene. In this work Zinin found that the two oxygen atoms of the nitro group are replaced by two atoms of hydrogen (39). Zinin himself named the reaction products (Benzid and Naphthalid, respectively), but Iulii Fedorovich Fritzsche (also known as C. J. Fritzsche), chemistry academician at the Academy of Sciences in St. Petersburg, soon noted that Benzid was identical to Anilin (40). Fritzsche had obtained aniline in 1840 by the decomposition of indigo.

The significance of this reaction soon became apparent. At the same time as Zinin was investigating this reaction, A.W. von Hofmann and several others began the difficult process of unraveling the constitution of coal tar. Continuing this work when he moved to London in 1845, Hofmann, together with his students, isolated twenty or so basic substances that became the foundation of the coal-tar dye industry. Zinin’s work on the reduction of nitrobenzene to aniline provided a key step in the production of various coal-tar dyes. In an obituary of Zinin written in 1880, Hofmann stated that “[i]f Zinin had done nothing more than to convert nitrobenzene to aniline, even then his name should be inscribed in gold letters in the history of chemistry”(41).

Zinin described his continuing investigation of methods to produce different aromatic amines in two papers in 1844 and 1845, his last publications before he left Kazan' University (42). The first paper examines the use of ammonium sulfide to form diaminobenzene from dinitrobenzene, and likewise for the analogous naphthalene compounds. In the second work Zinin described a method to produce benzidine from azobenzene and a method to produce azoxybenzene from nitrobenzene. To produce benzidine Zinin reduced azobenzene with ammonium sulfide, then treated the product with weak sulfuric acid. He showed that hydrazobenzene was formed from azoxybenzene, and then in the presence of acid it underwent a rearrangement to form benzidine. As in his earlier papers, Zinin did not include any discussion of possible theoretical significance for this work.

In 1847, Zinin learned that the *kafedra* of chemistry and physics at the Medical-Surgical Academy in St. Petersburg was vacant. An old friend of Zinin's, Professor P. A. Dubovitskii, who taught at the Medical-Surgical Academy and at that time was its secretary, urged Zinin to submit his name as a candidate for this position (43). At about this same time, Zinin delivered a public lecture at Kazan' University titled "A View of the Current Direction of Organic Chemistry" (44). In this speech, Zinin did not discuss his current work in organic chemistry or related studies but focused, instead, on two main themes. The first and main theme concerned the importance of organic chemistry for understanding the physiology of plants and animals. Zinin closely followed Liebig's ideas, particularly from *Chemistry and its Applications to Agriculture* (1840) and *Animal Chemistry* (1842), although he did not emphasize that fact. The other theme in this speech was a strong critique of *Naturphilosophie* and similar trends, which were grouped by Zinin with astrology and alchemy as not being scientific methods of analysis. In addition to being valuable as a reflection of his ideas at that time, this speech likely was connected to his attempt to obtain the position at the Medical-Surgical Academy. During his years in Kazan', Zinin had shown little interest in research on questions concerning physiology or agriculture although he did sometimes teach a course about physiology. Perhaps this public lecture was a way for him to indicate his acquaintance with the topics that he would be responsible for teaching at the Medical-Surgical Academy.

Apparently, Zinin did enter the competition for the position at the Medical-Surgical Academy since on Oc-

tober 20, 1847, the War Minister sent a petition to the Minister of Education stating that Zinin had been elected as ordinary professor of chemistry and physics at the Medical-Surgical Academy. The War Minister requested that Zinin be transferred to the authority of the War Ministry (45). However, the Minister of Education did not want to allow this transfer and used almost the same language in his reply that the curator had used in 1840 to thwart Zinin's move to Khar'kov University (46). When he found out about the decision of the Academy, Zinin quickly petitioned the rector of Kazan' University about a transfer to the War Ministry. His petition made it clear that his main reason for requesting this move was his desire to teach pure chemistry and not technology (47):

Your Excellency knows that I have devoted many years to the study of chemistry and the natural sciences necessary for a full understanding of this branch of knowledge. The duties of the *kafedra* of technology have diverted me particularly from laboratory work in chemistry, which has more affinity to my knowledge and abilities [than technology]. In addition, the Kazan' climate and provincial conditions of life have for some time been causing problems for my health. For these reasons and mainly from the desire for the opportunity to use my abilities for the benefit of society and science, I humbly request that Your Excellency petition the higher authorities to transfer me to service at the Medical-Surgical Academy.

Again, Zinin's request was not granted. This put him in an extremely difficult position. In order to leave Kazan' and finally shed his position as professor of technology, he would need to find some way to get around the refusal of the Ministry of Education to agree to his transfer to the War Ministry. Zinin finally resolved to request that he be released entirely from service in the Ministry of Education, and the Minister had little choice but to grant it (48). The Medical-Surgical Academy then again elected Zinin as ordinary professor of chemistry and physics, and the War Minister ratified the decision (49). At long last, Zinin could escape Kazan' and jettison the unwanted position as professor of technology.

After a period of scientific inactivity following his move to St. Petersburg, Zinin resumed his research by returning to materials that he had studied previously. In 1852, he published articles concerning the production of mustard oil, and in 1854 he studied the concept of substitution in organic compounds using mustard oil as a starting material. Later, he continued his work on reactions involving benzil, benzoin, and other substances.

In the 1860s, he was able to convince the Russian customs officials to provide him with samples of bitter almond oil that had been confiscated at the border. He then returned to the topic of his earliest studies, examining the processes of oxidation and reduction in various aromatic compounds in more detail, despite the fact that this was far from the cutting edge in current research, as Butlerov lamented in his obituary of Zinin (50). In the 1870s, Zinin branched out to study the compound lepidene, which later was determined to be tetraphenylfuran. Over the course of several years Zinin studied various reactions using lepidene, carefully separating the different isomers formed in the reactions. Soviet historians of chemistry credit Zinin with stimulating the study of hetrocyclic chemistry in Russia (51).

This brief outline of Zinin's life and career illustrates several general points about the history of chemistry in Russia during the nineteenth century as well as aspects specifically about Zinin himself. The most important thread running through his career was his embrace of "pure" chemistry and his avoidance of applied or technical chemistry. Zinin's biography suggests some possible reasons for his attitude. We remember that Zinin studied mainly astronomy and mathematics as an undergraduate student at Kazan' University, and he obviously intended to pursue these fields in his graduate training. He taught these subjects and assisted the astronomy professor in his research. He apparently had no desire to focus on chemistry until Curator Musin-Pushkin decided that the incumbent chemistry professor was incompetent and needed to be replaced. Since there were extremely few Russian students willing and able to pursue advanced training during the first half of the nineteenth century, the curator had little choice but to select Zinin to be the future chemistry professor. Zinin himself had little choice in the matter. Like so many Russian students during the first half of the nineteenth century, he was not from the elite nobility and had scant opportunities for advancement outside an academic career. The administration officials at Kazan' University selected the topic of Zinin's *magistr* dissertation, and they also drafted his plan for study abroad.

While Zinin sincerely enjoyed studying science, it is not certain that he wanted to devote himself to chemistry at this time. To me, this is the implication of the episode during his study abroad when—under the influence of fellow Russian students in Berlin who were studying medicine—he abandoned his study of chemistry and turned to medicine. Returning to the study of chemistry after a short interlude, Zinin soon decisively

embraced chemistry under Liebig's influence. Thus it must have been especially difficult for him to accept the switch to studying technology as demanded by Curator Musin-Pushkin. Again, Zinin had little choice in the matter, and he likely went along with the plan because it gave him an extra year of research abroad and because the new plan did not significantly alter his intended path of study. He displayed his feelings about having to teach technology, however, when, in 1840, he tried to obtain the position in chemistry at Khar'kov University instead of returning to Kazan' University to teach technology. After being frustrated in this attempt, he reluctantly returned to Kazan', but once there he devoted little attention to teaching technology or conducting any research with applications to technology. Moreover, Zinin fled Kazan' at the first opportunity to take a position at the Medical-Surgical Academy in St. Petersburg.

On the basis of these experiences, it is easy to see why Zinin did not devote more attention to the possible applications of his research in industry or agriculture. This neglect of practical applications is perhaps surprising in such a devoted follower of Liebig. Zinin not only adopted Liebig's ideas about complex radicals, which guided much of Zinin's research throughout his career, but he also supported many of Liebig's teachings outside of "pure" chemistry, as was shown in the public lecture given by Zinin in 1847. However, despite his evident attachment to Liebig, the Russian adopted only the "theoretical" side of Liebig's ideas as a guide to his research and not the "practical" side. The efforts of Kittary, Zinin's successor in technology at Kazan' University, show that ample opportunities existed there to promote technology.

Thus, when Zinin discovered an easy method to reduce nitrobenzene to aniline in 1842, he did not follow up this work with further investigations and did not explore the possibility of industrial or commercial uses for this reaction. Instead, it was Hofmann who seized upon Zinin's initial insight and developed its practical uses. Zinin was not the first to obtain aniline; several others had obtained it as early as 1826 by alternative methods. Aniline was originally discovered by Otto Unverdorben (as "Crystallin"), and it was subsequently obtained from coal tar in 1834 by Friedlieb Ferdinand Runge (as "Kyanol") and from the decomposition of indigo in 1840 by Fritzsche (as "Anilin"). Note, however, that each researcher gave a different name to the product, which obscured its identity. Not until 1843 did Hofmann demonstrate that all of these products were identical. Auguste Laurent was also interested in these

products, and in 1843, in collaboration with Hofmann, he managed to convert phenol into aniline (52). It is clear that aniline and its related compounds were important and active areas of chemical research at the time when Zinin developed his method for preparing aniline that was far simpler and of greater potential use than any of the earlier methods.

Zinin's aversion to the practical uses of his research was also a common feature of Russian chemistry during the nineteenth century. Very few Russian chemists had much contact with industrialists, and only a small number of Russian chemists were employed in the domestic chemical industry throughout the nineteenth century. The reasons for this lack of contact are not clear although it resulted partly from the emphasis on theory in the academic culture in Russia and partly from the insular nature of the Russian industrialists (53). In addition, Homburg's argument that the key players in the early development of the dye industry were the colorists and not the academic chemists indicates that we should not have expected Zinin to develop his discovery into a practical method for the dye industry (54).

On the other hand, some chemists in Russia—especially during the first half of the century—devoted a considerable amount of time to “practical” activities, such as serving as technical consultants for governmental agencies. These practical activities had little to do with direct industrial applications and were mainly pursued to gain the chemists a “local” reputation. As noted above, while he was in Kazan', Zinin did not have contacts with industrialists and did not undertake practical activities. However, this is in marked contrast to the years after he moved to St. Petersburg when he actively pursued these types of local activities. For example, during his first four years in the capital, he served as a member of the Manufacturing Council of the Ministry of Finance, traveled to the Caucasus region to study mineral water for the Ministry of Finance, served on the commission to build St. Isaac's Cathedral, and was the secretary of the Mineralogical Conference, among other activities. He continued his involvement in a wide range of committees and other assignments until his death (55).

This involvement in local, practical activities after his move to St. Petersburg helps explain, I believe, another facet of Zinin's scientific career. Despite his impressive research, especially that conducted while in Kazan', Zinin remained rooted in the “local” tradition of chemistry in Russia, not in the later “professional”

tradition. This was in contrast, for example, to Aleksandr Mikhailovich Butlerov, who in the late 1850s became one of the first professionalized Russian chemists (56). With this traditional outlook Zinin did not develop a strong interest in chemical theory and thus did not grasp the theoretical implications of his 1841 discovery. Hofmann, on the other hand, used Zinin's work as a key initial part of his far-reaching development of the chemistry of amines and his formulation of the ammonia type (57).

Zinin's work with aniline was not his only brush with a potentially useful compound. In 1853 Zinin conducted research on nitroglycerin as an explosive agent but did not publish this work nor follow it up. Shortly after this, another Russian began studies on large amounts of nitroglycerin. However, it was left to Alfred Nobel to transform nitroglycerin into dynamite and develop large-scale methods for its manufacture, as well as for blasting caps and other associated products. And how did Nobel learn about nitroglycerin? He learned about it from Zinin, who taught chemistry to Nobel in the 1850s.

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THE BEGINNINGS OF SYNTHETIC ORGANIC CHEMISTRY: ZINC ALKYLs AND THE KAZAN' SCHOOL

David E. Lewis, University of Wisconsin-Eau Claire

It is scant exaggeration to say that modern organic synthesis would be almost inconceivable without the important carbon-carbon bond-forming reactions involving the addition of organometallic reagents to aldehydes, ketones and acid derivatives. Today, the addition reactions of organometallic reagents of most elements of the periodic table have been explored in great detail, permitting the synthetic organic chemist to exploit the unique reactivity of the alkyl derivatives of many elements of the periodic table to obtain that degree of control that gives modern organic synthesis much of its power.

The rise of organometallic compounds as tools in organic synthesis is probably best traced to the development of the Grignard addition reaction in 1900 (1), but the real origins of organometallic synthesis date from some 30 years earlier in the city of Kazan', at European Russia's eastern frontier. The position of Kazan' at the crossroads between east and west had long been exploited in the name of trade. Its transformation to an educational center only began with the establishment of Kazan' University in 1804 at the urging of the intellectuals in St. Petersburg (with little enthusiastic support from the Kazan' community). Despite its isolation and its location at the fringe of society, Kazan' University had, by the end of the nineteenth century, established a school of chemistry that was pre-eminent in Russia, supplying many department chairs and professors of chemistry to Russian and foreign universities.

The two decades following Wöhler's 1828 discovery of the synthetic production of urea (2) were watershed years in the development of organic chemistry.

During the 1830s and 1840s the concept of the radical as an entity, which passed through chemical transformations unaltered, was established, thanks to the work of Liebig, Wöhler, Bunsen, and Dumas. Then, in 1852, Sir Edward Frankland published the paper in which he proposed that elements have a set saturation capacity—the first proposal of the concept of valence (3). In the course of this work, Frankland had synthesized the first organometallic compounds, the dialkylzincs (3), an achievement of crucial importance to the work that comprises the subject of this paper.

Thus, by the mid-1850s, the stage was set for the next great advance in the discipline of organic chemistry, and the last three years of the 1850's may, indeed, be characterized as a nexus in the development of organic chemistry. It was during these years that Friedrich August Kekulé and Archibald Scott Couper developed what has become known as the structural theory of organic chemistry. On the basis of the earlier work of Frankland and Kolbe, in which the concept of valence had been placed on a firm footing, Kekulé (4) and Couper (5) independently developed the concept of a compound as a material in which all valences of all participating atoms could be satisfied.

It is almost certain that this theory, as first proposed, was largely designed to accommodate the known facts; whether either Kekulé or Couper was completely aware, when he first proposed it, of the real potential of this new theory may be argued (6). This author contends that the full realization of what this new theory could do belonged first to the great Russian organic chemist, Aleksandr Mikhailovich Butlerov (1828-1886). It was

certainly Butlerov, who was a professor at Kazan' University at the time, and his students who first followed up experimentally on the predictive power of the new theory.

By this time, the Chemistry Department at Kazan' had already begun its rise under Nikolai Nikolaevich Zinin (1812-1880) and Karl Karlovich Klaus



A. M. Butlerov (1828-1886)

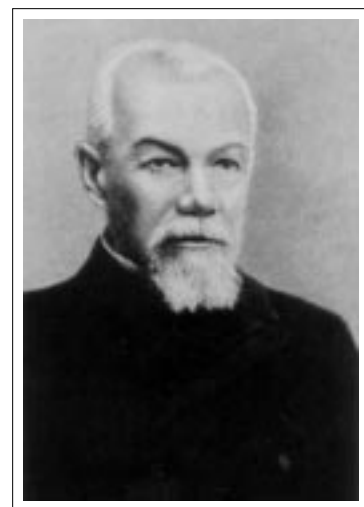
(1796-1864), whose contributions to chemistry have often been overshadowed by those of his more famous colleague. Butlerov had studied under both Zinin and Klaus, but his commitment to a career in chemistry at the time may have been marginal, at best (7). In fact, he had written his kandidat dissertation on the diurnal butterflies of the Volga region (8). However, with the departure of Zinin for St. Petersburg and Klaus for Dorpat, Kazan' University needed an instructor in chemistry, and Butlerov was appointed to the position, ultimately succeeding Klaus as Chair at Kazan'. The move was a fortunate one for Russian organic chemistry, for Butlerov became one of Russia's greatest organic chemists. Butlerov spent the years following his return in 1858 from a *komandirovka* (salaried study abroad) in Western Europe in developing and testing his own version of structural theory. It was Butlerov who first coined the term "chemical structure" and used that concept to systematize chemists' thinking about compounds. By 1860 he was expounding his structural theory of organic chemistry in his classes, and his textbook (9) was the first based solely on structural theory.

Butlerov saw that the wider acceptance of structural theory would depend in part on its ability to predict new isomers of organic compounds and on the experimental confirmation of the existence of these new isomers by synthesis, as he stated explicitly in his presentation to the Speyer Congress on September 19, 1861 (10). He immediately began using the theory first to predict the number of isomers of simple organic compounds and then to attempt the synthesis of these compounds. It is perhaps fitting, therefore, that Butlerov should have been among the first to confirm predictions

of the existence of new compounds by synthesis. It is uncertain how the possibility of the double displacement reaction between a dialkylzinc and an acid chloride occurred to him; but in his Speyer presentation on structural theory he explicitly mentioned the reaction between ethylsodium and carbon dioxide to form propionic acid, which had been reported by Wanklyn in 1858 (11). For whatever reason, in 1863 he took the step of treating phosgene with diethylzinc (12). The result was both historic, this being the first synthesis of a tertiary alcohol, and ironic. The existence of tertiary alcohols had been predicted by Kolbe (13), the most adamant opponent of the new structural theory, and this first synthesis was accomplished by Butlerov, its most ardent champion. This reaction, which he subsequently expanded into a general method for the synthesis of tertiary alcohols by the reaction between a dialkylzinc and an acid chloride, became known as the Butlerov reaction. Butlerov continued his research into tertiary alcohols and their dehydration products after his move to St. Petersburg in 1869, taking with him a tradition of organic synthesis begun at Kazan'.

Butlerov was succeeded at Kazan' by two of his students, Aleksandr Mikhailovich Zaitsev (1841-1910) and Vladimir Vasil'evich Markovnikov (1838-1904). Both had come to Kazan' University as students in economic science at a time when all students in that subject (*kameralisty*, many of whom were training for bureaucratic jobs in government) were required to complete two years of chemistry. This requirement thus brought them into contact with Butlerov, who was a dynamic and inspiring lecturer; both young men fell under the master's spell.

Butlerov may well have seen that the strengths of the two young men were complementary. Markovnikov was a daring and brilliant theoretician whose master's dissertation on structural theory (14) broached ideas that became widely accepted only decades later. Zaitsev, on the other hand, was a superb experimen-



A. M. Zaitsev (1849-1910)

talist, as his record plainly shows. As a student under Kolbe at Marburg, he had completed the first synthesis and characterization of a sulfoxide (15). He also accomplished the first synthesis of a sulfonium salt (16) and worked in Wurtz' laboratory on problems in carboxylic acid chemistry. Both Zaitsev and



V. V. Markovnikov (1838-1904)

and Markovnikov graduated in the *kameral* division.

At this time, graduates from the *kameral* division were not considered the equal of graduates in the physical-mathematical division when it came to assigning laboratory assistantships in chemistry. Zaitsev and Markovnikov are among the group of brilliant chemists whose graduation in the *kameral* division and desire for further study in chemistry resulted in a re-evaluation of this status; Butlerov helped to promote this agenda.

Despite what one might expect from their common admiration of Butlerov and the common path of their early careers (both worked under Butlerov and Kolbe, and both began their independent careers as extraordinary professors at Kazan'), Zaitsev and Markovnikov feuded bitterly for much of their lives. Indeed, Zaitsev's appointment to the second chair of chemistry as Markovnikov's junior colleague in 1870 may have been one of the minor precipitating factors in Markovnikov's rancorous departure from Kazan' shortly thereafter. (It should be noted that Markovnikov had been one of the official examiners of Zaitsev's master's dissertation and had written a report which, while overtly positive, carried a strongly negative subliminal message.)

One may speculate on the origins of this feud, but it is my opinion that one major contributing factor may be traced to the time both spent in Kolbe's laboratory. In the *kandidat* dissertation that Zaitsev submitted to Kazan' University in 1863, he had shown himself willing to compromise with Kolbe (17), who vigorously opposed structural theory. In contrast, Markovnikov remained inflexibly in the structural theory camp. Zaitsev's pliability may have seemed a betrayal of the "Russian" position to the intensely Russian nationalist, Markovnikov—an unpardonable sin.

At Kazan', Zaitsev continued the line of research into the reactions of dialkylzincs begun by Butlerov, and the credit for developing and extending the scope of this synthetic method really belongs to Zaitsev and his students. In 1865 Frankland and Duppa reported the reaction between diethylzinc and diethyl oxalate to give the ethyl ester of α -ethyl- α -hydroxybutyric acid (18). Much of Zaitsev's earliest work as an independent researcher involved extending the Butlerov reaction to include the interaction of organozinc compounds with other carbonyl compounds. Of greater importance, perhaps, was his insight that the notoriously sensitive dialkylzinc reagents could be replaced by a mixture of the alkyl iodide and zinc metal. This *in situ* formation of the alkylzinc iodide allowed much greater flexibility and ultimately led to the development of the Grignard reaction.

This new, general synthesis of tertiary alcohols was later extended by Zaitsev and his students to reactions between organozinc reagents and a variety of compounds. The co-author on many of these early works was another of the brilliant organic chemists to come from the Kazan' school: Egor Egorevich Vagner (1849-1903), who later became Professor of Chemistry at the University of Warsaw. Better known in the west as Georg Wagner, the terpene chemist, Vagner had entered Kazan' as a student in law, where he came under the influence of Zaitsev as his mentor had come under the influence of Butlerov when he himself had entered as a student in economic science. By the time Vagner was a student, the two-year chemistry requirement of graduates in the *kameral* division was no longer in force. However, like his own mentor, Zaitsev had an excellent reputation among his students, and it is not unreasonable to speculate that *kameral* students at Kazan' may well have passed along to incoming students their opinion that Zaitsev's lectures were worth attending. (Even today, it



E. E. Vagner (1849-1903)

is not uncommon for the student “underground” to recommend certain professors to students fulfilling science requirements in a nonscience major).

Zaitsev’s development of organozinc synthesis proceeded apace during the 1870s and 1880s. Under his direction, Vagner developed a general synthesis of symmetrical secondary alcohols from the interaction of ethyl formate with dialkylzincs (19). With his student I. I. Kanonnikov, Zaitsev extended the synthesis to the reaction between zinc and formate esters in the presence of a mixture of alkyl halides to give unsymmetrical secondary alcohols (20). He continued his work on the synthesis of unsymmetrical tertiary alcohols by exploring the reaction between alkylzinc halides and ketones (21). It was during this work that Zaitsev discovered, with his student D. Ustinov, that the reaction between the propylzinc reagent and 4-heptanone gave not the expected tertiary alcohol, but the reduction product, 4-heptanol (22). During this same period, Zaitsev’s brother and student, Mikhail Mikhailovich, studied the reaction between alkylzinc halides and anhydrides, which leads to the formation of ketones (23).

In 1875 Vagner was sent on a *komandirovka* at St. Petersburg to study directly under Butlerov, a move encouraged by Zaitsev despite the impact on his own research group of losing such a talented student. Continuing his study of alkylzinc halides, Vagner extended the Zaitsev synthesis to the addition of alkylzinc halides to aldehydes, thus developing a general synthesis of unsymmetrical secondary alcohols (24). This general synthesis of alcohols from alkylzinc halides and carbonyl compounds is generally referred to as the Zaitsev-Vagner synthesis. One of the more noteworthy features of the Zaitsev-Vagner synthesis is the success with which it yields alcohols from allylic halides. The formation of Grignard reagents from allylic halides is often problematic because of the facile coupling of the alkyl groups by S_N2 displacement of the halide from a second molecule of the allyl halide by the already-formed allylmagnesium halide. This cross-coupling reaction is much less a problem in the reactions of the less nucleophilic alkylzinc reagents.



S. N. Reformatskii (1860-1934)

Kazan’ and Zaitsev were fortunate that Vagner’s departure was followed fairly rapidly by the emergence of the next synthetic organic chemist from the “nursery” at Kazan’: Sergei Nikolaevich Reformatskii (1860-1934), who later became Professor of Chemistry at Kiev University. The son of a pastor, Reformatskii had been expected to enter the priesthood; but on graduation from the Kostroma Spiritual Seminary he entered Kazan’ University and instead encountered Zaitsev. Following his graduation with the gold medal in 1882, Reformatskii remained at Kazan’ and eventually began working on the reaction that bears his name, publishing the first paper in 1887 after he had become Privatdozent at Kazan’. It may well be that the successes obtained by using unsaturated, allylic alkyl halides suggested an extension of the Zaitsev-Vagner synthesis to α -haloesters in place of the allylic halides. The substitution was successful, and Reformatskii published what became the most enduring of the synthetic methods based on zinc alkyls (25). For the better part of a century the Reformatskii reaction was the method of choice for the synthesis of β -hydroxy carbonyl compounds until the design of elegantly controlled aldol additions in the 1980s.

The development of the Grignard synthesis just over a decade after Reformatskii’s first publication spelled the end of most organozinc syntheses of alcohols. The final paper to emerge from Kazan’ on the synthesis of alcohols from alkylzinc reagents (26) was a one by another Zaitsev student, Aleksandr Erminingel’ovich Arbuzov (1877-1968), who succeeded Zaitsev at Kazan’ and was to achieve international stature for his pioneering work with organophosphorus chemistry. The greater ease of formation and use of the Grignard reagent made it generally superior to the corresponding zinc reagent, especially in the hands of less experienced chemists. The very dominance of the Grignard reagent after 1900, however, pays silent testimony to the experimental ability of the Kazan’ chemists, who were able to use organozinc reagents to prepare alcohols with such success. Even so, the final chapter of the organozinc story may not yet have been written, for in the early 1980s, Noyori ob-



A. E. Arbuzov (1877-1968)

served that—in contrast to the Grignard reagents—dialkylzincs are amenable to asymmetric addition to aldehydes in the presence of a chiral dialkylaminoalcohol catalyst to give secondary alcohols with high levels of asymmetric induction (27).

In conclusion, it is no exaggeration to assert that modern organic synthesis would be inconceivable without the formation of carbon-carbon bonds by the reaction between an organometallic reagent and a carbonyl compound. Thus, modern organic synthesis owes a great debt, seldom acknowledged, to the chemists at Kazan' University and their pioneering chemistry with zinc alkyls.

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CUTTING-EDGE CHEMISTRY: SOME 19TH - CENTURY RUSSIAN CONTRIBUTIONS. A COMMENTARY

Seymour H. Mauskopf, Duke University

The Nature of Scientific Discovery

[M. Kaji, "D. I. Mendeleev and the Concept of Chemical Elements"]

This presentation follows the "classic" paper of Bensaude-Vincent (1) rather closely, but with some additional points and emendations to her argument. One of the first points Kaji makes—that Mendeleev was ambivalent about the status of the atomic theory—can be related to what Bensaude-Vincent delineates as the "strict positivist tradition" to which he belonged. Kaji, however, give this philosophical context concrete scientific grounding in his reference to Mendeleev's interest in so-called "indefinite compounds" (solutions, alloys, silicates, etc.).

In the same and following sections Kaji explores the relationship of the writing of the textbook, *The Principles of Chemistry*, and the discovery of the periodic law. Here Kaji appears to emend Bensaude-Vincent most fundamentally. She was at pains to dispel the "myth of a sudden discovery," stressing that the genesis of the concept of the periodic law for Mendeleev was a slow one, going back to ca. 1860. As a kind of indirect evidence, she analyzed the structure of *Principles*, suggesting that its odd structure, with the setting forth of the periodic law deep into the work (at the end of the first part) was, in fact, in line with Mendeleev's pedagogical aims of moving from concrete chemical facts to the more abstract conception of elements arranged in the periodic table. She noted that the first part moved successively through consideration of water, air, carbon

compounds, and common salt. The elements involved here (H, O, N, C, S, Cl) were to be heads of groups in the periodic table (with the exception of S). But S and Cl set the stage for what became systematic presentations pointing towards the periodic table: of the halogens, alkali metals, and alkaline earths. Then came the climactic presentation of the periodic law.

By contrast, Kaji at least implies something of a sudden discovery of this law and claims that one can see "when" it occurred through inspection of *Principles*. Examining the same first part of the textbook as Bensaude-Vincent, Kaji finds that the foci of the first part illustrate a pre-periodic conception of chemical "element" based upon *valency*. It was precisely at a particular point in the textbook (the chapter on heat capacity) that a disjunction occurred, with the discovery of the periodic law and the new conception of chemical element based on *atomic weight* and not on valency.

Continuing his analysis of the textbook (diachronically now), Kaji emends another assertion of Bensaude-Vincent: that Mendeleev never changed the presentation of his textbook. Kaji shows that extensive changes were made over the eight editions; however, he fails to make clear what the format for the first edition was. In his enumeration, the third edition (1877) seems to correspond most closely with his earlier outline of the work's structure

Despite these emendations to Bensaude-Vincent's analysis, there are fundamental agreements, most notably over Mendeleev's mature notion of elements as unchangeable entities, defined by atomic weight.

Science Across the Borders: National Patronage and Tradition vs. International Scientific Transfer

[R. E. Rice, "Hydrating Ions in St. Petersburg and Moscow; Ignoring Them in Leipzig and Baltimore"]

This paper deals with the reception of physical chemistry in Russia (or better, perhaps, the interaction between German and Russian theories of solution). Specifically, Rice recounts the vicissitudes faced by two Russian chemists, Kablukov and Kistiakovskii, in their espousal of physical chemistry, generally, and their attempts to reconcile the ionic theory and hydrate theory of solution. Regarding the latter, Mendeleev, who first set forth such a theory in Russia, plays as central (if more indirect) a role in Rice's paper as he does in Kaji's paper. Certainly Kablukov and perhaps Kistiakovskii (it is not clear from the paper) first become interested in the hydrate theory solution under Mendeleev's influence while studying at St. Petersburg University. Both also became enthusiasts for physical chemistry generally and arrange to take study leaves in Leipzig.

Upon their return to Russia, their stories diverge. Kablukov went back to Moscow University, where he was able to defend a dissertation, which Rice characterizes as "the first systematic discussion of the new physical chemistry in Russia." In it (and in his physical chemistry textbook of 1902), Kablukov suggested that the ion and hydrate theories of solution could be reconciled; however, he never produced the synthetic theory.

Kistiakovskii, who seems to have been much more determined to produce a synthetic theoretical explanation of solution than Kablukov, encountered great hostility toward physical chemistry in St. Petersburg and was effectively blocked from pursuing physical chemistry towards a degree or carrying out research there. There were clearly important local differences in attitudes towards physical chemistry in Moscow and St. Petersburg universities, which would merit some discussion. In particular, what role did Mendeleev play in all of this at St. Petersburg?

What does come clear is that, despite the efforts of two talented young chemists, physical chemistry did not readily take root and flourish in Russia. It would be interesting to compare and contrast its development in other "peripheries," such as the United States, for which we have an authoritative study by John Servos. In the

US, there was much more receptivity because there was no equivalent of Mendeleev with an anti-ionic theory of solution, and because there was an industrial "market" for chemists trained in physical chemistry.

Chemistry and Industrial Context: Issues of Pure vs. Applied Chemistry

[N. M. Brooks, "Nikolai Zinin and Synthetic Dyes: The Road not Taken"]

This paper, as well as that by Lewis, deals with aspects of the important 19th-century chemical "school" at the University of Kazan'. In Brooks' paper a number of characteristics of Russian chemistry are highlighted: the role of state administrators in determining what kind of academic career a would-be scientist will have (and where it would be); the tradition of the fixed-term study leave for dissertation research in a western European center of scientific activity; and, most important of all, the attitude towards practical chemistry. Brooks' thesis seems to be that "Zinin's aversion to the practical use of his research" inhibited his development of work on the reduction of nitrobenzene to aniline into a broader program on aniline chemistry for industrial uses, as Hofmann was to do in the 1840s and 1850s. I am not completely convinced of this thesis, at least as sketched out here; it was, after all, quite some time—some 13 years—after Hofmann initiated his work on coal tar chemistry that the first aniline dye was produced. But if Brooks is correct that the aversion to practical chemistry was "a common feature of much Russian chemistry during the nineteenth century," it might well tie into Rice's story about physical chemistry, which could also be styled "the road not taken." Namely, both Brooks' thesis about the anti-practical orientation of Russian chemistry and Rice's about the lack of receptivity of physical chemistry in Russia may have wider industrial contexts (or, better, lack thereof).

This, in turn, impels me to call for more information on one point of Zinin's career highlighted in this paper: his assignment to the *kafedra* of technology at the University of Kazan' at the behest of the Curator of the Kazan' Education District, Count Musin-Pushkin. How did the position come about? About what was the professor expected to teach? How did he interact with the extra-university commercial and industrial sectors, and were these private or state-owned and operated?

The Nature of Research Programs

[D. E. Lewis, "The Beginnings of Synthetic Organic Chemistry: Zinc Alkyls and the Kazan' School"]

This paper is perhaps the closest exemplar of the theme of this session. Lewis delineates a clear-cut (and very distinguished) Kazan' research tradition, originating, perhaps, with Zinin, but getting its main impetus from Butlerov: the synthesis of alcohols from alkylzinc reagents. On the chemistry itself, I have nothing to add. But I do have questions concerning some of the contextual issues—issues common to some of the other papers as well.

The first and most obvious is the University of Kazan' itself. Both Lewis and Brooks emphasize its "fringe" location as "the easternmost university in Europe." Yet, early in the century, it had had Lobachevskii in mathematics and in the second half, the distinguished sequence of chemists whose work is detailed in Lewis' paper. My question is why: Was the success in the sciences here explicable simply in terms of fortuitously lucky interpersonal interactions, or should we also look for other reasons? A possible one (just from the inspection of Lewis' paper) concerns the place of chemistry in the curriculum at Kazan'. All these chemists came to Kazan' with other career goals; and, unlike Zinin, they were not "drafted" into chemistry by state officials but freely chose chemistry after being exposed to it in the course of their university studies. How did this come about? In another paper (2) Lewis noted (regarding Zaitsev) that "all students in the Faculty of Law were required to pass two years of chemistry in order to graduate." Markovnikov had also been a law student and, presumably, was attracted to chemistry by the same curricular path as Zaitsev (through Butlerov's lectures). Vagner, too, had switched from law to chemistry under the impact of Zaitsev's and Markovnikov's lectures. What was the intent of this requirement, and were there similar ones vis-à-vis chemistry for other faculties of study at Kazan'? Reformatskii had been a seminarian; but he, too, switched to chemistry after "encountering" Zaitsev at Kazan'.

Secondly, what were the laboratory research conditions at Kazan', and how had they developed in the era between Zinin and Zaitsev? In an earlier paper on chemistry at Kazan', Lewis noted (3) that Markovnikov "frequently bemoaned the backwater conditions under which Russian scientists worked;" yet Zaitsev appears to have developed a vigorous research group after Markovnikov left Kazan'. Rocke (4) has recently emphasized the importance of state subsidies to academic chemical laboratories in accounting for the contrasting development of German and French chemistry after 1840. What was the situation in Russia, particularly at the University of Kazan'?

Lastly—more an observation than a question—in the two papers by Rice and Lewis there is an interesting interaction—one might almost call it a dialectic—in the development of chemists, between their domestic and foreign mentors: Ostwald and (or *versus*) Mendeleev in the case of the physical chemists; Kolbe and Butlerov in the case of Zaitsev. This is quite different, I think, from the contemporary analog of American chemists' going abroad for advanced work: unlike Russia, there were no domestic giants whose mentorship could interact in this way with that found in the "high" centers of scientific research in Germany or France. Significantly, by 1875, the research leave for Vagner was in Russia itself, at St. Petersburg.

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OPPOSITION TO THE FORMATION OF THE AMERICAN CHEMICAL SOCIETY: NOTED ADDED IN PROOF⁽¹⁾

James J. Bohning, Lehigh University

The formation of the American Chemical Society (ACS) on April 6, 1876 in New York has often been linked in different ways to the Centennial of Chemistry celebration held in Northumberland, Pennsylvania on July 31 and August 1, 1874. A typical example is one drawn from the 50th anniversary of the ACS in 1926, when Samuel Goldschmidt, who was present in Northumberland in 1874, commented that “from this meeting sprang the present Society, the largest and strongest scientific society in the world (2). Goldschmidt’s implication is that there is a direct link between 1874 and 1876.

The intent of my previous paper (1) was to show that this link is very tenuous at best. As that issue of the *Bulletin* was going to press, a letter (3) was found in the

archives of Pennsylvania State University that adds considerable support to my premise that care must be used when associating the origin of the ACS with the 1874 Centennial of Chemistry celebration.

This letter was written by Charles L. Parsons, Secretary of the ACS, on official ACS stationery. It was address to Gerald L. Wendt, then dean of the School of Chemistry and Physics at Penn State, and dated August 5, 1926. Parsons was responding to Wendt’s invitation to join the celebration at the Joseph Priestley House in Northumberland, when a small Museum of Priestley artifacts would be dedicated as part of the ACS Golden Anniversary celebration. In his typical fashion, Parsons succinctly told Wendt his opinion of the relationship between 1874 and 1876:

There is one thing that I want to bring to your personal attention, but I do not want you to get the idea that I am an iconoclast or that I am worrying myself seriously about the absolute correctness of history. However, if you will read the Twenty-Fifth Anniversary Number of the American Chemical Society (4) and study it with care you will, I think, see clearly that altho [sic] some people have attempted to claim so, *the little meeting at Northumberland had little or nothing to do with the organization of the American Chemical Society*. It was the precursor of Section C of the American Association for the Advancement of Science, but the American Chemical Society was started quite independently two years later, and I fail to find anywhere in the statements of those years that the calling together of a preliminary meeting for the American Chemical Society in New York *had the slightest connection with the meeting two years before at Northumberland*.

It is simply one of those traditions which has grown like the tradition that has been in my family for a good many years that a certain pair of silk stockings had been worn by one of my ancestors when he signed the Declaration of Independence. The silk stockings surely look as if they might have been worn by one of my ancestors, but the Josiah Bartlett who was my ancestor was a farmer down in Lebanon, Connecticut, and was a very different man from the Josiah Bartlett of New Hampshire who actually did the signing. With all respect, however, to the silk stocking. Their names simply happen to be the same (5).

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4. *Twenty-Fifth Anniversary of the American Chemical Society*, Chemical Publishing Company, Easton, PA, 1902.
5. I am indebted to Professor Roy Olofson of Pennsylvania State University for calling this letter to my attention.

FUTURE ACS MEETINGS

April 7-11, **2002**—Orlando, FL
August 18-22, **2002**—Boston, MA
March 23-27, **2003**—New Orleans, LA
September 7-11, **2003**—New York, NY
March 28-April 1, **2004**—Anaheim, CA
August 22-26, **2004**—Philadelphia, PA
March 13-17, **2005**—San Diego, CA
August 28-September 1, **2005**—Washington, DC
March 26-30, **2006**—Atlanta, GA
September 10-14, 2006—San Francisco, CA
March 25-29, **2007**—Chicago, IL
August 19-23, **2007**—Boston, MA
April 6-10, **2008**—San Antonio, TX
August 17-22, **2008**—Philadelphia, PA
March 22-26-, **2009**—Salt Lake City, UT
August 16-21, **2009**—Washington, DC
March 21-26, **2010**—San Francisco, CA
August 22-27, **2010**—New York, NY
March 27-31, **2011**—Anaheim, CA
August 28-September 1, **2011**—Chicago, IL
March 25-29, **2012**—San Diego, CA
August 19-23, **2012**—Boston, MA

FOUR GIANTS IN A COLLEGE CHEMISTRY DEPARTMENT: OBERLIN COLLEGE, 1880-1966*

Norman C. Craig, Oberlin College

Although the teaching of chemistry at Oberlin College began a year after the founding of the college in 1833, a distinct chemistry department dates from just before 1880. This paper focuses on the 86-year period from 1880 to 1966. To give this brief historical account shape and texture, the emphasis is on four prominent figures who were chemistry faculty members during this time period. Those persons are Frank F. Jewett, Harry N. Holmes, Luke E. Steiner, and J. Arthur Campbell. Holmes, Steiner, and Campbell were nationally known. Jewett joined the faculty in 1880, another reason for the starting date of this account. Steiner retired from the faculty in 1966, the reason for the final date. Campbell left the faculty in 1957 to become one of the founders of Harvey Mudd College. The many other faculty members who contributed much to making chemistry at Oberlin College a vital and effective program during this time period are listed in Table 1.

Frank F. Jewett

Frank F. Jewett (faculty member from 1880–1912) is best known as the mentor of Charles M. Hall, who discovered the electrolytic process for refining aluminum

metal in Oberlin in February 1886, within eight months of his graduation from college, and who in 1888 became one of the founders of the Pittsburgh Reduction Company, known today as Alcoa. Figure 1 is a photograph of Frank Jewett when he was about 40 years old and working with Hall. Jewett was as well educated in chemical science and as widely experienced as any American academic of his day. He had received his B. A. from Yale in 1870 and had returned two years later to do master's degree work in chemistry and mineralogy at the new Sheffield Scientific School at Yale. He then spent a year (1874-75) studying in Friedrich Wöhler's laboratory in Göttingen, the leading laboratory of chemical science in Germany in those years (1, 2).



Figure 1. Frank F. Jewett at about forty years of age when C. M. Hall was developing the process for refining aluminum metal.

Jewett returned to the US to take a position as assistant to Wolcott Gibbs at Harvard (1875-76). At the end of a year with

Gibbs, Jewett was persuaded by the president of Yale to accept an appointment at the Imperial University in Tokyo, Japan. Having been one of the first half-dozen westerners to teach chemical science in Japan, he returned to the US after three-and-one-half years to ac-

cept an appointment in 1880 as Professor of Chemistry and Mineralogy at Oberlin College (3).

Frank Jewett took the place of William K. Kedzie, who had known Jewett when both were graduate students at Yale. Kedzie was the son of William C. Kedzie, who became well known as the president of Michigan State College. The younger Kedzie, who brought to Oberlin enthusiasm and modern instruction in chemistry, including laboratory work for students, succumbed to a respiratory illness after a year and a half but not before “naming” Jewett as his successor. When Jewett arrived in Oberlin in the summer of 1880, he found a “new” laboratory building fashioned out of an old public school building, which was shared with the professor of biological sciences. This building, called Cabinet Hall, is shown in Fig. 2. Equipment for experiments was barely adequate and did not include a good analytical balance. Jewett described having to crawl under the floorboards in cold winter weather to thaw water pipes with a Bunsen burner and characterized these facilities as distinctly inferior to the new and well-equipped ones he had known in Japan. Finding financial support for adequate equipment was a continuing challenge for him (1).

At first the only chemistry course that Jewett taught was a general inorganic course for juniors. He also taught mineralogy and some other courses such as rhetoric. Qualitative and quantitative analysis and a course in organic chemistry were soon added, all taught by Jewett. Laboratory work for the students remained optional until 1895, when Jewett finally had an assistant to help with the laboratories. When the north wing of the laboratory building was sacrificed to build a new college building in 1886, Jewett inherited the whole of the remaining structure (1).



Figure 2. Cabinet Hall in the early 1880s when it housed the departments of chemistry and biological sciences.

The great respect for Frank Jewett as a teacher of chemistry and the mentor of Charles Hall was recognized when the father of one of his former students provided financing for the construction of a first-class chemistry building. Louis Severance, college trustee and treasurer of the Standard Oil Company, donated funds for the building, for equipping it, and for endowing the Severance professorship. Jewett was ready with plans, having taken the occasion of a sabbatical year (1895–96) to visit new chemistry laboratories in Berlin and Leipzig and then, in the US, to visit the laboratories at Amherst, Williams, and Yale. Severance Laboratory, shown in

Fig. 3, was completed in 1901. Following his remarks at the dedication, Ira Remsen, distinguished chemist and president of Johns Hopkins University, said that he wished he had as good a laboratory himself (1).

A chemist's whim was expressed in Severance

Laboratory. The library on the second floor was shaped as an elongated benzene ring, made possible by the truncated intersection of the two wings of the building. Remarkably, commodious Severance Laboratory, complete with three instructional laboratories, was built for Jewett and one assistant. It was sufficiently large to serve the department of chemistry well until 1961, when it housed six faculty members, a laboratory manager, a departmental secretary, and a few M. A. students, as well as providing adequate space for classrooms, four instructional and some research laboratories.

In effect, Jewett and Hall exchanged places on the world stage. Hall was the technical innovator behind the worldwide aluminum industry; he was so recognized in his lifetime. After Jewett came to Oberlin in 1880, he became deeply involved in building up a compre-

hensive program in chemistry and in working for the community. He supported missionary teaching in Asia, served on the City Council, developed one of the first municipal water treatment facilities, for which he did the analyses, and served as the official US weather observer in Oberlin. Other than several editions of a locally produced laboratory manual, his publications were few in number (4).

In addition to Charles Hall, another famous student of Jewett was Robert Millikan, Nobel prize winner in physics and developer of Caltech. Jewett also maintained a lifelong friendship with Edgar Fahs Smith, distinguished chemist, historian, and president of the University of Pennsylvania, whom Jewett addressed as "Chum" in correspondence (5). They had been students together in Göttingen. For a private publication following Frank Jewett's death, his wife chose to name the booklet *The Beloved Teacher*, an apt choice for Jewett's life work and impact (3).

After Jewett's retirement in 1912, Alan W. C. Menzies, a Scotsman with a recent Ph.D. from Chicago, was appointed to the headship of chemistry, in competition with offers from Chicago and Columbia. The chemistry faculty was then three in number. Menzies remained in Oberlin for only two years before he left for what he undoubtedly regarded as a more prestigious and research-active position at Princeton. He was probably also concerned that his doubts about religion were incompatible with Oberlin College in those days (6).

Harry N. Holmes

In 1914 Harry N. Holmes (faculty member from 1914-1945) was appointed to the chemistry faculty and subsequently developed for himself and the department a national reputation. Figure 4 is a photograph of Harry Holmes. He had received his Ph.D. with Ira Remsen and J. C. W. Frazer at Johns Hopkins in 1907 and had taken a position as the sole teacher of chemistry at Earlham College, where he remained for seven years before moving to Oberlin (1). Holmes had equal interests in teaching and in research. In an exchange of views

with W. A. Patrick of Johns Hopkins in the first volume of the *Journal of Chemical Education*, Holmes made his position clear regarding the importance of research in a college. After citing several well-known academics who supported doing research with undergraduates, he wrote (7):

A stimulating freshness and a feeling of authority come to the college teacher as he unravels the secrets of science. The teacher profits, the great body of science profits, and the pupil profits. The pupil feels that he's near one of the fresh springs that feed the stream of knowledge into which he has been dipping.

Patrick felt that combining teaching with research reduced the quality of both and that teachers should limit their scholarship to combing the journals for the latest developments (8). Although Holmes had little time and no

coworkers to do research at Earlham, he investigated ozone levels as a function of changing weather by carrying starch iodide paper in an open test tube in his coat pocket. These observations led to his first independent paper entitled "Atmospheric Ozone" (9). No doubt, the modern and extensive facilities in Severance Laboratory, inherited from the Jewett era, attracted Holmes to the headship at Oberlin, where he joined two other faculty colleagues.

At Oberlin, Harry Holmes taught organic chemistry and general chemistry for a while and then settled into teaching general chemistry and colloid chemistry. A natural showman with an engaging manner and a commanding presence, Holmes made a lasting impression on students in general chemistry. His popular lectures were extensively illustrated with lively dem-



Figure 3. Severance Chemical Laboratory, completed in 1901.



Figure 4. Harry Holmes at the time he was President of the American Chemical Society.

onstrations. After discussing chemical explosives, for example, Holmes did not hesitate to toss a sample of TNT to an unsuspecting student and expect him to catch it. He once led a whole general chemistry class on tip-toe out of the lecture room, leaving a sleeping student in the front row to awake in unexpected isolation. He played leading roles in community dramas (10).

Holmes's widely used text, *General Chemistry*, first published by Macmillan in 1921 along with a laboratory manual, went through five editions until 1949. He was an early advocate of incorporating semi-micro qualitative analysis into the general chemistry laboratory. As early as 1920, he had written instructions for such a qualitative analysis program in an unpublished pamphlet. Soon after his first book, two other introductory texts appeared: *Introductory College Chemistry*, 1925, and *Elements of Chemistry*, co-authored with L. W. Mattern, a high school teacher in Washington, DC, in 1927, both published by Macmillan. Richard Remsen Holmes, Harry Holmes's chemist son, recalls that his father's income from texts often exceeded his income from the college. Holmes also wrote several popularizations of chemistry, including *Out of the Test Tube*, *Have You Had Your Vitamins?* and *Strategic Materials and National Strength*.

Holmes's research interests were in three areas. One was colloid chemistry, for which he taught a laboratory course and wrote a manual, *Laboratory Manual of Colloid Chemistry*, first published by John Wiley in 1922. A text with the title, *Introductory Colloid Chemistry*, followed in 1934. His interests in colloids led to a second area of research, the early use of alumina, silica gel, and other adsorbents for column chromatography. In the early 1930s Holmes's students were among the first to make extensive use of column chromatography to purify substances (11). This work led to a third area of research on vitamins, including the first crystallization of vitamin A. For this work with vitamins, techniques were developed to carry out column chromatography at dry-ice temperature. His coworkers were also among the first to do what is today called "flash chro-

matography" in an attempt to purify penicillin in the 1940s, the increased pressure being achieved with a bicycle pump. Fig. 5 shows the flash chromatography apparatus developed in Holmes's laboratory.

Holmes's interest in vitamins led him to be an early proponent of megadoses, especially of vitamin C. Of course, Linus Pauling was a more recent advocate of large doses of vitamin C to ward off the common cold. That he was aware of Harry Holmes's earlier advocacy was revealed when he met an Oberlin faculty member at a conference in 1986 and, as an item of conversation, Pauling said so (12).

Some regarded Holmes as more showman and publicist than a scientist (13). There can, however, be no question about his overall effectiveness at Oberlin and at the national level. Many former students have attested to the inspiration they received from his teaching and to his ability to attract able chemistry students to Oberlin (10). These talents as a teacher were recognized in 1955 with the James Flack Norris

Award of the Northeastern Section of the American Chemical Society. In 1954, Holmes was also the first to receive the ACS Award in Colloid Chemistry, sponsored by the Kendall Company.

In contrast to Frank Jewett, Harry Holmes had an enviable publication record and was widely known. In addition to his many textbooks, he was the author of 70 research papers and 9 patents. The culmination of his career was election as President of the American Chemical Society in 1942. Another high point near the end of his career was the graduation in 1943 of three students who have made outstanding contributions to chemical science: Ralph Hirschmann, who, while at Merck, was a leader in the first synthesis of an active enzyme, ribonuclease; David Gutsche, who, at Washington University, developed early synthetic examples of molecular recognition in calixarenes; and James Boggs, who has made notable experimental and computational contributions in the field of molecular structure at the University of Texas.



Figure 5. An apparatus to do flash chromatography in 1943. The photograph was supplied by C. David Gutsche, who did this work as part of his honors research.

Comparable to Holmes's interest in chemistry was his interest in golf. An excellent player, he helped in many ways with the local golf club. During the 1930s, he redesigned and participated in rebuilding the nine-hole golf course in Oberlin (14). In his latter years he also became an ardent painter with oils on canvass. For the Chicago ACS meeting in 1950, he organized a show of paintings by a number of chemists.

At least twice during his tenure on the Oberlin faculty, Harry Holmes received enticing outside offers. One was to become Dean of the School of Chemistry and Chemical Engineering at Penn State. Another was to become director of the Battelle Institute. Although Oberlin College had an undifferentiated salary schedule within faculty ranks in those days, the college responded by establishing the Hall Instructorship that provided Holmes with a regular postdoctoral appointee (10).

Luke E. Steiner

Luke E. Steiner (faculty member from 1928-1966) joined the Oberlin College faculty in 1928. An Oberlin graduate of the class of 1924 and a student of Holmes, Steiner had completed a Ph.D. in chemical thermodynamics under John Johnston at Yale in 1927 and had served as an instructor there for one year. Steiner was the first member of the faculty to hold a Ph.D. in physical chemistry and the first to have a good grasp on the rapidly developing theoretical basis of chemistry (15). The 1920s were, of course, the

decade in which quantum mechanics was developed and in which thermodynamics and statistical thermodynamics became accepted parts of the curriculum in the leading institutions. Fig. 6 is a photograph of

Luke Steiner with many thermodynamics texts on the shelves behind him.



Figure 6. Luke Steiner in 1961 with many thermodynamics texts on the shelves behind him.

Over his 38-year career on the Oberlin faculty, Steiner developed a "school" of thermodynamics. Soon after his appointment to the faculty, he began writing a text, *Introduction to Thermodynamics*. After a number of tryouts in his senior/graduate-level course, this book was published by McGraw-Hill in 1941 and went through a second edition. Among the students who prepared notebooks filled with solutions to the numerous, challenging problems from this text and who went on to make notable contributions in thermodynamics were Henry A. Bent (Connecticut, Minnesota, North Carolina, and Pittsburgh), William C. Child (Carleton), Norman C. Craig (Oberlin), Howard J. DeVoe (Maryland), Eric A. Gislason (Illinois at Chicago), William B. Guenther (University of the South), Reed A. Howald (Montana State), Roger C. Millikan (General Electric, UC Santa Barbara), Kenneth H. Sauer (American University in Beirut, UC Berkeley), and John C. Wheeler (UC San Diego). Other Oberlin chemistry students in Steiner's time who made major contributions to thermodynamics but who did not take the course were J. Arthur Campbell (Oberlin, Harvey Mudd), Ward N. Hubbard (Argonne Laboratory), Hilton A. Smith (Tennessee), and Stephen S. Wise (Mobil Oil). In 1969 after Steiner's retirement, the Division of Chemical Education held a symposium on the teaching of thermodynamics, at which two of his former students presented papers and at which he was acknowledged for his many contributions in this area of science (16).

Upon Harry Holmes's retirement in 1945, Steiner became head of the department of chemistry and held this position until one year before his retirement in 1966. By that time at Oberlin College, with few exceptions department chairmanships had become rotating positions. In the early 1950s Steiner negotiated the conversion of the Hall Instructorship into a regular faculty position to give the department a faculty of six.

In addition to teaching thermodynamics, Steiner regularly taught general chemistry. Despite having to compete with Holmes's commanding personality as the teacher of other sections of this course, Steiner had his adherents among the students for his more fundamental and challenging approach to the subject and his remarkable patience. Although he also kept his hand in research and remained an uncompromising advocate of undergraduate research experience, especially the college's Honors program for seniors, his principal contributions were in the area of chemical education.

Steiner wrote texts at several levels in the college curriculum and for high school students as well. In 1938



Figure 7. Kettering Hall soon after it opened in 1961. The quartz aggregate section in the foreground housed the Science Library and the main lecture halls; the chemistry half of the building is immediately to the left.

he completed the fourth edition of *Second Year College Chemistry* (John Wiley), whose author, William Chapin, Steiner's colleague, had suffered a stroke. A new edition of the accompanying laboratory manual followed in the mid 1940s. From its publication in 1922, *Second Year College Chemistry* was exceptional in presenting an introduction to physical chemistry and analytical chemistry in a single text. With J. Arthur Campbell as coauthor Steiner wrote a laboratory manual for general chemistry and a modern first-year text, *General Chemistry*, which were published by Macmillan in 1955. This text, like Pauling's pathbreaking 1950 text, had many illustrations of space-filling models of chemical substances. This writing in the general chemistry area soon led to Steiner's authorship of the text, *Modern Chemistry*, for John Baxter's 1958-59 television series, "Continental Classroom." In the final episode of this TV series, Baxter said, "More than any other person, Professor Luke E. Steiner of Oberlin College helped set the tone and content of the course. To this wise and kindly teacher I owe a debt I can never repay. Those who have been fortunate enough to have worked with him know whereof I speak (17)."

Shortly after writing *Modern Chemistry*, Steiner served as one of the lead writers for the text for the National Science Foundation-sponsored ChemStudy program that revolutionized the teaching of high school chemistry in the 1960s. In 1963 Steiner also served as the Chair of the Division of Chemical Education. After retirement he spent two years at Berkeley making strong contributions to texts in the Science Curriculum Improvement Study (SCIS), designed for pre-high-school

students. The wide range of Steiner's textbook writing prompted a colleague to say that Steiner covered chemistry from the cradle to the grave.

Steiner's final great contribution to chemistry at Oberlin was guiding the planning of a new science building, Kettering Hall, to a successful completion. Fig. 7 is a photograph of Kettering Hall, which was shared with the biology department and completed in 1961. It not only had outstanding space for instructional laboratories and a new science library, but it provided each faculty member with first-class research laboratory space. Kettering Hall also proved easily adaptable to the age of intensive use of instrumentation that was dawning in the early 1960s. The fine facilities spawned an era of exceptional research productivity at Oberlin College.

J. Arthur Campbell

J. Arthur Campbell (faculty member from 1945-1957) replaced Harry Holmes in 1945, as a most worthy successor. Art Campbell, who liked bow ties in his early days, appears in Fig. 8. An Oberlin graduate of the class of 1938 who had studied with both Holmes and Steiner, Campbell had acted in plays during his undergraduate years. A tall, commanding figure with an actor's flair, similar to Holmes, Campbell was unusually effective in the classroom. He was an engaging presenter of lecture demonstrations. An example is the famous "blue bottle" experiment, described and explicated in his book, *Why Do Chemical Reactions Occur?* (18).

After graduating from Oberlin, Campbell spent a year completing an M.S. at Purdue but then moved on to UC Berkeley, where he completed a Ph.D. in 1942 in physical chemistry under Joel Hildebrand. While using X-ray methods to study the local structure in liquid mercury and liquid xenon, he also became infected with Hildebrand's enthusiasm for teaching undergraduates. Upon completing his Ph.D., Campbell joined the Manhattan project at Berkeley, where he served for three years as

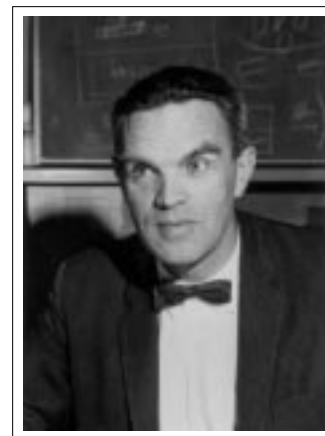


Figure 8. J. Arthur Campbell during his days as an Oberlin College faculty member.

an instructor and a researcher focusing on electrochemical methods for reducing uranium (19).

Campbell was an energetic innovator. Soon after he began teaching physical chemistry upon the retirement of James McCullough in 1949, he introduced the identification of an unknown organic liquid as the organizing principle for applying a variety of physical methods in the laboratory. He designed and had made in the college shop large, space-filling molecular models and a periodic table displaying atomic radii with wooden spheres. Subsequently, charts showing these atomic radii graced the walls of classrooms and lecture halls throughout the country. Campbell was one of the first to use Walter Moore's revolutionary new text, *Physical Chemistry*, despite its numerous, student-challenging errors. In the general chemistry laboratory, Campbell introduced limited unknowns, which gave qualitative inorganic analysis a more exciting, research-like character. He used Linus Pauling's *The Nature of the Chemical Bond* to teach seniors and M. A. students modern ideas about bonding.

Exceptionally interested in students, Art Campbell and his wife Dorothy held weekly open houses at their home on Sunday afternoons. Campbell continued Holmes and Steiner's practice of hosting the Alchemists Club, monthly afternoon teas complete with beakers for cups and citric acid and sucrose for flavoring, at which the best students in general chemistry met informally with the teacher and learned about new research developments in chemistry. Campbell's interest in students and his effectiveness in classrooms and laboratories drew many students into chemistry. Campbell was a dedicated practitioner of the Socratic method. As a student at Oberlin College, the author heard it said of Campbell, "Don't bother to ask him a question about chemistry. He'll ask you twenty questions, and it will turn out that you knew the answer all along."

Although Campbell's principal interest was in chemical education, he, like Steiner and Holmes, was a staunch advocate of research experiences for undergraduates. He regularly sponsored student research projects during the academic year but chose to spend most summers teaching elsewhere, at Ohio State, Michigan State, and Wisconsin. A year's research leave, spent in part at Cambridge, England, gave him expertise in applying X-ray methods to analyzing crystal structures. Some of this work was continued at Oberlin with the equipment in the physics department. His research emphasis at Oberlin, however, was the application of

thermal analysis to the decomposition of chromate salts and of photometric methods to understanding the pH dependence of the equilibrium between chromate and dichromate ions. During his 12 years on the Oberlin faculty, Campbell published several research papers. In the area of chemical education, as already noted, he and Steiner produced a laboratory manual and the text, *General Chemistry*, in 1955. In addition, numerous papers in chemical education appeared throughout Campbell's career.

Fresh from his participation in the Manhattan Project, Campbell was a public spokesman for peaceful uses of atomic energy. On at least one occasion, he was selected by the members of the senior class in the college to give an all-campus assembly talk. He chose to speak about atomic energy as well as the importance of science. In general, he was a public figure on the campus. In 1948 in an issue of *Isotopics*, which he edited for the Cleveland section of the ACS, and in a letter to the then-president of the college, Campbell raised questions about the legality of the pressures being brought to bear on scientists because of hearsay evidence of Communist affiliations (20). He began a term as chair of the Division of Chemical Education in 1950, a mere five years after he began teaching at Oberlin College. He spent the 1956-57 academic year in Washington, DC working as Director of Institutes at the National Science Foundation and did not return to the Oberlin faculty.

In the spring of 1956, Campbell was invited to Claremont, CA as a candidate for the presidency of Harvey Mudd College, which was in its prenatal period. Although Campbell was not interested in the presidency, by the end of the fall of 1956 he had agreed to be one of the founders of the college and the first professor of chemistry. When asked why he had decided to leave Oberlin, he said, "At age 40, one should get a new wife, a new house, or a new job. I chose a new job." Being a founder of a new science-oriented college and a shaper of its chemistry program was a powerful attraction, as was returning to California, which he and his wife had grown to like during their years in Berkeley.

Soon after his appointment to the Harvey Mudd faculty, Art Campbell was tapped by Glenn Seaborg to be the director of the NSF-sponsored ChemStudy program. Through its formative years, Campbell played a crucial role in directing this national program that transformed the teaching of high school chemistry. Campbell was very interested in the innovative use of films in edu-

cation. Consequently, he acted in a number of the ChemStudy films and guided the production of many others (19).

Art Campbell led in the emergence of Harvey Mudd as the premier science college in the US and wrote several more texts. A frequent traveler for UNESCO, he became known throughout the world for his contributions to chemical education (19). Campbell's career, which had such a strong start during his 12 years on the Oberlin faculty, skyrocketed during his 29 years on the Harvey Mudd faculty. Had he not been diagnosed with bulbar ALS in 1986, he would not have withdrawn as a

candidate for the presidency of the ACS. He would surely have been a very strong candidate and a very likely choice of the electorate.

Epilog

Much of significance has occurred in the chemistry department at Oberlin College since the mid 1960s. Already noted is the extent to which a balance between teaching and research, as advocated so clearly by Harry Holmes, reemerged. This change occurred without the support of graduate students through most of this time

Table. Chemistry Faculty Members, Oberlin College, 1834-1966*

1834-78	James Dascomb (M.D., Dartmouth)
1878-80	William K. Kedzie (B.S., Agricultural College of Michigan; M.S., Yale)
1880-1912	Frank F. Jewett (B.A., M.S., Yale)
1899-1900	Joseph S. Chamberlain (B.S, M.S., Iowa State; Ph.D., Pennsylvania)
1895-96, 1901-06	Thomas M. Taylor (B.A., Oberlin; Ph.D., Pennsylvania)
1906-07, 1910-37	William H. Chapin (B.A., Oberlin; Ph.D., Pennsylvania)
1907-49	James C. McCullough (B.S., M.S., Case Institute)
1912-14	Alan W. C. Menzies (B.Sc., M.A., Edinburgh ; Ph.D., Chicago)
1914-45	Harry N. Holmes (B.A., Westminster; Ph.D., Johns Hopkins)
1917-18, 1920-21	Edwin H. Cox (B.S., Earlham; M.S., Louisville; M.A., Harvard; D.Sc., Geneva, Switz., 1922)
1921-22, 1925-44	Alfred P. Lothrop (B.A., Oberlin; Ph.D., Columbia)
1922-25	Edna H. Shaver (B.A., M.A., Oberlin; Ph.D., Chicago, 1937)
1928-66	Luke E. Steiner (B.A., Oberlin; Ph.D., Yale)
1937-75	Werner H. Bromund (B.A., Chicago; M.A., Oberlin; Ph.D., New York University, 1942)
1942-43	Clara M. Deasy (B.A., M.S., Ph.D., Cincinnati)
1944-78	William B. Renfrow (B.A., Furman; Ph.D., Duke)
1945-57	J. Arthur Campbell (B.A., Oberlin; M.S., Purdue; Ph.D., UC Berkeley)
1949-51	Robert E. Lyle, Jr. (B.A., Emory; Ph.D., Wisconsin)
1952-58, 60-63	Barbara H. Bunce McGill (B.A., Bryn Mawr; Ph.D., Harvard)
1952-84	Peter J. Hawkins (B.Sc., Ph.D., London)
1956-59	Carl W. Kammeyer (B.A., Carthage; Ph.D., Illinois)
1957-2000	Norman C. Craig (B.A., Oberlin; Ph.D., Harvard)
1958-60	Norman J. Hudak (B.A., DePauw; Ph.D., Cornell)
1960-93	Richard C. Schoonmaker (B.Chem.Eng., Yale; Ph.D., Cornell)
1963-66	James S. George (B. A., Allegheny; Ph.D., Illinois)
1963-2000	Terry S. Carlton (B.S., Duke; Ph.D., UC Berkeley)

*Omitted are persons who held one-year appointments except for Chamberlain.

period, the masters degree program having been discontinued in 1975, or of postdoctorals. The challenge of finding funds for modern instrumentation and for the support of students has been met again and again. With few exceptions faculty members have devoted summers to working closely with undergraduate students in the research laboratories. The era of textbook writing, such a prominent theme in the time of Holmes, Steiner, and Campbell, is now but a memory. Yet, the four giants described in this account stand proudly in the background and provide palpable challenges to the present faculty. The Jewett Scholarship award for sophomores, the Steiner Lectureship, and the Holmes Award for seniors are welcome reminders to students as well as faculty of these remarkable individuals. Oberlin College awarded honorary degrees to Luke Steiner (1978) and J. Arthur Campbell (1988).

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ABOUT THE AUTHOR

Norman Craig holds a B. A. in chemistry from Oberlin College, where he was a student of Luke Steiner and J. Arthur Campbell. The author holds an M.A. and a Ph.D. in physical chemistry from Harvard University. In 1957 he replaced J. Arthur Campbell on the Oberlin chemistry faculty. He is the author of two articles about Charles Hall, Frank Jewett, and Julia Hall, Hall's sister. These articles are "Charles Martin Hall—The Young Man, His Mentor and His Metal," *J. Chem. Educ.*, **1986**, 63, 557-559; and "Julia Hall—Coinventor?" *Chemical Heritage*, **1997**, 51:1, 6-7, 36-37. Another article on the history of chemistry is "Correspondence with Sir Lawrence Bragg Regarding Evidence for the Ionic Bond," *J. Chem. Educ.*, in press.

EDGAR BUCKINGHAM: FLUORESCENCE OF QUININE SALTS

John T. Stock, University of Connecticut

Malaria, an often-fatal disease, has been a worldwide plague for several thousand years. The discovery of the efficacy of substances present in the bark of various *cinchona* trees, native to the Andes, provided some relief. A real anti-malarial drug was not available until 1820, when Joseph Baptiste Caventou (1795-1877) and Josephe Pelletier (1788-1842) isolated *quinine* from the bark (1). Eighty years after their discovery, a statue honoring these chemists was erected in Paris (Fig. 1).

Other workers established the formula for quinine, showed that it acts as a diacid base, and that it is a methoxy derivative of a companion alkaloid, cinchonine. The elucidation of the structure of these compounds, largely due to the work of Wilhelm Königs (1851-1906) and Paul Rabe (1869-1952), was finally published in 1908 (2). More than three decades passed before the partial synthesis of quinine was achieved (3). The first completely stereoselective, total synthesis of this compound was reported in 2001 (4). However, despite the discovery of other antimalarial drugs, quinine is still manu-

factured from cinchona trees that are cultivated in South America and in the Far East.



Figure 1. Caventou and Pelletier

It must have been known since ancient times that certain substances appear to have one color when viewed by transmitted light and another when viewed obliquely. Mineralogists recognize a type of fluor-spar, pale green when viewed against the light, but appearing blue when viewed at an angle to the light. Unrefined petroleum shows the same kind of effect, as do certain substances when in solution. Fluorescein, used both in the laboratory as an indicator and industrially for the location of leaks in waste water systems, is a familiar example. Another is *quinine* or, because of its low solubility in water, one of its salts. The solution, colorless when viewed directly, appears blue when viewed at an angle to the incident light. The phenomenon exhibited by these various sys-

tems is termed *fluorescence*. With modern laser instrumentation and highly sensitive detectors, fluorescence has become a powerful analytical technique. For example, the laser-induced fluorescence detection of derivatized angiotensin peptides is applicable to quantities as small as a few hundred zetamoles (5).

The systematic study of fluorescence was initiated by Astronomer Royal, John Frederick Herschel (1792-1871) (Fig. 2). He named the phenomenon *epipolic dispersion*, derived from the Greek for "surface," because he believed that the effect originated in a layer adjacent to the entrance of light. For Herschel and his suc-



Figure 2. John F. W. Herschel

cessors, the usual light source was the sun or daylight. Because the "detector" was the eye, the observations were not numerical but merely comparative. Colored glass or sometimes a prism was used to select spectral portions of the incident or emergent light. Observations had to be made in a dark room or enclosure, with the incident light entering through a hole or slit.

In 1845 Herschel described his experiments with solutions of quinine tartrate (6,7). He noted that when an approximately 1% solution is placed in a tall glass before an open window, the blue color can be seen by looking down into the glass. When the solution was trickled from one glass to another, the thin film seemed to be equally effective as the bulk solution. Herschel commented that light transmitted through a "quiniferous solution," thus producing a "dispersion," did not produce a dispersion in a second portion of solution.

In fact, the phenomenon described by Herschel had been noted earlier by David Brewster (1781-1868) (Fig. 3). He used a lens to focus sunlight and was able to demonstrate that the "dispersion was not confined to the surface layer, but extended well into the solution (8)."

George Gabriel Stokes (1819-1908) greatly extended the observations of Herschel and Brewster. With a box-like enclosure that enabled him to observe without darkening the room, Stokes examined quinine sulfate, solutions of various plant extracts, certain glasses, and even uranium compounds (9). He thus demonstrated that many systems exhibited phenomena similar to that shown by quinine salts. In a later report, Stokes used "fluorescence" to replace the older term (10). An apparently universal effect, that the fluorescence was emit-

ted at a wavelength longer than that of the incident beam, became known later as Stokes' Law.

Stokes noted that the quinine salts of numerous acids exhibited fluorescence, exceptions being the salts of HCl, HBr, and HI. In fact, the addition of one of these acids to a fluorescing quinine salt solution destroyed the effect. However, the fluorescence returned when the interferent, or quenching agent, was removed; e.g., by treatment with HgO. Mercury halides did not quench the fluorescence.

Other workers, notably Victor Pierre (1819-1886) (11), Jacob Edward Hagenbach (1833-1910) (12), and Cornelius Joseph Lommel (1837-1899) (13), extended the study of fluorescence. Pierre showed that a given substance does not fluoresce if the wavelength of the incident light is greater than a certain minimum. Hagenbach examined the fluorescence of numerous, mainly organic substances, including quinine sulfate. He found that the spectrum of a solution of this salt exhibited two maxima. One of Lommel's discoveries was that the fluorescence radiated by a volume element of a substance is proportional to the amount of the exciting light absorbed.

This was approximately the state of affairs when Edgar Buckingham (Fig. 4) began his work on fluorescence, particularly that of quinine salts. Born in Philadelphia on July 8, 1867 and graduated from Harvard in 1887, Buckingham spent a period in Stra_burg before moving to Leipzig in 1890, where he began the work mentioned. His aims were to extend the then-known facts and to interpret the results in terms of the Arrhenius ionic theory, which was strongly promoted in Ostwald's laboratory. Buckingham's optical equipment was simply the Stokes dark box, with colored glass filters for sunlight and, occasionally, artificial light (14). The availability of electrolytic conductance apparatus was a major asset, allowing him to assess the ionic state of his solutions.

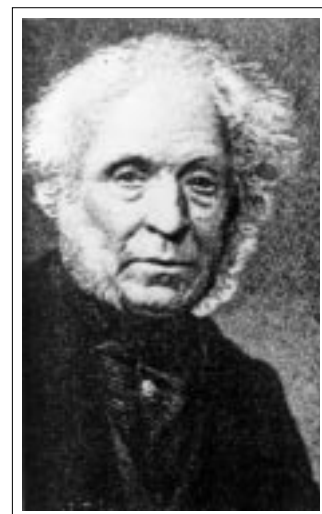


Figure 3. David Brewster

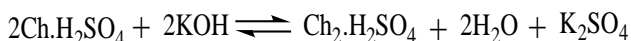
Preliminary experiments were carried out with eosin (tetrabromofluorescein), which behaves as a dibasic acid. Its red solution exhibits a green fluorescence. These experiments convinced Buckingham that the intensity of the effect was governed by the concentration of the *ions* of the solute. He then turned to quinine, known to contain two basic nitrogen atoms and thus capable of forming two series of salts. Because the basic properties of quinine are weak, however, Buckingham pointed out that, with respect to electrolytic dissociation, the salts formed with one equivalent of acid per molecule tend to act like binary neutral salts such as KCl.

Buckingham experimented with the hydrochloride, acetate, monochloroacetate, nitrate, and sulfate of quinine, as well as with the hydrogen sulfate, which he termed "bisulfate." With approximately millimolar solutions of each of the salts, he found that the hydrogen sulfate fluoresced more strongly, the acetate less strongly than the other salts, excluding the hydrochloride. As had been found by Stokes, the hydrochloride was nonfluorescent. From the German, "Chinin," Buckingham used the contraction "Ch" to indicate this compound. Quinine hydrogen sulfate was thus written $\text{Ch.H}_2\text{SO}_4$, or $(\text{Ch.H})\text{HSO}_4$. The fluorescence of a solution of this salt decreased as KOH was added, vanishing when the molar concentrations of this salt and of added KOH had become approximately equal. Because of the low solubility of free quinine in water, the experiments were conducted in approximately 64% alcohol.

In molecular terms, the reaction was presumed to be:



This implied that free quinine does not fluoresce. In a possible alternative reaction:

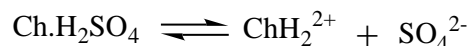


the (normal) sulfate, $(\text{Ch.H})_2\text{SO}_4$, would be formed; but the absence of fluorescence implied that the normal sulfate was also inactive. However, a 5mM 60% alcoholic solution containing both KOH and the normal sulfate produced a distinct, if weak, fluorescence, thus suggesting that the reaction indicated by equation (2) was unlikely.

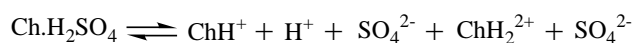
Because quinine acts as a univalent base in aqueous alcoholic solution, Buckingham assumed that the fluorescent species was the cation ChH^+ , formed by the reaction:



The addition of alkali destroyed this cation and also the fluorescence. However, the fluorescence was increased by the addition of HNO_3 . Another possibility considered was that the salt dissociated as follows:

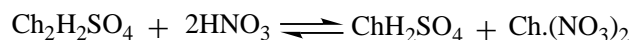


From an extensive series of measurements of electrolytic conductivity, Buckingham argued that, in solution, quinine hydrogen sulfate partially dissociates to give *both* univalent (ChH^+) and divalent (ChH_2^{2+}) cations:

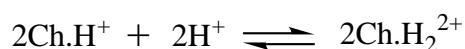


Buckingham came to the conclusion that the fluorescence was due to the quinine cations, and that the divalent species was the more effective. The addition of HNO_3 (*i.e.*, of hydrogen ion) to a solution of $\text{Ch.H}_2\text{SO}_4$ favors the conversion of the univalent to the divalent cation, with corresponding increase in fluorescence. Conductometric measurements of the quinine salts of strong acids (other than HCl, etc.) at millimolar concentration indicated almost complete dissociation. The stronger fluorescence of the hydrogen sulfate thus cannot be due to dissociation greater than that of the other salts.

If the above explanations are correct, the addition of excess strong acid to equimolar solutions of the various univalent quinine salts should cause the fluorescence to rise to the same maximum. Buckingham proved this experimentally (halides excluded) and found that even weaker acids in greater excess were also effective. He also found that if *small* amounts of HNO_3 were added to a millimolar quinine sulfate solution (cation, Ch.H^+), the conductance *decreased*. Because HNO_3 is an excellent conductor, this seems surprising. This result was attributed to the conversion of the univalent to the divalent quinine cation, with consequent removal of the highly conducting hydrogen ion:



If only the cations are considered, the equation becomes:



Obviously, the amount of hydrogen ion (*i.e.*, of HNO_3) added must be less than that implied by equa-

tions (6) and (7). Buckingham demonstrated this experimentally with amounts of HNO_3 that ranged from 1/5th to 1/50th of the amount of quinine nitrate. Through the common-ion effect, the addition of K_2SO_4 to a solution of quinine sulfate might be expected to depress the dissociation of the quinine salt, and thus diminish the fluorescence. In fact, the latter increased, a fact attributed to partial conversion of Ch.H^+ into divalent Ch.KH^+ ions.



Figure 4. Edgar Buckingham

Finally, Buckingham turned to the well-known quenching of fluorescence by halide ions. He repeated the experiments by Stokes, looking for possible causes of the effect. Halide solutions absorb active portions of the incident light or the fluorescent light itself. However, this light from a quinine salt solution was not extinguished when its container was surrounded by HCl solution. The presence of halides may have caused the formation of double or polymolecules of quinine. However, neither conductometric measurements nor freezing-point determinations supported this view. To obtain any quenching effect by HgCl_2 , which is only slightly dissociated in solution, a one hundred-fold excess is needed. Thus it is the chloride ion, and not merely a soluble chloride salt, that causes the quenching. Finally, when Ch.HCl is added to $\text{Ch.H}_2\text{SO}_4$, the fluorescence of the latter is strongly depressed. Thus the effect of halide ions does not depend upon their source.

Although Buckingham had examined and eliminated various possible causes of the quenching effect, he had to admit that he could not explain this effect. More than 30 years after he had finished this work, the following statement appeared in a paper by other workers: "This curious effect of halogen ions remains unexplained (15)."

In 1928 a double-beam photoelectric fluorimeter was used to make a careful study of the quenching of the fluorescence of 0.0025M quinine bisulfate solution by increasing concentrations of additives (16). The results are summarized in Fig. 6. These confirm that the quenching effect is essentially due to the additive anion; Ag^+ is the only cation with appreciable activity. The increasing order of quenching efficiency, indicated in

the Table below, is similar to that of the lyotropic series of ions that is relevant to various physicochemical phenomena such as the precipitation of colloids.

Refractive index measurements were used to obtain the numbers beneath the symbols. The numbers are measures of ionic deformability, *i.e.*, the looseness of the binding of the outer electrons. The authors suggested that the high deformability of the halide ions (CNS^- , known to be a powerful quencher, was not evaluated) enabled the excited quinine cations to return to normal conditions by radiationless transfer of energy through collision with the halide ions.

The work of Francis Perrin (1901-1992) was quoted in support of this collision theory. He showed that as the viscosity of the solvent is increased, a greater concentration of the fluorescing solute is needed to obtain maximum emission (17). Presumably the frequency of collision between the quinine ions, and hence their activation, is diminished in a more viscous medium. This decrease should also apply to collisions between the quinine ions and the quenching ions. The diminution of the quenching power of the halide ions is thus analogous to the increased concentration of quinine ions needed for maximum emission when the quencher is absent.

On his return to the U.S. Buckingham taught physics and physical chemistry at Bryn Mawr College from 1893 to 1899 and then was briefly affiliated with the University of Wisconsin. Apparently, he never returned to the quinine topic. He once remarked that he had studied harmony, not physical chemistry, under Ostwald (17). This is a reminder that Ostwald, by no means a regular attendant at lectures as a

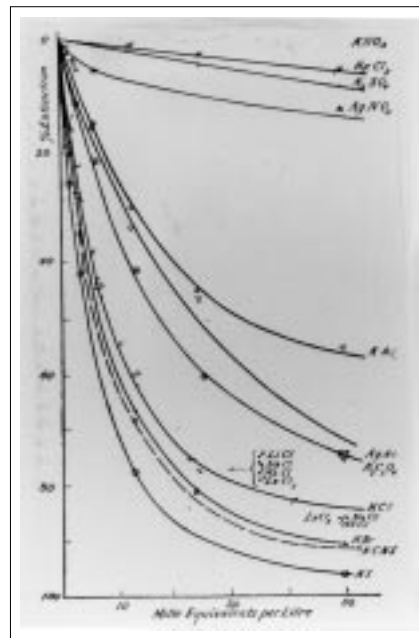


Figure 5. Quenching effect of salts on the fluorescence of quinine sulfate

Table. Quenching Efficiency of Various Ions

Quenching Ion:

 $F^- < NO_3^- < SO_4^{2-} < \text{Acetate} < \text{Oxalate} < Cl^- < Br^- < CNS^- < I^-$

Rel. Deformability:

2.5 3.66 3.65 8.7 12.2 18.5

university chemistry student, did manage to learn the viola parts of all of the 83 Haydn string quartets. This facet of Ostwald's interests must have appealed to Buckingham, who later took miniature scores to symphony concerts.

In 1902 Buckingham became a physicist in the U. S. Department of Agriculture and then transferred to the U.S. Bureau of Standards (now the National Institute of Standards and Technology). Here he published extensively on thermodynamics, hydraulics, fluid dynamics, and engineering physics. He retired in 1937 but remained scientifically active until his death in Washington, DC on April 29, 1940.

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DULONG AND PETIT: A CASE OF DATA FABRICATION?⁽¹⁾

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Introduction

The famous law of Dulong and Petit was based upon their own specific heat data first reported in 1816. For at least 15 years there has been public expression of doubt about the reliability of their data, however. Peter Macinnis spoke on this subject on a radio program of the Australian Broadcasting Corporation during the 1980s (2), and Paul Schwarz published a letter in *Chemical and Engineering News* in 1987 (3). Much of what follows is an elaboration of their work for a scholarly audience. I propose to examine the data, compare it to modern data, and develop reasons for questioning their numbers. The inference can reasonably be drawn that they fabricated some of that data; obviously, however, no one who really knows has an opportunity to testify.

Brief Biographical Sketches

Pierre-Louis Dulong was born in Rouen in 1785. Orphaned at the age of 4, he was raised by an aunt. He entered the *École Polytechnique* in Paris in 1801 but withdrew from it in his second year. He practiced medicine for a time, but he eventually ran out of money in that occupation. He turned next to botany and then to chemistry, working with Thenard and then Berthollet. He held teaching posts at the *École Normale* and then the *École Vétérinaire d'Alfort*. In the early 1810s, Dulong discovered nitrogen trichloride, whose explosiveness cost him a finger and the sight in one eye. He began working with Petit in 1815, a collaboration that led to three papers on heat, of which the paper announcing the law of constant atomic heats in 1819 was the

last. Dulong was appointed Professor of Chemistry at the *Faculté des Sciences* in Paris in 1820. That same year he was appointed Professor of Physics at the *École Polytechnique*—a post vacated by the premature death of Petit. After Petit's death Dulong continued to work on heat, including the specific heat of gases. He was appointed to the physics section of the *Académie des Sciences* in 1823, serving as president in 1828. He died in Paris in 1838 (4).

Alexis-Thérèse Petit was born in Vesoul in 1791. He was a prodigious student, satisfying the entrance requirements for the *École Polytechnique* before age 11; he enrolled there at age 16 (the minimum permissible age). He graduated first in his class—in a class by himself, actually; for he placed “before the line” so that the next student was designated “first.” He was first Professor of Physics at the *Lycée Bonaparte* in Paris and then at the *École Polytechnique* in 1815. He died in 1820 from tuberculosis, which he had contracted in 1817 (5).

The Law: Its Reception and Subsequent Use

The first joint paper by Dulong and Petit in 1816 treated the expansion of materials important to thermometry, such as mercury (6). Their paper the following year (7) on the expansion of gases and mercury and on cooling earned them a 3000-franc prize from the *Académie des Sciences* (8). In the course of this investigation, they measured several specific heats over a wide range of temperatures. In their third paper (1819) they announced the law of constant atomic heat capacities and discussed some theoretical questions concerning heats of reaction

(9). Because this paper figures so prominently in the following analysis, I will refer to it below as “the” DP paper, data from it as the DP data, etc.

The table from this paper is reproduced as Table I. It contains a column of specific heats (on a scale in which water is unity), a column of atomic weights (on a scale in which oxygen is unity), and a column containing the product of the first two. The product, as noted in the paper, is significant because it represents the heat capacities of the atoms. The numbers in that product column are strikingly similar indeed. As the authors state, “The simple inspection of these numbers exhibits an approximation too remarkable by its simplicity not to immediately recognize in it the existence of a physical law capable of being generalized and extended to all elementary substances. ... The atoms of all simple bodies have exactly the same capacity for heat.”

The law was never established to be quite so general or exact as Dulong and Petit presented it (10). Indeed, the law proved to be only approximate. For one

thing, several nonmetals have atomic heat capacities that deviate from the law. For another, heat capacities are temperature-dependent, with different temperature dependencies—a criticism of the law that dates back at least to John Dalton (11).

At the time of Dulong’s death, the law was not even mentioned in one short summary of his work (12), but it was to receive more attention and prominence later on. Stanislao Cannizzaro’s “Sketch of a Course in Chemical Philosophy” (13), which was widely influential in establishing a consistent set of atomic weights and formulas, made extensive use of “the law of the specific heats of elements and of compounds.” Statistical me-

chanics eventually provided an explanation as to why the law holds even approximately at relatively high temperatures, and its breakdown at low temperatures was explained through the use of quantum mechanical energy expressions in statistical thermodynamic treatments (14).

Data Fabrication

1. Suspicions

Suspicions of data fabrication arise if one compares the DP data table to a corresponding table of modern values. Assembling a set of modern data for comparison,

however, is not as straightforward as one might guess. Any number of contemporary reference books and textbooks contain molar heat capacities of the elements at 25°C. Dulong and Petit, however, reported that they measured their heat capacities by cooling samples in ice water from a temperature 5-10° above the temperature of that medium. *The International Critical Tables* (15) are a convenient (if rather old) source

of temperature-dependent heat capacities, and I have employed 0°C values from that source. Allotropism is an additional complicating factor in making a comparison to modern data. Two elements on the DP list have two common forms, whose molar heat capacities differ by 1-2 J K⁻¹ mol⁻¹. Tin has a gray α and a white β form. The gray form is thermodynamically more stable at 0°C. The transition temperature is 13°C (16), so the white form is the standard state at the commonly used reference temperature of 25°C. Sulfur also has two forms, rhombohedral α and monoclinic β . The rhombohedral form is the standard state of the element at both 0°C and 25°C, as the transition temperature is about 93°C (16). In the tables below the heat capacities of the thermody-

TABLE 1. Table from Petit and Dulong 1819 (9)

Element	Specific heats	Relative weights	Products of the weight of each atom by the corresponding capacity of the atoms
Bismuth	0.0288	13.30	0.3830
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.0314	11.16	0.3740
Tin	0.0514	7.35	0.3779
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Tellurium	0.0912	4.03	0.3675
Copper	0.0949	3.957	0.3755
Nickel	0.1035	3.69	0.3819
Iron	0.1100	3.392	0.3731
Cobalt	0.1498	2.46	0.3685
Sulfur	0.1880	2.011	0.3780

namically stable form at 0°C for both tin and sulfur are used. Although this is a natural, perhaps even canonical, choice, it is nevertheless arbitrary, because Dulong and Petit did not provide any descriptions of their samples. Fortunately, the statistical analyses presented below do not depend a great deal on this selection, as will be discussed below.

Table 2 displays the product of atomic weight and specific heat, the quantity that Dulong and Petit correctly interpreted as an atomic heat capacity, the constancy of which is the law that they announced in 1819. The DP atomic heat capacities differ from modern values by no more than 10% in either direction; the DP value for sulfur is 10% greater than the modern value, the largest error. The DP molar heat capacities are remarkably constant—a bit too constant, in fact. The range of the DP data (difference between largest and smallest value) is only 1.04 J mol⁻¹, compared to 3.19 for the modern data. The range is the most obvious, if not the most telling, measure of variability, a subject to be explored more rigorously below. For now it is worth considering the question of how one can obtain such low variability in a set of data based on measurements that presumably have larger errors than modern data.

Table 3 displays DP atomic weights in modern atomic mass units (amu, where ¹²C = 12) and the corresponding modern atomic weights. The DP atomic weights of platinum, tellurium, and cobalt are anomalously low, by 9%, 49% and 33% respectively. All other values vary by less than 4% from the modern figures. Large atomic weight errors are understandable for tellurium and cobalt, because the determination of atomic weights was dependent on chemical analyses as well as on assumptions about formulas. From accurate analytical data on TeO₂, one would obtain an atomic weight half the true value for tellurium if the analyte was believed to be TeO. Similarly, an atomic weight two-thirds of the true value for cobalt would be inferred from accurate analytical data on CoO if it was believed to be

TABLE 2. Atomic heat capacity at 0°C (J K⁻¹ mol⁻¹)

Element	DP (9)	modern (15)
Bismuth	25.64	25.41
Lead	25.40	26.19
Gold	24.80	25.44
Platinum	25.04	25.71
Tin*	25.30	4.5
Silver	25.16	25.11
Zinc	25.01	25.10
Tellurium	24.60	25.58
Copper	25.14	24.33
Nickel	25.56	25.34
Iron	24.98	24.51
Cobalt	24.67	24.40
Sulfur*	25.30	23.0

*allotropes: see text

Co₂O₃. The assumptions employed in atomic weight determinations were arbitrary and were recognized to be so by at least some chemists of the time, including Dulong and Petit (17). Therefore, the deviations of the tellurium and cobalt atomic weights from modern values are understandable and justifiable. The same can be said for the fact that DP used different atomic

weights than the most recent ones reported by Berzelius, a fact noted by several writers (8, 18, 19, 20). The atomic weight of platinum may well be a misprint, as several authors have commented. In any event, the DP atomic heat capacity of platinum is not equal to the product of the numbers that appear in the atomic weight and specific heat columns. (See discussion below.) Otherwise, there is nothing obviously improper about the reported atomic weights.

TABLE 3. Atomic weight (amu, ¹²C = 12)

Element	DP	modern (16)
Bismuth	212.79	208.98
Lead	207.19	207.2
Gold	198.87	196.967
Platinum	178.55	195.08
Tin	117.60	118.71
Silver	108.00	107.868
Zinc	64.48	65.39
Tellurium	64.48	127.6
Copper	63.31	63.546
Nickel	59.04	58.69
Iron	54.27	55.847
Cobalt	39.36	58.933
Sulfur	32.17	32.066

TABLE 4. Specific heat ($\text{J g}^{-1} \text{K}^{-1}$)

Element	DP	modern (21)	DP – modern
Bismuth	0.1205	0.1216	-0.0011
Lead	0.1226	0.1264	-0.0038
Gold	0.1247	0.1292	-0.0045
Platinum	0.1314	0.1318	-0.0004
Tin	0.2151	0.206	0.009
Silver	0.2330	0.2328	0.0003
Zinc	0.3878	0.3839	0.0040
Tellurium	0.3816	0.2005	0.1811
Copper	0.3971	0.3829	0.0142
Nickel	0.4330	0.4318	0.0013
Iron	0.4602	0.4389	0.0214
Cobalt	0.6268	0.4140	0.2127
Sulfur	0.7866	0.717	0.069

Table 4 displays DP specific heats expressed in modern units of $\text{J g}^{-1} \text{K}^{-1}$, the corresponding modern data (21), and the difference between them. Note that Dulong and Petit reported that they measured specific heats of several solids by a method of cooling. They described the method involving cooling of the experimental samples and a standard through a common temperature range, in this case from 5-10°C to 0°C. It is indeed a valid method (22). Rates of cooling through a given temperature range are directly proportional to the heat capacity of the cooling body. Dulong and Petit would have preferred to use an ice or water calorimeter; however, they said that the samples they had were not large enough (less than 30 g) for such methods to yield precise data. Their paper described the apparatus in some detail, including an accurate and finely graded thermometer good to 1/200th of a degree. They did not give a formula that related specific heat to their measurements, though, because the many correction terms would take them too far afield (9).

The DP specific heats of tellurium, cobalt, and sulfur are anomalously high, by 90%, 51%, and 10%, respectively. All other values fall within 5% or less of modern figures. The first suspicious observation is that the largest errors in both specific heat and atomic weight are in the same elements, tellurium and cobalt. The errors in specific heat are large ones, and the property is based solely on mass and temperature measurements, independent of the arbitrariness that attended atomic weights and atomic formulas. Furthermore, the large

errors in both elements compensate the atomic weight errors such that the product of atomic weight and specific heat is very nearly the same as for the rest of the elements in the table. The improbability of independent compensating errors is the main assertion made previously by both Paul Schwarz (3) and Peter Macinnis (2).

2. Statistical Analysis

The law Dulong and Petit proposed was literally too good to be true. In one sense, that fact has been well known for a long time: the law holds only approximately. The data on which the law was based are also too good to be true, as the following analyses suggest.

The variance is a statistical measure of the variability of data within the data set, a much more telling measure than the range. The sample variance, s^2 , is defined as the sum of the squares of the differences between each data point and the mean of the data set. For the 13 DP atomic heat capacities, the sample variance is less than one sixth as great as the variance among modern values for the same elements (0.102 vs. 0.670). A statistical test known as the F test may be used to compare variances of two samples, to assess the probability that the samples were drawn from populations with the same variance (23). The test statistic is the ratio of the sample variances:

$$F = \frac{s_1^2}{s_2^2}$$

where $s_1 > s_2$. The computed F value (6.58) exceeds the critical value for the 0.5% significance level for 13 observations per sample (4.91), supporting the hypothesis that the variance of the modern values is really greater than that of the DP data set. That is, the test strongly suggests that the DP data and the modern data do not reflect measurements of the same quantities with randomly distributed errors (24).

By themselves, the variance data are suggestive. It is difficult to imagine how data based on measurements that a modern observer would expect to be cruder than modern measurements could legitimately lead to a smaller sample variance than modern data. This anomalously small variance in the DP atomic heat capacities, however, is even more dubious when combined with the large errors in DP specific heats.

If the DP specific heats were measured by a valid

method without systematic error, one would expect the deviations of the DP values from the true values to be randomly distributed with a normal distribution. Specific heat errors are displayed in Table IV. They are plotted in Figure 1 on a normal or Gaussian scale. If the data points were normally distributed, they would fall along a straight line. Clearly these points do not. A statistical test of the hypothesis that the errors were randomly taken from a normal distribution indicated that they were not, with a significance level of less than 0.1%.

The errors for cobalt and tellurium are suspiciously large (as Macinnis and Schwarz had previously pointed out). Combined with the fact that they compensate errors in atomic weight (however legitimate) to yield atomic heat capacities with anomalously low dispersion stretches credulity past the breaking point. The DP data are truly stuck on the horns of an improbability dilemma: it is difficult to escape the conclusion that Dulong and Petit made up at least some of the specific heats they claim to have measured.

One additional way to see that Dulong and Petit used specific heat data that are not particularly accurate to obtain atomic heat capacities that are remarkably constant is to compare the average error in specific heat to the average deviation in DP atomic heat capacities. That is, for each element, compute the absolute value of the error in specific heat c , and divide it by the true value of the specific heat: –

$$\frac{|c(\text{DP}) - c(\text{modern})|}{c(\text{modern})}$$

The mean of these specific heat errors is 13.3% for the whole set of 13 elements, and it is still 2.9% when cobalt and tellurium are excluded. Now for each element, compute the absolute value of the deviation of DP atomic heat capacities from their mean value, and divide it by that mean atomic heat capacity:

$$\frac{|C(\text{DP}) - \langle C(\text{DP}) \rangle|}{\langle C(\text{DP}) \rangle}$$

The mean of these deviations is just 1.0%.

As mentioned above, the selection of modern data to be used for comparison to DP data is somewhat arbitrary. The computations carried out above employed the heat capacities of the thermodynamically stable form at 0°C for both tin and sulfur, the two elements that have two allotropes. In the case of tin, the 0°C allotrope (gray) has a heat capacity closer to the DP value than the less stable one (white); in the case of sulfur, the 0°C allotrope (rhombohedral) has a heat capacity further from the DP value than the less stable one (monoclinic). Giving the DP data the benefit of a doubt by using the modern data that are closer to those DP data (i.e., keeping the more stable form of tin and using the less stable form of sulfur) still leads to a strong conclusion of fraud.

Using an atomic heat capacity of 24.0 J mol⁻¹ K⁻¹ (instead of 23.0) and a specific heat of 0.748 J g⁻¹ K⁻¹ (instead of 0.717) for sulfur does indeed reduce the range (to 2.19, compared to 3.19) and variance (to 0.419, compared to 0.670) of the modern atomic heat capacities. (After all, sulfur was, and remains, the element with the lowest atomic heat capacity.) The F statistic becomes 4.11, no longer significant at the 0.5% level, but still significant at the 2.5% level. The assertion that atomic heat capacities are just too constant is still a probable

one, but one which cannot be asserted with quite the same level of confidence. The other horn of improbability, however, is even stronger with this choice of modern data. With the modern atomic and specific heat capacities for sulfur more in line with the rest of the DP data, the DP specific heats of tellurium and cobalt stand out as all the more anomalous. The distribution of specific heat errors is still not normal. The error of

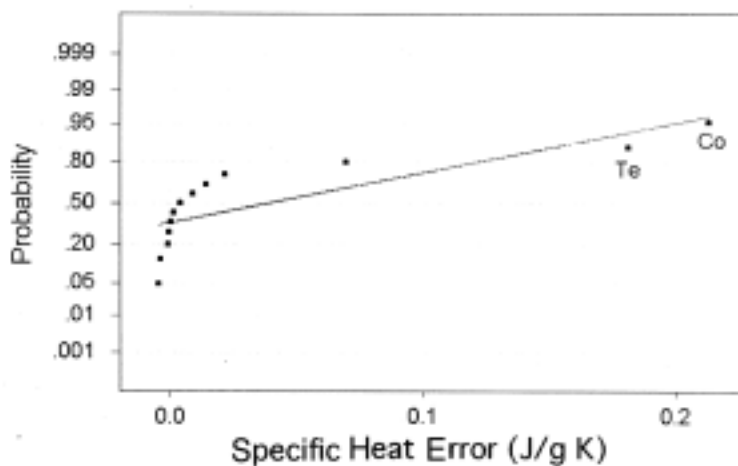


Figure Normal probability plot of errors in DP specific heat. The plotted points are distributed along the horizontal axis as the actual errors are distributed and along the vertical axis as normally distributed errors. If the actual errors were normally distributed, they would fall approximately along a straight line.

specific heat for tellurium is more than 13 standard deviations away from the mean error defined by the other 11 data points; that of cobalt is nearly 16 standard deviations away. How such specific heat outliers can lead to atomic heat capacities even as constant as the modern data (let alone even slightly more constant) is inexplicable.

To test the robustness of the statistical conclusions, I used yet one more set of modern data, a tabulation of heat capacities of the elements at 25°C and 1 bar (25). Although there are good reasons to believe that this set of data is less appropriate as a reference set than the previous ones (mainly because of the different temperature), it is worthwhile to see whether such a perturbation in the reference data alters the statistical conclusion. These room-temperature data have slightly different heat capacities because of the temperature difference, and they reflect yet another selection of allotropes, white tin and rhombohedral sulfur. The DP atomic heat capacities still have a smaller variance than the reference data ($F = 10.9$, significant at 0.5% level). The distribution of specific heat errors is still not normal. The error of specific heat for tellurium is more than seven standard deviations away from the mean error defined by the other 11 data points; that of cobalt is more than eight standard deviations away.

3. Discussion

It is natural to speculate: (a) that Dulong and Petit concluded the atomic heat capacity was constant, either empirically on the basis of fewer elements than they listed or theoretically, and (b) that they computed specific heats consistent with their law and with their best estimates of atomic weights for at least some of the elements in their table, including tellurium and cobalt. Is there any evidence to support this speculation? Is there any way of knowing whether tellurium and cobalt were the only two pieces of fabricated data? Are there ways to explain the data without fabrication of specific heat data (including fabrication or biased selection of atomic weight data)? Carrying out the F test without data on tellurium and cobalt still suggests that the DP data are too good to be true. In other words, tellurium and cobalt appear certainly fraudulent, because they neatly compensate large errors in atomic weight, but other specific heats appear to have been chosen to give a product of specific heat and atomic weight close to the constant value as well. (The F statistic for the 11 data points without cobalt or tellurium is 11.2, still much greater than the critical value of 5.85 (0.5% significance level,

one-tailed test) (26). Which other data were made up, however, is not obvious.

Dulong and Petit had reported specific heats of several substances in their 1817 paper concerned primarily with thermometry and cooling laws (7). In that paper, they reported specific heats measured over a wide range of temperatures by the method of mixtures (plunging a sample into a liquid of known specific heat). Interested in the variation of specific heat with temperature, they reported mean specific heats for the ranges 0-100°C and 0-300°C for seven elements. Five of these (iron, zinc, silver, copper, and platinum) would later appear in the table of data on which the Dulong and Petit law was based; the other two were mercury and antimony. One might guess that Dulong and Petit formulated their law on the basis of these specific heats and then fabricated some of the others; however, this is simply speculation (27).

Three of the elements (copper, zinc, and silver) listed in both papers have identical specific heats to four figures, which is in itself rather suspicious. After all, the 1819 values were measured by the method of cooling over a temperature range reported to be at most 0-10°C; the 1817 values were measured by the method of mixtures over a temperature range reported to be 0-100°C. The absolute agreement to four figures of two methods at two slightly different temperature ranges is suspicious, particularly in light of the quite notable temperature differences reported in the 1817 paper: specific heats at 0-100°C were some 5-10% lower than those reported for 0-300°C. Perhaps Dulong and Petit did not measure the specific heats of these elements again in 1819 by the method described. A fourth element, iron, has only a minuscule difference in specific heats (0.2%) between the two papers. The fifth element common to both papers, platinum, raises additional questions.

The comedy of errors surrounding the platinum data makes it very difficult to judge whether fraud, or simply carelessness, was at work. In the 1819 paper the numbers printed for platinum do not "add up;" the actual product of the printed specific heat (0.0314) and atomic weight (11.16) is 0.3504, not 0.3740 as printed. Because the printed value of 0.3740 is clearly in the narrow range of atomic heat capacities listed by Dulong and Petit, whereas the actual product would be a serious outlier (more than five standard deviations away from the mean of the remaining atomic heat capacities), it is fairly clear that the product is printed correctly and that one of the factors was misprinted. Which factor? That

the atomic weight of platinum is a misprint has been proposed by several authors, for the printed 11.16 is close to, but not a simple multiple of, Berzelius' 1818 atomic weight of 12.15. But the product of specific heat 0.0314 and putative atomic weight 12.15 is 0.3815, not the printed 0.3740. If 11.16 were a misprint, then, it would have to be a misprint for $0.3740/0.0314 = 11.91$. Could a printer's error have rotated the digits 16 into 91 (28)? It is also possible that the specific heat is the misprinted factor, and that the intended specific heat was $0.3740/11.16 = 0.0335$. A transcription error of 0.0314 for 0.0335 is plausible when one notes that the number directly below the specific heat of platinum is that of tin, 0.0514. Jan van Spronsen found additional provenance for the figure 0.0335 in a German translation of the 1817 paper of Dulong and Petit (which he cited as *J. Chem. Phys. (Schweigger)* 1819, 25, 304); the French original has 0.0355 instead. Van Spronsen asserted that the German translation had the correct value, and that the original French publication had 0.0355 as a misprint (19). Although the profusion of misprints sounds improbable, I propose two additional reasons for believing van Spronsen was correct. First, in the 1817 paper (French version), platinum was the only substance listed as having an identical specific heat over the 0-100°C and 0-300°C ranges; although the specific heat of platinum does, in fact, have a weaker temperature dependence than the other elements studied in the 1817 paper, it is not much smaller than that of silver and copper, for which Dulong and Petit reported different specific heats over the different temperature ranges. Therefore, it is quite likely that the specific heat measured for platinum in 1817 over either 0-100° or 0-300° was not the printed value of 0.0355. Second, we have already seen Dulong and Petit recycle specific heats from their 1817 paper in their 1819 paper (29).

This detailed scrutiny of the figures reported for platinum leaves unanswered (so far) the question of the provenance of the atomic weight (whether we take it to be 11.16 or 11.91), which is not simply related to published atomic weights available at the time. In light of the suspicion of fabrication already cast, is it not reasonable to guess that the atomic weight was fabricated, obtained by dividing 0.3740 by the measured specific heat (0.0335 or 0.0314)?

If so, another question must be raised—one that ought to be brought up in any event.

Is it possible that Dulong and Petit actually measured specific heats and simply adjusted atomic weights or even selected atomic weights (from a variety of published sources) with a bias that led to the constancy of atomic heat capacities? Note that I am not referring here to arbitrary factors of small-integer ratios mentioned above, but to atomic weights based on assorted chemical analyses published by different investigators.

At first blush, this appears to be a promising alternative. After all, platinum seems to be an example of atomic weight fabrication or selection. Furthermore, the DP paper explicitly stated that they measured specific heats, including a detailed description of how they did so, whereas it said next to nothing about sources of their atomic weight data. Dulong and Petit stated that published specific heats then available were highly unreliable, showing great variation from one experimenter to another, and including values "three or four times as great as they ought to be" (9). Surely they would not have made such pointed remarks about the measurement of specific heats if they had fabricated specific heats.

Upon further examination, however, the hypothesis of atomic weight fabrication or biased selection must fall. For one thing, notwithstanding their statements to the contrary, Dulong and Petit recycled some specific heat measurements from a previous paper, despite their descriptions of method and apparatus. More conclusively, it is quite clear that Dulong and Petit used a single set of atomic weights (based on analyses published in 1818 by Berzelius (30)), with the apparent exception of

TABLE 5. Atomic weight ($\alpha = 1$)

Element	DP	Berzelius (30)	Berzelius/DP
Bismuth	13.30	17.738	1.334
Lead	12.95	25.8900	1.999
Gold	12.43	24.8600	2.000
Platinum	11.16	12.1523	1.089
Tin	7.35	14.7058	2.001
Silver	6.75	27.0321	4.005
Zinc	4.03	8.0645	2.001
Tellurium	4.03	8.0645	2.001
Copper	3.957	7.9139	2.000
Nickel	3.69	7.3951	2.004
Iron	3.392	6.7843	2.000
Cobalt	2.46	7.3800	3.000
Sulfur	2.011	2.0116	1.000

platinum, as the basis for their atomic weights (31). Table V displays the DP atomic weights and the 1818 Berzelian atomic weights and their ratios; with the exception of platinum, the ratios are those of small integers to at least three significant figures. Dulong and Petit may have selected the small-integer ratios to make the law work (32); however, they did not search for atomic weights that narrowed the variation among their atomic heat capacities.

Historiography of the Dulong and Petit Law

Why was this alleged fabrication undetected for so long? First of all, it is not surprising that it escaped detection of Dulong and Petit's contemporaries. Accurate atomic weights and specific heats were not available at the time. (Indeed, one can find the DP specific heats for cobalt and tellurium in a textbook published more than 20 years later (33)!) Furthermore, the statistical concept of variance and inferential statistical tests such as the F test were not yet available either. Although the accuracy of the Dulong and Petit law was questioned and tested since its announcement, the provenance of the data was not.

Two history of science papers from the 1960s involved the Dulong and Petit law: Robert Fox, "The Background to the Discovery of Dulong and Petit's Law" (8) and Jan van Spronsen, "The History and Prehistory of the Law of Dulong and Petit as Applied to the Determination of Atomic Weights" (19). In neither case did the authors suspect Dulong and Petit of data fabrication. Although both provided valuable insights, including leads relevant to this paper, there are, naturally, some conclusions in these papers incompatible with data fabrication.

In particular, Fox begins his paper by examining a story told by Jean-Baptiste Dumas that Dulong and Petit were pushed into announcing their law by a "calculated indiscretion" of François Arago, Petit's brother-in-law. Fox was initially skeptical of this account, told 60 years after the fact solely by someone (Dumas) who was not there. Fox concluded, however, that the account was essentially substantiated, that the Dulong and Petit law was indeed unexpected and not part of a deliberate program of research. Of course, a fabricated result cannot be unexpected, so the present work is clearly contradictory to Fox on this point. On the other hand, pressure to announce the law hastily could have provided a motive for data fabrication.

Van Spronsen makes note of the compensating errors in the DP specific heat and atomic weight of tellurium, stating that Dulong and Petit found an inaccurate value for the specific heat, which led them to elect an atomic weight value half of the true value.

Slightly earlier, Gates wrote a brief note to the *Journal of Chemical Education* on Dulong and Petit, responding to a paper on the development of calorimetry (18). His letter clearly identifies the source of the DP atomic weights; however, it is less perceptive about suspicious data, speaking of compensating errors (about platinum in this case). More than 20 years later, when Schwarz discovered "at least, a bit of wishful thinking" in their results, Gates wrote another letter defending Dulong and Petit, who, he said, simply adjusted the atomic weights of cobalt and tellurium, as they had adjusted many other atomic weights, by small-integer ratios. In these cases, however, the adjustment was wrong because it was "based on grossly inaccurate specific heat measurements" (34).

Schwarz was researching relationships among atomic heat capacities, a subject upon which he reported to the Chemical Education division at the Spring 1986 National Meeting of the American Chemical Society. The currency of the topic of cheating in research prompted him to write a letter to *Chemical and Engineering News* the following year in which he reported the suspicious tellurium and cobalt data (3). To the best of my knowledge, this letter is the first and only accusation of fraud that has appeared in the chemical literature.

Meanwhile Macinnis, an Australian science writer and educator, noted and discussed the fabrication of some of the DP data on the Australian Broadcasting Corporation radio program "Ockham's Razor." That program was included in a book of scripts from the show. Macinnis has repeated the tale for a computer list on fraud in science, and in personal correspondence to the author (35).

Macinnis told me that the fabrication had been noted in print, somewhere around 1985, he thought, possibly in the *Journal of Chemical Education*. I have not been able to find such a paper (except for Schwarz's letter) in either the chemical literature or the history of science literature. I made an informal inquiry to the history of chemistry internet list (CHEM-HIST) for leads on the possible "fudging" of data by Dulong and Petit. The only responses I received mentioned the adjustment of

atomic weights by small-integer ratios. I am, therefore, left with the impression that the insights of Macinnis and Schwarz have not penetrated the history of science community because of where those insights appeared.

Conclusion

At least some of the data upon which Dulong and Petit based their law of constant atomic heat capacity appears to have been fabricated. In particular, the specific heats of cobalt and tellurium, which Dulong and Petit state they measured, appear to have been fabricated. Other specific heats may have been fabricated as well, or at least recycled from an earlier publication that was supposed to have involved a different measurement method and temperature range. Any suspicion of data fabrication seems to have gone unnoticed, or at least unreported, until the middle 1980s; and it has not appeared in a scholarly publication until the present article.

ACKNOWLEDGMENTS

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- were unequal, a two-tailed test would be appropriate, and the quoted critical value would represent a 1% confidence level (0.5% at each end of the distribution).
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 27. Fox (Ref. 8) noted of the heat capacities reported in this paper, "So accurate were the results obtained that the Dulong and Petit law could easily have been deduced from them." Because they made no such deduction, Fox inferred that Dulong and Petit were not interested in atomic heat capacities at that time.
 28. Paul Schwarz raised this point during the discussion period following the presentation of this paper in San Diego. Close inspection of the typeface used in the 1819 paper shows that the "r" has 180° rotational symmetry, while the "6" and "9" are related by a 180° rotation about the center of the closed loop.
 29. The statistical analyses reported above, in particular the extent to which specific heat errors for tellurium and cobalt are outliers from the rest of the reported DP specific heats, are unaffected by the choice of the printed 0.0314 or the inferred 0.0335 as the DP specific heat of platinum.
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BOOK REVIEWS

Scaling Up: The Institution of Chemical Engineers and the Rise of a New Profession. Colin Divall and Sean F. Johnston, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000, 347 pp., £83 (£50 to IChemE members).

Chemical engineering, as a profession, has traditionally found itself at the intersection of chemistry and engineering (especially mechanical engineering in its early history). Balancing itself between these two has not always been an easy task. As a result, the role of the chemical engineer has not always been clearly understood. Indeed, George E. Davis, considered by many as one of the “founding fathers” of chemical engineering, stated in the very beginning of his seminal work, *A Handbook of Chemical Engineering* (1901), “The functions of the Chemical Engineer are very generally misunderstood.” Excerpts from this work are included in the authors’ book.

This misunderstanding, along with a strong resistance of industrial chemists to relinquish any of their “turf” to this new profession, created significant challenges to the development of chemical engineering. The authors have effectively covered the problems of this burgeoning profession as it struggled for acceptance in Britain. They have done an excellent job of meshing the history of the profession with the history of its professional society in Britain, the Institution of Chemical Engineers (IChemE). Both aspects are covered in sufficient detail to provide a complete story but not in such excess detail as to make it burdensome for the reader.

James F. Donnelly has contributed an excellent chapter on the early history of chemical engineering before the First World War. The authors show how the development of university courses in chemical engineering (often taught by chemists) influenced the growth of the profession. They also show the effect of the two world wars on the development of the profession and its acceptance by both government and industry. They discuss the influence of these two entities on the formation and expansion of IChemE. The authors cover the rapid growth of the chemical and petrochemical industries following the Second World War and how this helped to promote both the profession and IChemE. They show the relationship between the institution and other chemical and engineering organizations and how these relationships impacted, both positively and negatively, its development.

Scaling Up is an excellent history of the chemical engineering profession in Britain and the development and growth of the Institution of Chemical Engineers. It is well laid out and the text is generally easy to read. The authors use a number of acronyms, many of which are not readily recognizable to someone from the U.S., but they define each at first use and include a list for ready reference. Unfortunately, there are very few illustrations and no photographs.

Overall, it is a highly recommended book for anyone interested in the history of chemical engineering. The price is a little high, but worth it for those who really want to learn how it all began. *Stanley I. Proctor, Proctor Consulting Services, Chesterfield, MO 63017.*

Mauve: How One Man Invented a Color that Changed the World. Simon Garfield, W. W. Norton & Company, New York, 2001. 222 pp, Cloth (Typeset), \$ 23.95.

The days when accounts of the romance and history of chemical industry attracted a large readership among the public are long gone. It has become increasingly difficult to find any powerful nostalgic pull. Enthusiasm has been replaced by cynicism, chemistry is no longer the leading science, and industrial organic chemistry has often reinvented itself as the life-sciences industry. Those publications on the development of chemical industry that do appear nowadays tend to be self-serving corporate promotional exercises, or short-run, low-readership, over-priced academic tomes (generally prepared from camera-ready copy). In the meantime, many of the great chemical firms that dominated the 20th-century scene and developed the products on which modern society relies have lost their identities, generally through takeovers, mergers, bankruptcy, and dismemberment, particularly the process known as “spin off.”

While we cannot expect much in the way of lamentation for lost corporate names, it is a sad state of affairs when, at a time of great technological and business change, the achievements and contributions of chemical industry as part of the “old economy” are hardly known outside of industry and a handful of historians. But, perhaps, all is not lost. A new genre of industrial histories may well be on the way—well-researched, balanced, readable, and exciting. The authors are award-winning journalists and science writers. And, in their fascination with history and quest for accuracy, they rely on original sources, interviews, and—most heartening—the academic scholarships of both historians and practitioners of chemistry.

Mauve is one of the first of the new breed. Its author, Simon Garfield, is recipient of the prestigious Somerset Maugham Prize. His beautifully produced small-format volume charmingly informs the layperson that there is a direct lineage from William Perkin’s much-heralded discovery of the first aniline dye to such corporations as BASF, Bayer, Hoechst, ICI, Du Pont, Ciba, and Geigy. While this is the theme, and there is plenty of detail of the early years, there are frequent and disarming changes of focus, though always linked, one way or another, by the color mauve or the range of human activities that it helped to spawn.

Garfield’s main story is perhaps too well-known to readers of this journal to justify more than a reminder.

In the Easter vacation of 1856 the teenaged William Perkin, inspired by a suggestion put out by his boss, August Wilhelm Hofmann, head of the Royal College of Chemistry in London, attempted to synthesize the important natural drug quinine from allytoluidine. Perkin’s experiment failed, but his efforts were not in vain. On repeating the reaction with aniline, he obtained a solution that dyed silk a beautiful purple. Believing that he had stumbled across a useful commercial colorant (and why not, since some of the most successful were made from all manner of waste, including bird excrement), Perkin decided to file a patent for the process. Though he had little idea of what the market was worth, he gained the confidence of his father and brother George, who together erected a small factory in a remote part of northwest London called Greenford Green. By the end of 1858 they were in the business of manufacturing from coal-tar benzene what was originally called Tyrian purple, but that in 1859 acquired the name mauve from the fashionable ladies of London. It was the beginning of synthetic dyestuffs and, by extension, the modern organic chemical industry.

This odyssey is divided into two main sections, Invention and Exploitation. The first deals with the discovery and manufacture of mauve and the second with where it led. The account of Perkin’s early work is accessible in both style and content, providing a fresh interpretation for the historian, and an ideal conceptual framework for the lay reader through joining the moment of discovery with celebratory events in 1906 and 1956. Mauve fired the hearts and imaginations of generations of chemists. Perkin, however, retired from the business in 1873 after making a second fortune with synthetic alizarin. He realized then that the Germans had cornered the science, the technology, and the markets.

Garfield’s biographical details are based on his own thorough research, as well as the many accounts that have appeared in the United Kingdom and the United States. The gallery of greats that get into the story include individuals such as Caro, Duisberg, von Baeyer, Graebe, and Liebermann, and all major firms that have dabbled in synthetic dyestuffs. Garfield leads us through the myriad connections between the 19th-century coal-tar colors and the 20th century successors, particularly, salvarsan, prontosil, the sulfonamides, and Bakelite. He goes on to the present, when phthalocyanine colorants, a British invention of the 1930s, are employed in cancer therapy, natural dyes are being reinvestigated as inks for computer printers, and, of course, the fashion world

continues to expect its colors on demand. He does not forget environmental problems and difficulties with toxic byproducts encountered and produced by the industry, starting with the 1860 fuchsin process that employed arsenic acid as an oxidant.

The great achievement of this book is that Garfield has taken a story that has been endlessly rewritten for different audiences and at different times, and refashioned it into a form that will appeal strongly to modern-day readers—not just students and teachers of science, but anyone interested in the origins of our modern world.

The nature of journalism is often to make things more important than they are, or might really be. While there may be good reason to criticize or condemn this approach, it is certainly an effective tool, as used here, in drawing the public's attention to what we are trying to tell each other in our muted tones. That is one of several reasons why this book should also be read by serious historians. *Anthony S. Travis, Sidney M. Edelstein Center for the History of Science, Technology, and Medicine, The Hebrew University of Jerusalem, Jerusalem ISRAEL 91904.*

Linus Pauling: Scientist and Peacemaker. Clifford Mead and Thomas Hager, Ed., Oregon State University Press, Corvallis, OR, 2001. [x] + 272 pp, Cloth, ISBN 0-87071-489-9. \$35.00.

The preface to this centenary volume for Linus Pauling indicates that it is modeled on those for Albert Einstein and Niels Bohr published by Harvard University Press about twenty years ago. Thus, even though the editors do not specifically say so, the intended audience should, by analogy, be “the general public, as well as professional [chemists] and teachers of science.” Like those two earlier volumes, this one also presents a variety of pieces by and about its subject, and the collection includes some material in print for the first time from the Ava Helen and Linus Pauling Papers at Oregon State University. The variety of pieces is both the strength and weakness of this collection.

According to the editors, the pieces were chosen for this volume on the basis of their “quality and comprehensiveness” though there is no claim for a complete picture of this “multi-faceted crystal with many dimensions,” as Pauling once described himself. The book consists of three major sections, The Man, The Science, and The Peace Work; a shorter fourth section entitled Facets; and a Selected Bibliography, which lists about one hundred of Pauling's 1100 published articles, most of his sixteen books, and twenty books and articles about Pauling. Facets is in some ways the most interesting part of this collection. Certainly the best for browsing,

it contains snippets of writing both by and about Pauling. These snippets provide insights—often humorous ones—into Pauling's character in terms of what he tended to notice and what others tended to notice about him.

For example, one snippet suggests that Pauling did not suffer the same fate that Niels Bohr did, as noted by the editors of the latter's 1985 centenary volume: “Bohr . . . is different [from Einstein] in that his name, although known to every student of natural science, is not widely recognized by the public.” Early one morning in the 1960s Richard Feynman “found himself sharing a ride through the desert with a trio of [Las Vegas] prostitutes . . . and when Feynman told the group that he was a researcher at Caltech, he was surprised to hear one of the women reply, ‘Oh, isn't that the place where the scientist Pauling comes from?’ . . . The women . . . had read about him in a recent issue of *Time* magazine, in a cover story about U.S. science that they had combed through for pictures of the youngest and handsomest researchers.” Of course, Pauling's name became even more widely recognized by the public with his winning of the Nobel Peace Prize for 1962 and his notoriety in the 1970s and 1980s in connection with combating maladies from colds to cancer with megadoses of vitamin C.

In another anecdote William Lipscomb tells how Pauling had his beard shaved off during a transcontinental train ride in the 1930s. “Ever conscious of his image as seen by others, he returned to his seat by Ava

Helen and pretended to make advances which sprained the eyebrows of several other passengers who were saying 'Just wait 'til the guy with the beard comes back.'" And another story about Pauling as he was leaving the office of one of his graduate students: he paused and picked up "a small device consisting of an eyepiece with a lens containing a photograph which could only be viewed by looking directly into it against a strong light. The photograph was that of a beautiful girl, completely naked, standing on a large black rock in the middle of a rushing mountain stream. Pauling . . . clapped it to his eye. 'Hmmm,' he said. 'Basalt.' And he walked out without another word."

The three major sections are less humorous and somewhat more uneven. Each contains pieces by Pauling, an interview with Pauling, and, except for the third section (The Peace Work), pieces by others about Pauling. The first section begins with "The Roots of Genius" by Tom Hager, one of the editors. He notes that while it is easy to understand the events of Pauling's life—he has, in fact, written two of the some half dozen biographies—"understanding Pauling at deeper levels" is more difficult. Adept at posing penetrating questions, Hager admits that many of them remain unanswered, but this piece does offer valuable insights into "Pauling's sometimes contradictory genius" and provides clues about his character to keep in mind while reading subsequent pieces.

Hager also has an interesting piece in the second section, The Science. "The Triple Helix" examines Pauling's loss to Watson and Crick in determining the structure of DNA and provides a counterpoint from Pauling's perspective to Watson's version in *The Double Helix*. Watson, as well as some historians of science, has attributed Pauling's failure with DNA to the Federal government's refusal to issue him a passport to travel to England in May 1952 since that prevented him from seeing Rosalind Franklin's X-ray photographs. As a result of the ensuing uproar, however, Pauling did receive a passport in time to attend two international meetings in France in July 1952. Afterwards, he spent a month in England without ever bothering to visit Franklin or trying to see her data. Hager argues that Pauling's failure was actually due to three unrelated factors: his focus on proteins, his lack of adequate data, and his pride. Pauling's youngest son Crellin adds another twist to this story in a snippet in Facets. In August 1948 Pauling crossed the Atlantic on the same ship as Erwin Chargaff, whose findings that adenine and thymine, as well as guanine and cytosine, are present

in equal amounts in DNA were crucial in Watson and Crick's eventual unraveling of the DNA structure. Pauling later mused that if he hadn't heard about those results "straight from the horse's mouth"—a horse that had a reputation for being headstrong—and had read about them instead, he might have paid more attention to them and recognized their true significance. But, of course, he didn't, and that's part of the story of DNA.

Although Pauling is invariably the most interesting writer on Pauling, *The Man and The Peace Work* might have benefited from insights by others. Other views—particularly about his antinuclear activities, the Nobel Peace Prize, his opinions about vitamin C, and his difficulties at Caltech—could have added more corners to the "cubistic view" of Pauling in each of the three major sections. The transcript of Pauling's 1958 interview on *Meet the Press* is one of the few pieces that deals with the negative popular attitudes toward Pauling and his antiwar activities at the time. It is particularly surprising that there are no pieces by Ava Helen Pauling—if such pieces exist—since Pauling characterizes his meeting her as "the event that had the greatest effect on my life." He also describes her specific influence on him in the late 1940s in his becoming a social activist in "An Episode That Changed My Life."

The Science section does contain interesting pieces by other writers, especially "The Scientific Contributions of Linus Pauling" by Jack Dunitz, which was taken from an appreciation that appeared in *Biographical Memoirs of Fellows of the Royal Society*. The majority of pieces in this section, both by Pauling and by others, focus on biological topics, and this section expanded my view of him as a scientist. Many of the pieces in this section, as well the other sections, are not dated—nearly half in all. This is understandable for reminiscences by Pauling that he may have left undated, but the editors should have noted the dates of other pieces when they were known.

This is a minor drawback to a collection that is far stronger on the positive side than the negative. Although I might quibble with a few of the editors' choices, they are generally interesting and informative and contribute to the overall "view of a fascinating man." The book is strewn with wonderful photographs of Pauling from every stage of his life, from a five-year-old in furry chaps to an old man with his trademark beret. There is even one of Pauling "as a good-looking little gal" at a fraternity smoker in 1920! The photograph of Linus and Ava Helen Pauling at the Nobel ceremonies in 1963 shows

how much they came to resemble each other after forty years of marriage since several pictures of them as a young couple show no such resemblance. There are also short quotes from interviews conducted by Tom Hager dispersed throughout the book as Marginalia. Although these occasionally duplicate material in the text, they add to the “cubistic view.”

This collection expanded my view of Pauling considerably, from that of primarily a physical chemist, the author of *The Nature of the Chemical Bond*, and an originator of the valence-bond model, to a scientist broadly interested in applying his knowledge of chemistry to biological and medical problems, as well as one committed to using his own prestige for social activism in warning the world of the dangers of nuclear war. In comparing how he valued the two Nobel prizes, Pauling wrote, “the Nobel Prize in Chemistry pleased me immensely, but . . . it was given to me for enjoying myself—for carrying out researches in chemistry that I enjoyed carrying out. On the other hand, I felt that the Nobel Peace Prize was an indication to me that I had done my duty as a human being—my duty to my fellow human beings.” This collection succeeds in presenting

the picture of a remarkable human being, who divided his energies between what he enjoyed doing and what he felt obligated to do.

The editors specifically refer to two kinds of readers of this book. The “more knowledgeable scholars” whom they mention in the preface may find “new and perhaps valuable source materials” here, but I doubt that “first-time readers about Pauling” will find this a particularly satisfying book. It succeeds quite well on its own terms, a “mosaic . . . almost cubistic view . . . of one of the central scientists in twentieth-century history,” but it is too fractured a view for someone wanting to learn about Pauling for the first time. Instead, a reader who has some knowledge of Pauling’s life and work, but who wants to learn more, should find this a fascinating collection. I found it more and more intriguing as I went back and dipped into it here and there after initially reading it straight through. It has motivated me to read more about Pauling, especially one (or perhaps even both) of the books by Tom Hager. *Richard E. Rice, General Education Program, James Madison University, Harrisonburg, VA 22807.*

Chemical Sciences in the 20th Century. Carsten Reinhardt, Ed., Wiley-VCH, Weinheim, 2000. 281 pp, ISBN 3-527-30271-9, DM 158.

Chemistry in the twentieth century has seen unprecedented growth in both the depth and the breadth of its understanding of scientific phenomena. The complexity and the varied interrelationships among the sciences and their changing perspectives on what constitutes a particular area of study have caused many science historians to examine this area of twentieth century chemistry in a new light. Indeed they have expressed a strong interest in cross-disciplinary studies involving this era. It was the European Science Foundation, desirous of bringing together an international network of historians of chemistry and of addressing the new realities of twentieth century chemistry, that began a five-year program focusing on the evolution of chemistry. They formed the Commission on the History of Modern Chemistry in 1997. The first confer-

ence of the commission, focused on “Between Physics and Biology: Chemical Sciences in the Twentieth Century,” was held in Munich in 1999. Most of the papers and clearly the main ideas in this collection came out of the conference. The aim of this book is to bridge the boundaries between chemistry and the other sciences as well as to illustrate how chemistry interfaces with technology and mathematics.

The contributors propose to explore these interdisciplinary developments in three sections covering the areas of theoretical chemistry, nuclear chemistry and cosmochemistry, and the newest area of solid-state chemistry and biotechnology. An important addition was the chapter on disciplinary changes in organic chemistry, which is actually divided into four areas of study. The contributing authors are internationally recognized in their areas and able to address the issues raised in their respective disciplines. The number of references and notes per chapter varied from four in a short chap-

ter to 118. The editor reminds the reader early that disciplines create unity, that the existence of hybrid fields helps to forward the unity of science, that disciplinary identity in chemistry does exist and yet most chemists are involved in activities from the territory of several disciplines.

The first chapter covers the various factors that have impacted on the development of organic chemistry since 1900 and how organic chemistry played a major role in the creation and expansion of the new discipline of bioinorganic chemistry. Three central areas are explored. It is pointed out how this dominant area of organic chemistry is impacted by physical chemistry to give rise to physical organic chemistry. Then it is noted that classical structural chemistry is replaced by physical instrumentation with a major impetus coming from industrial companies that promoted techniques such as ultraviolet spectroscopy, infrared spectroscopy, nuclear magnetic resonance, and X-ray crystallography. Lastly, the origin and growth of bioinorganic chemistry are traced as chemists seek to understand biological reactions at the level of organic reaction mechanisms; and the areas of chemistry and biology secure a small degree of unity.

In the next section one explores the origin and development of quantum and theoretical chemistry. Several questions are examined, such as the reduction of chemistry to physics: the degree to which mathematics should enter chemistry; and to what extent theoretical methods can explain chemical behavior. The emergence of quantum chemistry is explored by considering the impact of textbooks and computers and how specific chemical ideas such as the chemical bond and resonance are affected. Two chapters in this section describe the efforts of Giovanni Bonino to establish quantum chemistry in Italy and of Jean Barriol in setting up the theoretical chemistry laboratory in Nancy, France. The influence that social and political factors can have in the establishment of a discipline is also examined in these two chapters.

The following section covers changes from radiochemistry to nuclear chemistry and cosmochemistry, which are viewed as completely interdisciplinary fields. Chapter 6 outlines the section and identifies four critical issues to consider: the approaches to weigh physical evidence in these areas; the relationship between identification and production of a new element; the way

in which artificial elements are viewed relative to natural elements; and relationships illustrated by these new fields. The interplay between chemistry and physics is presented in the next two chapters. The work of the Noddacks in their successful discovery of element 75-Rhenium but their failure with element 43 is traced to their utilization of traditional chemical means but not of newer nuclear techniques. Then follows a description of the delay of discovery of nuclear fission, caused by limited interdisciplinary collaboration, and how this discovery resulted in improved knowledge of nuclear behavior and clarification and extension of the periodic table. The last chapter of this section shows how cosmochemistry grew from achievements in geochemistry, meteorite science, astrophysics, and nuclear physics to become an established field of science that is completely interdisciplinary in nature.

The last section comprises an introductory chapter and four other chapters focusing on solid-state chemistry and biotechnology. In chapter eleven it is argued that biotechnology is not a new area but existed in an earlier decade and was reflected in academic/industrial cooperation in such areas as hormone production, fermentation advances, and plant hormone studies that resulted in various agricultural herbicides. The next chapter covers the building of polymer science from organic chemistry and the physical chemistry of polymers. Chapter 13 is a case study of the work of Michael Polanyi, who used both chemistry and physics in his scientific work but also became a philosopher who reflected on the boundaries of science and the humanities. The last chapter is a reflection on various aspects of the history of the still emerging area of material science research covering such developments as the contributions of metallurgy and polymer science to the beginning of materials science and the triumph of function over structure that resulted in composite materials.

Overall this book will be a useful addition to the library of anyone interested in recent chemical trends. Many challenging ideas are presented, which are to be evaluated by the individual reader; and this is part of the strength of this book. It is hoped there will be additional studies in this emerging area of the history of chemistry. *Robert H. Goldsmith, Department of Chemistry, St. Mary's College of Maryland, St. Mary's City, MD 20686.*

Transforming Matter. A History of Chemistry from Alchemy to the Buckyball. Trevor H. Levere, Johns Hopkins University Press, Baltimore, MD, 2001, 215 pp, paper, \$17.95.

This new history of chemistry is impressive in its coverage with only 199 pages of text (16 pages for notes and index)—much shorter than Brock's history published about ten years ago. It could be very useful for chemistry courses and for courses in history of all the sciences. Levere's book is short enough to be used and would enable better coverage of chemistry than usually happens in such survey courses. The writing is excellent with occasional insightful epistemological comments. For example, p. 51, "Words change their meaning as time passes."

Levere's history of chemistry is particularly strong from alchemy through Lavoisier. Alchemy and other developments preceding Lavoisier are presented in depth. Black, Hales, Cavendish, and Priestley are covered very well with an economy of words. Lavoisier's

work is beautifully explained with detailed drawings of the gasometer and the ice calorimeter. With each drawing is an explanation of how experiments were carried out with the instrument. Such inserts with drawings and explanations are a feature of this book. The last chapter, "Where Now and What Next? New Frontiers", is only 18 pages but includes five of these presentations which give those topics (e.g., Buckyball and DNA) some depth. On p. 23 is a marvelous short summary of Renaissance metalworking with a drawing taken from Agricola.

After Lavoisier, the chapters are: 8. The Rise of Organic Chemistry; 9. Atomic Weights Revisited; 10. The Birth of the Teaching-Research Laboratory; 11. Atoms in Space; 12. Physical Chemistry; 13. The Nature of the Chemical Bond; and 14. New Frontiers.

Brock's "The Norton History of Chemistry" covers more areas of modern chemistry, but in only 199 pages of text Levere gives impressive insight into the development of chemistry. *Paul Haake, Wesleyan University, Middletown, CT 06459*

Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production. V. Smil, The MIT Press, Cambridge, MA, 2001, xvii + 338 pp. Hardcover, \$34.95.

This comprehensive account of the discovery and commercialization of ammonia synthesis by Fritz Haber and Carl Bosch extends from historical uses of nitrogen in agriculture to the use of synthetic fertilizers and their impact on the environment. The author, Vaclav Smil, Distinguished Professor of Geography at the University of Manitoba, provides extensive notes and references for each chapter, along with graphs, charts, and appendixes to accompany the text.

The book begins by highlighting the important discoveries that elucidated the role of nitrogen in agriculture. Although the significance of nitrogen in agriculture was recognized by the late 1830s, the mechanism by which it was assimilated was unknown. Justus von Liebig pondered, "How and in what form does nature

furnish nitrogen to vegetable albumen, and gluten, to fruits and seeds?" Jean-Baptiste Boussingault became the first researcher, in 1838, to recognize the ability of legumes to restore nitrogen to the soil. Subsequent work by Théophile Schloesing in 1877 demonstrated the ability of bacteria to fix nitrogen. The biospheric nitrogen cycle was complete when researchers led by Ulysse Gayon isolated pure cultures of bacteria capable of reducing nitrates.

Chapters Two and Three examine agricultural sources of nitrogen, both pre- and post-Industrial Revolution. Restoration of nitrogen to the soil initially involved crop rotation, planting of leguminous species, and application of manure. As the need for nitrogen fertilization increased, nitrogen sources expanded to include guano and sodium nitrate. Additional sources for sequestering nitrogen for agricultural use included the recovery of byproduct ammonia from coking, synthesis of cyanamide from calcium carbide and nitrogen, and generation of nitric oxide by passing an electric arc

through air. All of these processes were highly energy intensive, however; and a more efficient, economical method for fixing nitrogen was required to meet the nutritional needs of the world's growing population.

The stage was set for Haber's synthesis of ammonia, a discovery that built upon work by numerous chemists such as Claude-Louis Berthollet, Wilhelm Ostwald, and Henry Louis Le Châtelier. Haber began his work on ammonia synthesis in response to a request from the Österreichische Chemische Werke in Vienna, initially focusing on the position of equilibrium of NH_3 around $1,000^\circ\text{C}$. Despite the low yield of ammonia obtained by passing N_2 and H_2 gases over iron and nickel catalysts, Haber's calculations predicted higher yields with decreasing temperature. Haber suspended his work on the synthesis of ammonia for three years, when a dispute with Hermann Walther Nernst prompted further experiments that yielded more ammonia at lower temperatures and higher pressures. Haber collaborated with Robert Le Rossignol in designing a high-temperature, high-pressure apparatus for ammonia synthesis that was patented in 1908 and is the basis for every ammonia plant in operation today. The high-pressure synthesis was completed when osmium was identified as the best catalyst for the process.

Bosch was instrumental in transforming Haber's bench-top process into a commercial success. Not only did Bosch recommend that BASF proceed with the commercialization of Haber's process, but he also set up a technical workshop to resolve the three key obstacles to full-scale implementation: a low-cost supply of hydrogen and nitrogen; the identification and production of effective and stable catalysts; and the construction of durable, high-pressure converters. Bosch designed a converter made up of two tubes that employed interior heating generated by the ignition of air forced into the hydrogen-rich mixture inside the converter. Along with his colleagues, he devised instruments for continuous monitoring of temperature, pressure, flow rates, and other parameters. Alwin Mittasch and coworkers used a systematic approach in identifying a catalyst to replace the rare and easily oxidized osmium employed by Haber. Extensive trials showed that a mixed catalyst, composed of magnetite (Fe_3O_4) and a catalyst promoter such as alumina or magnesium oxide, was effective and economical. Finally, an inexpensive source of hydrogen gas became available when a catalytic process for producing water gas was developed. Incredibly, only ten months passed between Haber's bench-top demonstration and the production of ammonia at BASF's experi-

mental site. The first full-scale, commercial plant for ammonia synthesis began operation on September 9, 1913 at Oppau, Germany. The BASF ammonia synthesis was redirected to nitric acid production for munitions applications during World War I.

Following the end of the First World War, the Haber-Bosch process was adopted in other countries, including France, Great Britain, and the United States. Although the basic process remains essentially unchanged, a number of innovations have increased both size and efficiency of ammonia synthesis plants. In particular, reforming of natural gas provides a source of hydrogen while methane serves as the principal source of process energy. Plants based on natural gas account for approximately 80% of the world's ammonia production capacity. Ammonia synthesis capacity was further expanded by the introduction of single-train ammonia plants.

The final four chapters of the book are devoted to the use of synthetic fertilizers, their impact on the environment, and the nitrogen cycle. Increasing use of nitrogen fertilizers has driven the synthesis of ammonia since the end of World War II. Smil summarizes our dependence on the Haber-Bosch synthesis of ammonia as follows:

For about 40% of humanity it now provides the very means of survival; only half as many people as are alive today could be supplied by prefertilizer agriculture with very basic, overwhelmingly vegetarian, diets; and prefertilizer farming could provide today's average diets to only about 40% of the existing population.

The author identifies the Haber-Bosch process as the single largest cause of human-driven intensification of the biospheric nitrogen cycle. The consequences of this global experiment are not yet fully appreciated, although environmental problems such as eutrophication of lakes and coastal waters caused by fertilizer runoff have already been recognized.

A Postscript chapter summarizes the lives of Bosch and Haber after the development of the ammonia process. Following World War I, Bosch became chair of the BASF board and then the first chairman of the I.G. Farben board of directors in 1926. He was instrumental in promoting the development and commercialization of coal hydrogenation to produce liquid fuels from lignites. Bosch received the Nobel Prize in 1932 for the synthesis of ammonia, the highlight of his professional career. He died on April 26, 1940, depressed and fearful following the Nazi takeover of Germany. Haber's

life took a tragic turn during World War I when he began working on gas warfare despite the Hague Conventions ban on the use of gases during war. His wife, Clara, committed suicide in 1915; he married Charlotte Nathan in 1917; but, despite the arrival of two children in 1918 and 1920, suffered from a deepening postwar depression. He was recognized for the synthesis of ammonia from its elements with the 1918 Nobel Prize. In his Nobel address, Haber noted:

It may be that this solution is not the final one. Nitrogen bacteria teach us that Nature, with her sophisticated forms of the chemistry of living matter, still understands and utilizes methods which we do not as yet know how to imitate.

Haber died in 1934 during a brief visit to Switzerland.

This book provides an excellent framework for the significance of Haber and Bosch's development of the ammonia process. By including extensive information on agricultural practices, nitrogen assimilation, and nutritional needs of the global population, Smil goes well beyond a standard biography by placing this scientific discovery in context. The industrial synthesis of nitrogen from its elements has directly impacted the lives of the six billion people who inhabit the earth today. *Mary M. Kirchoff, Green Chemistry Institute, American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036.*

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