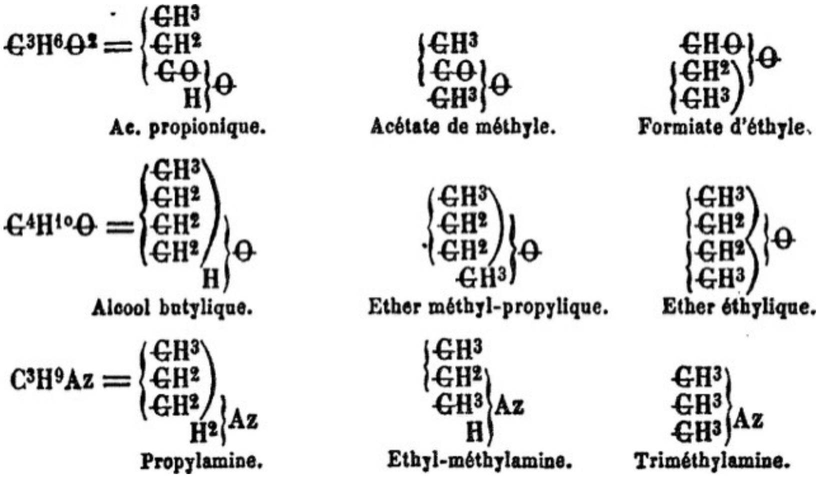
BULLETIN FOR THE HISTORY OF CHEMISTRY

Division of the History of Chemistry of the American Chemical Society

VOLUME 44 Number 2 2019

Butlerov



Markovnikov

Did the student lead the teacher?

BULLETIN FOR THE HISTORY OF CHEMISTRY
VOLUME 44 CONTENTS

NUMBER 1

NUMBER 2

The Cover... Did Markovnikov influence the structural theory of his teacher, Butlerov (p 77)

1860-1861: MAGIC YEARS IN THE DEVELOPENT OF THE STRUCTURAL THEORY OF ORGANIC CHEMISTRY (1)

David E. Lewis, Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54702-4004, USA; lewisd@uwec.edu

Introduction

The logical way to start this talk is by briefly looking at a chronology of organic structures. The first contribution in this area was the observation by Friedrich Wöhler (1800-1882, Figure 1) and Justus Liebig (1803-1873, Figure 1), that a substructure $C_{14}H_5O_2$ (C=6, O=8) survived unchanged through a large number of transformations of oil of bitter almonds (Bittermandelöl). They called this group benzoyl (2) and published it in a series of papers in contemporary outlets in both German (3) and French (4). The reactions used by Wöhler and Liebig to support their theory are gathered in Figure 2.

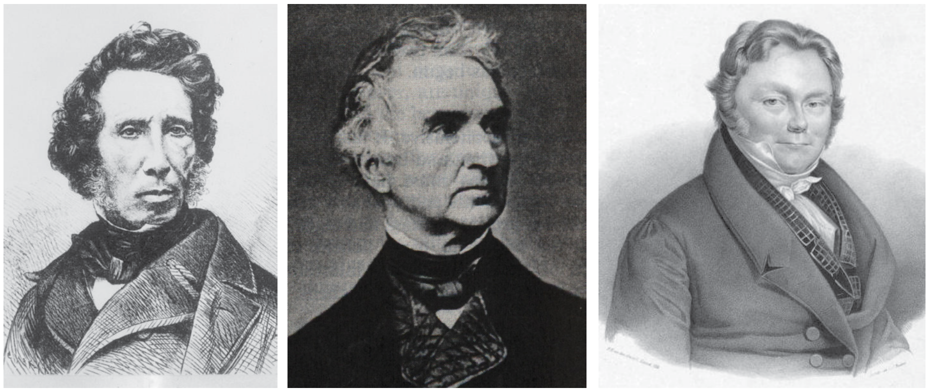


Figure 1*. (l-r): Friedrich Wöhler (1800-1882), Justus (von) Liebig (1803-1873) and Jöns Jacob Berzelius (1779-1848). Public domain images downloaded from Wikipedia.*

It is ironic that just two years later, Wöhler wrote to his former mentor, Jöns Jacob Berzelius (1779-1848, Figure 1), "Organic chemistry just now is enough to drive one mad. It gives me the impression of a primeval forest full of the most remarkable things, a monstrous and boundless thicket, with no way of escape, into which one may well dread to enter" (5)—right after he himself had done exactly that.

Substitution Theory

Between 1832 and 1839, Jean-Baptiste André Dumas (1800-1884, Figure 3), Charles Frédéric Gerhardt (1816-1856, Figure 3), and Auguste Laurent (1807-1853, Figure 3) had taken the complex radicals of Liebig and Wöhler and built the first "modern" theory of organic chemistry, Substitution Theory (6). This theory arose from the observations of Dumas, in particular, that substituting certain hydrogen atoms of an organic compound with chlorine, for example, did not dramatically affect its physical or chemical properties: the difference between trichloroacetic acid and acetic acid was one of degree, not basic reactivity. Its proposers did not explicitly specify that it applied solely to organic com-

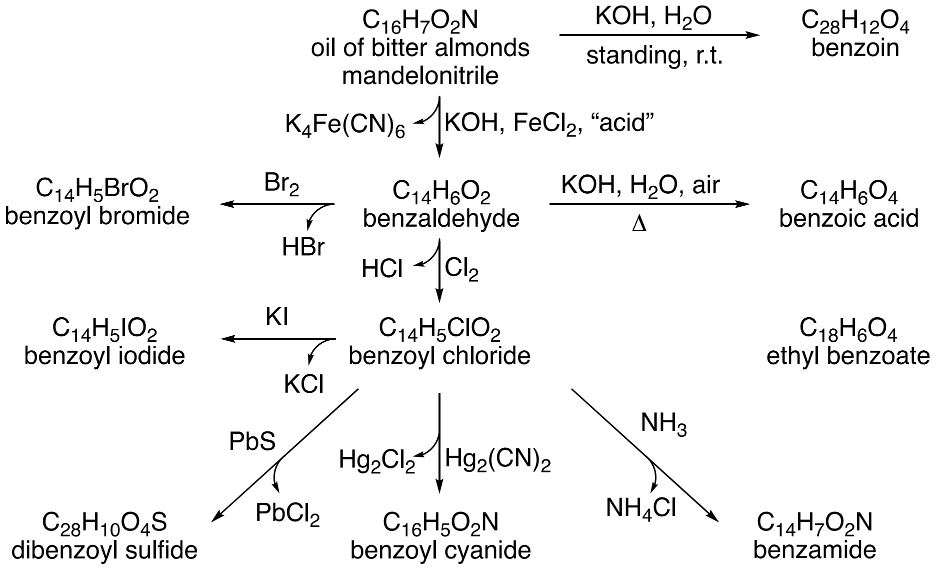


***Figure 2**. Transformations used by Wöhler and Liebig in their studies in the benzoyl series [C=6, O=8, S=16].*

pounds, so this new theory was not without opposition. Wöhler wrote a parody of it (7), under the pseudonym S. C. H. Windler, where he described the complete replacement of all atoms in manganous acetate by chlorine without any change in the properties of the material: *reductio ad absurdum*.

Nevertheless, the logic behind the theory is clear when one compares the effects of the same substitution in a pair of inorganic compounds and a pair of organic compounds (Table 1). Replacing an electropositive element (e.g., hydrogen) by an electronegative element (e.g., chlorine) leads to a dramatic change in physical and/or chemical properties, as we see when the hydrogen in sodium hydride is replaced by chlorine: the highly reactive, strongly basic, sodium hydride, which reacts violently with water instead of simply dissolving, becomes the benign, very weakly basic sodium chloride. If, instead, we replace the electropositive element in sodium chloride with chlorine, the product is chlorine gas—producing a substance that is clearly obviously not the same or even remotely similar. It is worth noting that to chemists of this era, hydrogen was always electropositive.

On the other hand, when a chlorine atom replaces one of the methyl hydrogens of acetic acid, the chloroacetic acid obtained has physical and chemical properties only slightly different from the acetic acid used to start with; the same effect is observed when the

***Figure 3**. Top row (l-r): Jean-Baptiste André Dumas (1800-1884), Charles Frédéric Gerhardt (1816-1856), and Auguste Laurent (1807-1853). Bottom row (l-r): Alexander William Williamson (1824-1904) and August Wilhelm Hofmann (1818-1892). Public domain images downloaded from Wikipedia.*

Table 1. Comparison of Substitution Theory for Organic and Inorganic Compounds.

Inorganic Compounds	Organic Compounds
Replacing an electropositive element (e.g., hydrogen) by an electronegative element (e.g., chlorine) leads to a dramatic change in physical and/or chemical properties.	Replacing an electropositive element (e.g., hydrogen) by an electronegative element (e.g., chlorine) leads to only a small change in physical and/or chemical properties.
Comparing NaH and NaCl, the replacement of hydrogen by chlorine in the ionic sodium hydride dramatically changes the chemical character of the compound from a strong base (H^-) to a very weak base (Cl^-)	Comparing CH_3CO_2H and CCl_3CO_2H, the replacement of the methyl hydrogens in acetic acid by chlorine gives a carboxylic acid that exhibits chemical and physical properties very similar to those of acetic acid

substitution is reversed. The properties of acetic acid and its chlorinated derivatives are summarized in Table 2.

Table 2. Comparison of Properties of Acetic Acid and its Chlorinated Derivatives

Acid	m.p. (°C)	b.p. (°C)	D_4^{20} (g mL^{-1})	n_D	pK_a
CH_3CO_2H	16-17	118-119	1.049	1.371	4.756
$ClCH_2CO_2H$	63	189.3	1.58	1.4351 (55 °C)	2.86
Cl_2CHCO_2H	9-11	194	1.5643 (20 °C)	1.466	1.35
Cl_3CO_2H	57-58	196-197	1.62 (20 °C)	1.62	0.66

Type Theory

The successor to Substitution Theory was Type Theory, which was proposed in 1839 by Dumas (8). It was subsequently extended by Alexander William Williamson (Figure 3), who described the "water" types (9), and August Wilhelm Hofmann (Figure 3), who described "ammonia" types (10, 11). Then, in 1853, Gerhardt published what has come to be known as "New Type Theory" (12).

The general features of Type Theory are summarized in Figure 4, where the formulas are based on the equivalent weights C=6 and O=8. Organic compounds could be viewed as being derived from the characteristic hydride by replacement of the hydrogen atoms by radical groups. Four basic Types were proposed: the hydrogen type (HH), the hydrochloric acid type (HCl), the ammonia type (NH_3), and the water type (H_2O_2 [H_2O]). Subsequently, Kekulé added the "marsh gas type," (C_2H_4 [CH_4]) (13). These Types made it possible to standardize organic chemistry, based on the functional groups characterized by each type. When we examine Type Theory, it is difficult not to perceive in it, an embryonic precursor to the theory of functional groups.

The year 1857 was pivotal in the development of the Structural Theory of Organic Chemistry. In that year, August Kekulé (1829-1896, Figure 5) was formulating his theory of organic structure in Heidelberg—and converting his fellow Privatdocent, Emil Erlenmeyer (1825-1909, Figure 5) to his views at the same time. In Paris, discussions in the laboratory of Adolphe Wurtz

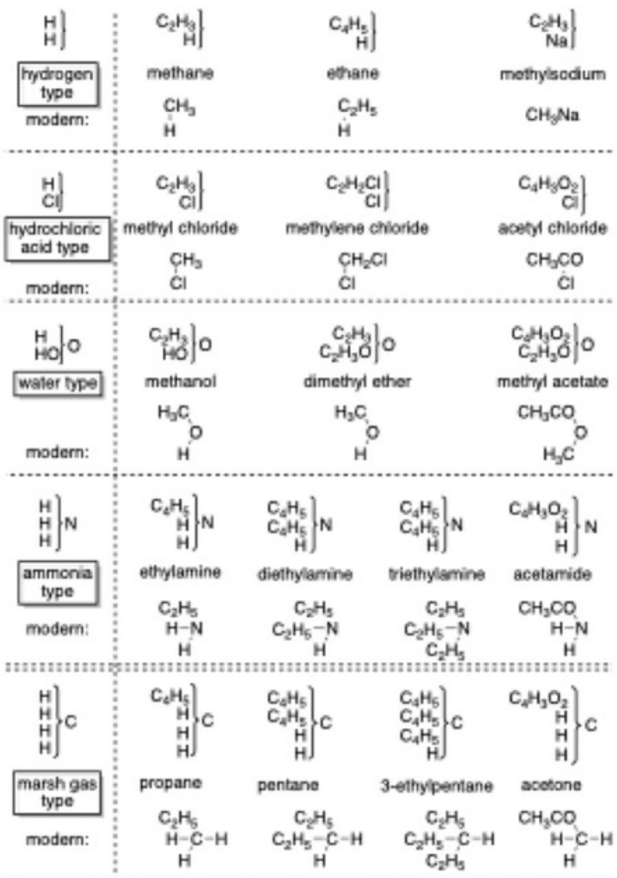


Figure 4. *The four original Types to 1853, and then, below the double lines, after Kekulé's addition of the "marsh gas type" in 1857.*

(1818-1886, Figure 5) were often devoted to papers on the structures of organic compounds (14), as were the meetings of the fledgling Société chimique de Paris. Archibald Scott Couper (1831-1892, Figure 5) was among the early members of this society; he was admitted to membership in January 1858.

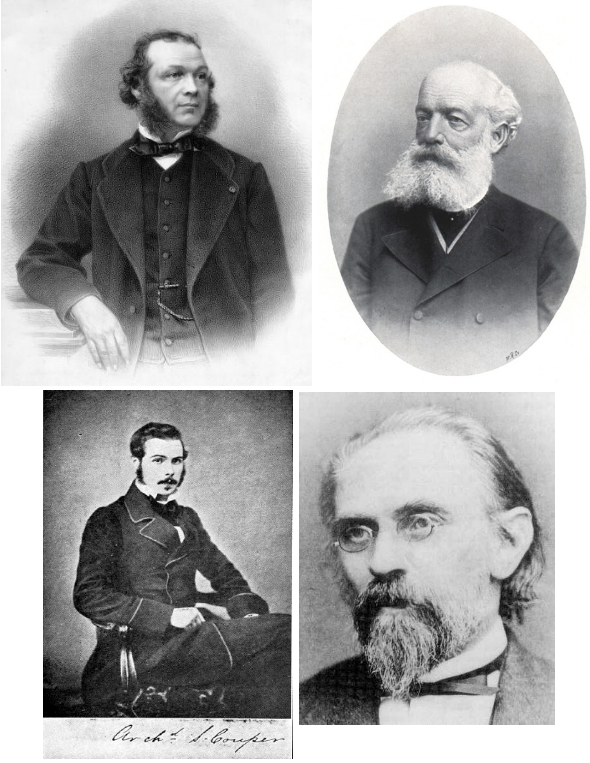


***Figure 5**. (l-r): Charles Adolphe Wurtz (1818-1886), Friedrich August Kekulé (1829-1896), Archibald Scott Couper (1831-1892), Richard August Carl Emil Erlenmeyer (1825-1909) Public domain images downloaded from Wikipedia.*

The Emergence of Structural Theory

Kekulé first proposed his "marsh gas type" in the course of reporting his conclusions concerning the tetravalency of carbon in 1857. At the same time, Type theory itself had begun to unravel, and the structure of compounds had become possibly the most intriguing question in organic chemistry. The problem with Type theory emerged when a molecule could be assigned to multiple different types—e.g., ethane could be viewed as ethyl hydride, $H–C_2H_5$, belonging to the hydrogen type, or as methyl methylide, $CH_3–CH_3$, belonging to the marsh gas type. Obviously, a better (i.e. more general) theory was needed. That theory was the Structural Theory of Organic Chemistry.

Before the new theory could emerge, however, the confluence of three intellectual concepts was necessary: 1) just what constitutes an atom, as opposed to an equivalent of an atom, had to be settled, especially for what we now call polyvalent elements; 2) the tetravalent carbon atom had to be conceived; and 3) the idea of catenation had to be conceived.

The question of atomicity had been nagging chemists for a number of years (15) and would not really be settled until the Karlsruhe Conference of 1860. In 1858, there were two sets of atomic weights and symbols for carbon and oxygen: Kolbe used the older equivalent weights, C=6 and O=8, which required doubling the number of these atoms in formulas [giving the formula $C_2H_3C_2(O_2)OOH$ for acetic acid], while Kekulé used the newer values, indicated by "barred" symbols (Ꞓ = 12, Ɵ = 16). Kekulé had proposed in a footnote to his 1857 paper. already referred to (13), that carbon is always tetravalent. The concept of catenation was proposed by both Kekulé (16) and Couper (17) as the key component of their independent versions of the Structural Theory of Organic Chemistry in 1858.

At that time, Kekulé was a docent at Heidelberg, which allowed him to publish his work immediately. (As a member of the faculty, he did not require approval to submit his manuscript.) Couper, on the other hand, was a student in Wurtz' laboratory, and had no similar freedom to publish—obtaining Wurtz's approval would have been imperative. Moreover, Wurtz was not yet a member of the Académie des Sciences, so he could not present the paper before the Académie without a sponsor. This meant that Kekulé's paper appeared first, allowing him to claim priority for the theory thenceforth. Couper blamed Wurtz for the delay in the publication of his paper, and immoderately and impoliticly (but not necessarily unjustly) scolded his mentor for delaying publication. The relationship between the two men rapidly soured, and shortly thereafter Wurtz summarily dismissed Couper from his laboratory (18). The eminent historian of chemistry, Alan J. Rocke, suggested to this author that "immoderate" may well be an understatement given the level of offensiveness required to bring the normally placid Wurtz to such a rage (19). Within two years, Couper's scientific career had been ended by a nervous breakdown.

Kekulé's version of Structural Theory was the more conservative of the two, and was much more widely accepted by the chemistry community. It retained many of the concepts of Type Theory familiar to chemists, so the (generally conservative) chemistry community felt more comfortable with it and found it easier to accept than the

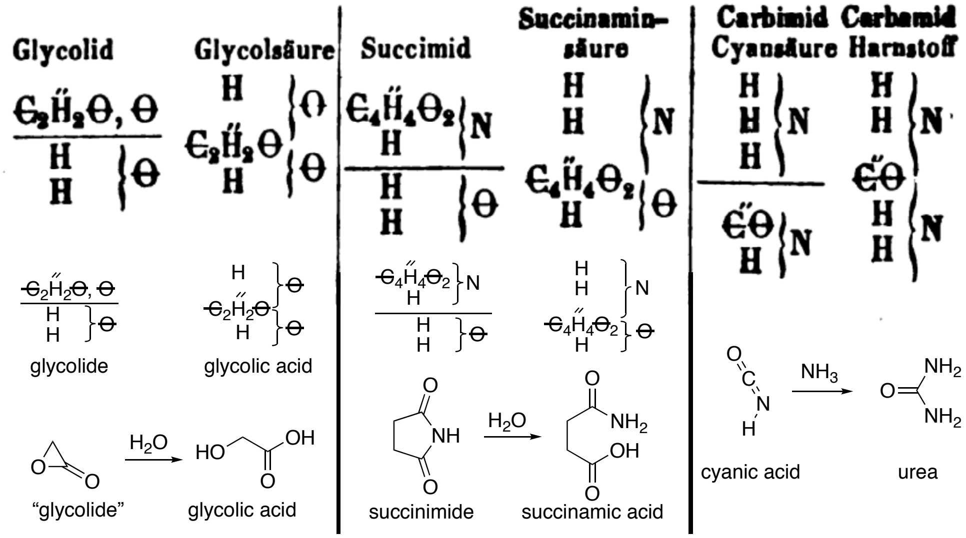


***Figure 6**. Kekulé's versions of the hydrolyses of glycolide and succinimide, and the ammonolysis of isocyanic acid. In these formulas, C=12 and O=16 (Ref. 16 , p 139).*

more radical versions of the theory. Even in his *Lehrbuch* (20), which was published in a series of fascicles over the ensuing decade, Kekulé still retained many of the trappings of Type Theory throughout. (It is fascinating to speculate, also, that this may have been done with an eye towards sales of the book.)

In Figure 6, Kekulé's originals and modern structural formulas for the hydrolysis of glycolide, the partial hydrolysis of succinimide and the ammonoloysis of isocyanic acid are shown. In Kekulé's formalism, the reactants are stacked vertically, so we see water in the lower row in the hydrolysis reactions and the ammonia in the top row for the ammonolysis. It is worth noting that Kekulé's formula for glycolide is $C_2H_2O_2$, i.e., the empirical formula rather than the molecular formula; it actually corresponds to the α-lactone.

Couper's version of Structural Theory went much further than Kekulé's. Where Kekulé had retained many of the characteristics of Type Theory, Couper advocated that it be discarded completely, and that the new theory be built *ab initio*. This is what he did, but for many chemists—including Butlerov (later to become Structural Theory's most ardent champion)—this was a step too far (21). Couper's theory made many organic chemists uncomfortable, as Butlerov's objections show. Butlerov clearly disagrees with Couper's statement that theory is the purpose of scientific investigations:

- Butlerov saw the foundation of new chemical *Laws* as the purpose of science.
- Butlerov saw a theory as a series of analogies in behavior from which laws could be deduced.
- Butlerov discounted any theory that went beyond what could be deduced from experimental observations—he accepted *deductive* reasoning, but was less trustful of *inductive* reasoning.
- Butlerov still saw no reason to abandon Gerhardt's Types, despite their occasional minor disagreements with observation.
- Butlerov noted that double decomposition reactions (the basis of Gerhardt's theory) did not provide any information about the internal structure of substances. He did not doubt that this might become possible, but he did not concede that Couper's theory was the answer.

As is evident from Figure 7, Couper's structures were much closer to modern structural formulas, and it was not long before Butlerov himself would come to prefer them.

The differences between the two versions of the theory are illustrated by the two structural formulas in Figure 8. In Kekulé's structure of succinamic acid, for example, the backbone of the molecule is not visible, and the molecule is drawn as a "mixed" type. The part of the molecule contained in the box is written as a divalent group in the formula. In Couper's structural formula of tartaric acid, in the other hand, the backbone of the

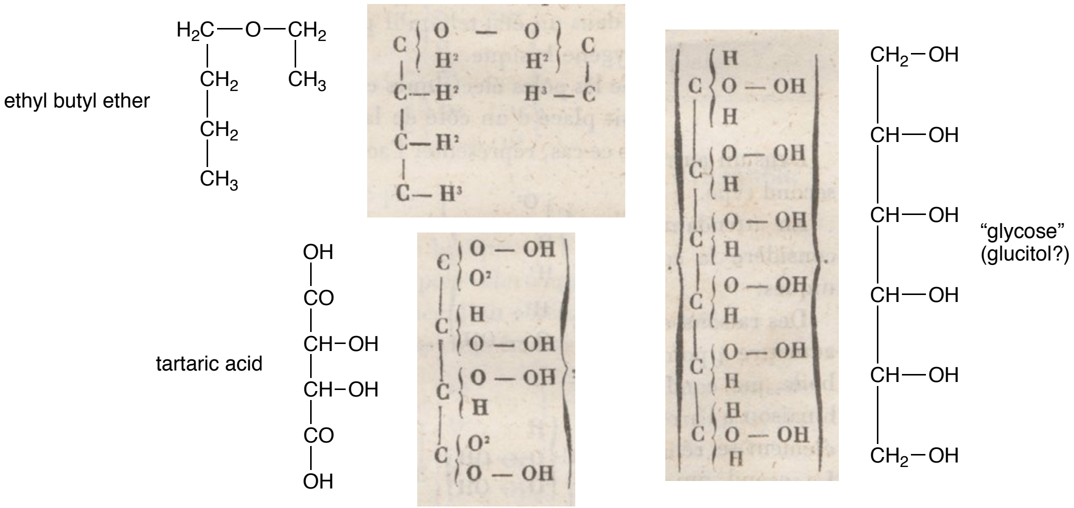


Figure 7. Couper's structural formulas. For these formulae, C=12 and O=8. (Ref. 17b).

molecule is shown explicitly, and the formula much more closely resembles the modern representation.

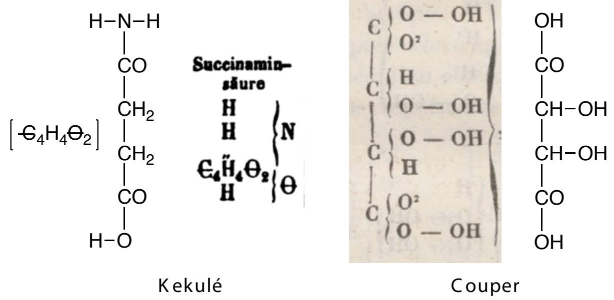


Figure 8. Comparing the structural formulas of the Kekulé and Couper versions of Structural Theory

There was also a third bloc of chemists, to whom neither version of Structural Theory was acceptable. Hermann Kolbe, who abjured the new theory in favor of his own concept of Rational Constitution, led the opposition to both new theories (22). This resistance to new ideas was typical of Kolbe. He had an inherent distrust of new theoretical ideas that he perceived not to have a firm basis in experiment, but rather from the application of deductive and inductive logic. His 1874 response to van't Hoff's postulate of the tetrahedral carbon atom is illustrative of this (23).

Butlerov

One of the major protagonists of this presentation, the Russian chemist Aleksandr Mikhailovich Butlerov (Бутлеров, Александр Михайлович, 1828-1886, Figure 9) (24) was born to the minor Russian nobility and was educated at Kazan University in Russia. As a student at Kazan, Butlerov had been strongly influenced by Nikolai Nikolaevich Zinin (Зинин, Николай Николаевич, 1812-1880, Figure 9); Zinin had become an adherent of the unitary theory of Gerhardt while on *komandirovka* (official study leave) in western Europe in 1837. Thus, although he had begun his study of chemistry under Karl Karlovich Klaus (Клаус, Карл Карлович, 1796-1864, Figure 9), who was a strong adherent of Berzelius' dualistic theory, Butlerov soon gravitated to Zinin with his more modern perspectives. When Zinin left for to the St. Petersburg Medical-Surgical Academy, instead of returning to study under Klaus, Butlerov reverted to his first love, entomology, and wrote his *kandidat* dissertation on the diurnal butterflies of the Volga region (25).

After Butlerov had graduated as *kandidat*, the University administration chose to retain him for the professoriate—not as an entomologist, but as a chemist—and he was appointed as Assistant to Klaus in 1850. In 1851, he submitted his successful dissertation (26) to Kazan University for the degree of *Magistr Khimii* (*M. Khim.*) and was promoted to Adjunct (Assistant Professor) in Chemistry by a 21-3 vote of the University Council. In 1852, he submitted a dissertation for the degree of *Doktor Khimii* (*Dr. Khim.*). At the time, the Chair of Chemistry was vacant following Klaus' move to Dorpat, so Modest Yakovlevich Kittary (Киттары, Модест Яковлевич, 1825-1880, Figure 9), the Professor of Technology, and Aleksandr Stepanovich Savel'ev (Савельев, Александр Степанович, 1820-1860, Figure 9), the Professor of Physics, were appointed to examine the dissertation. Savel'ev returned a vote of "not acceptable" (24g), so the degree was not awarded.

***Figure 9**. Top row (l-r): Aleksandr Mikhailovich Butlerov (1818-1886), Nikolai Nikolaevich Zinin (1812-1880). Middle row: Karl Karlovich Klaus (1796-1864). Bottom row (l-r): Modest Yakovlevich Kittary (1825-1880), Aleksandr Stepanovich Savel'ev (1820-1860). Public domain images courtesy of the Butlerov Museum of the Kazan Chemistry School (Butlerov, Zinin, Klaus, Kittary) and downloaded from Wikipedia (Savel'ev).*

In May, 1853, Butlerov submitted his re-written dissertation (27) and his *M. Khim*. diploma to Moscow University for the degree of *Dr. Khim*, and in March 1854 he was awarded the degree. Neither his *M. Khim*. nor his *Dr. Khim*. dissertation has ever been published as a stand-alone volume, although both were published in German in the *Bulletin de la Classe physico-mathématique de l'Académie impériale des Sciences de St.-Pétersbourg* (26b, 27b), and are contained as Russian translations in Butlerov's selected works (*Sochinenie*) (26c, 27c). Neither dissertation, at least as revealed by the papers in the *Bulletin*, presages the brilliant chemist who emerged just a few years later. Nevertheless, six months later, he was promoted to Extraordinary Professor on a 23-1 vote, and this was followed in March 1857 by his promotion to Ordinary Professor by a 20-1 vote. In June the same year, his *komandirovka* "to attend lectures in Germany, Switzerland, Italy, France and England during one year" was approved (28). As had Zinin before him, Butlerov managed to turn a strictly lecture-hall experience into a research experience, an event that proved critical in the development of the Kazan Chemistry School.

Butlerov's *komandirovka* could hardly have come at a more opportune time. The organic chemistry community, in particular, was obsessed with the "hot topic" of atomicity and of just what constituted the structure of a compound. During his trip, Butlerov met twice with August Kekulé at Heidelberg, as well as with Erlenmeyer, who was one of the first to adopt Kekulé's perspectives on the structure of organic compounds. During his six months in the Paris laboratory of Adolphe Wurtz, the Société Chimique de Paris was founded; Couper and Butlerov both became members. As alluded to above, the structure of organic compounds was a frequent topic for discussions in the laboratory and at meetings of the Société, so Butlerov witnessed the early development of a structural theory of organic chemistry first-hand. He would certainly have been aware of Couper's stance on the question.

By the beginning of 1859, the battle lines were fairly clear (Figure 10): Kolbe remained unyielding in his opposition to Structural Theory, whereas its two major protagonists were Couper, who advocated the complete replacement of Type Theory, and Kekulé who advocated retaining certain aspects of it. Wurtz was not an adherent of Structural Theory, but neither was he as obstinately opposed to it as Kolbe; he held a position rather between those of Kekulé and Kolbe. In January 1858, Butlerov had read a paper before the Société in which he espoused ideas similar to those of Kekulé, Kolbe and Wurtz. Unfortunately, this paper has not survived, except as referred to in the minutes of the Société (14). It may, however, provide a rationale for his 1859 criticism (21) of Couper's theory in the *Annalen der Chemie und Pharmacie*.

Butlerov returned to Kazan in 1859 to take up the chair of Chemistry left vacant by the departure of Kittary for Moscow. At the same time, he continued his research begun in Paris, and also continued to ponder the details of the new theories. While he was teaching

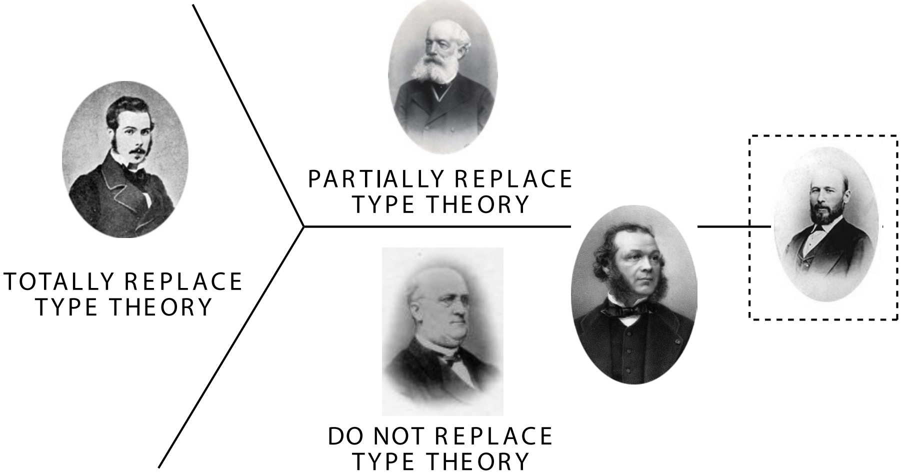
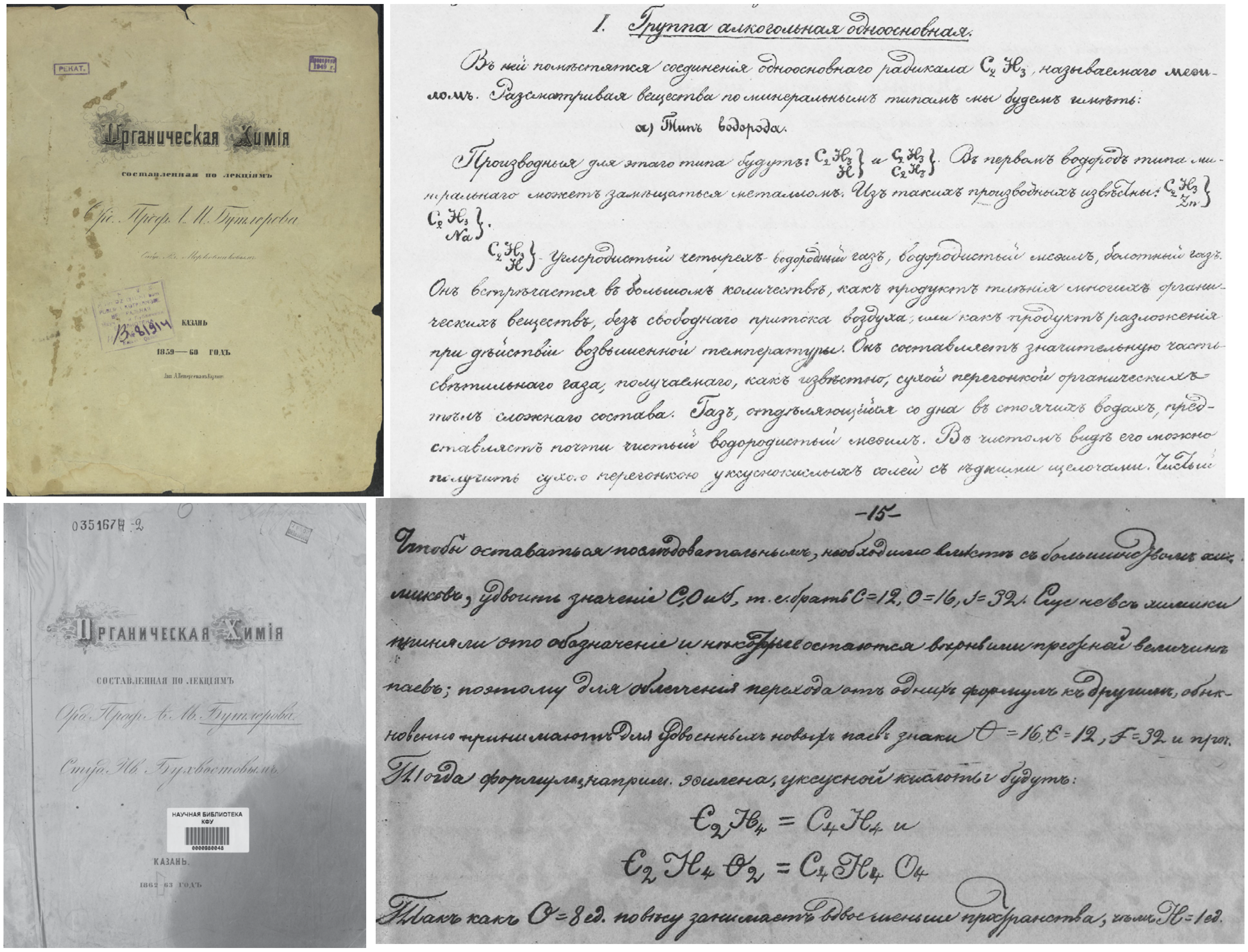


***Figure 10**. The attitudes of the major figures towards Structural Theory in 1859*

organic chemistry in 1859, he held the views contained in his "Bemerkungen" paper, and taught a course based on equivalent weights and Type Theory. This is clear from the notes (29) taken by his student, Vladimir Vasil'evich Markovnikov (1838-1904) (Figure 11, top row). By 1862, he had completely reversed his position on the merits of Structural Theory, and now taught a course based on modern atomic weights and his version of the theory,



Органическая Химія
составленная по лекціямъ
Орд. Проф. А. М. Бутлерова
Студ. Вл. Марковниковымъ
КАЗАНЬ
1859—60 ГОДЪ
Лит. А. Петерсена въ Казани

I. Группа алкогольная одноосновная.

Въ ней помѣстятся соединенія одноосновнаго радикала C_2H_3, называемаго метиломъ. Разсматривая вещества по минеральнымъ типамъ мы будемъ имѣть:

α) Типъ водорода.

Производныя для этаго типа будутъ: $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}$ и $\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}$. Въ первомъ водородъ типа минеральнаго можетъ замѣщаться металломъ. Изъ такихъ производныхъ извѣстны: $\left.\begin{matrix}C_2H_3\\Zn\end{matrix}\right\}$ $\left.\begin{matrix}C_2H_3\\Na\end{matrix}\right\}$.

$\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}$ - Углеродистый четырехъ-водородный газъ, водородистый метилъ, болотный газъ. Онъ встрѣчается въ большомъ количествѣ, какъ продуктъ тлѣнія многихъ органическихъ веществъ, безъ свободнаго притока воздуха; или какъ продуктъ разложенія при дѣйствіи возвышенной температуры. Онъ составляетъ значительную часть свѣтильнаго газа, получаемаго, какъ извѣстно, сухой перегонкой органическихъ тѣлъ сложнаго состава. Газъ, отдѣляющійся со дна въ стоячихъ водахъ, представляетъ почти чистый водородистый метилъ. Въ чистомъ видѣ его можно получить сухою перегонкою уксуснокислыхъ солей съ ѣдкими щелочами. Чистый

Органическая Химія
составленная по лекціямъ
Орд. Проф. А. М. Бутлерова
Студ. Ив. Бухвостовымъ
КАЗАНЬ.
1862–63 ГОДЪ

-15-

Чтобы оставаться послѣдовательными, необходимо вмѣстѣ съ большинствомъ химиковъ, удвоить значенія C, O и S, т. е. брать C=12, O=16, S=32. Еще не всѣ химики приняли это обозначеніе и нѣкоторые остаются вѣрными прежней величинѣ паевъ; поэтому для облегченія перехода отъ однихъ формулъ къ другимъ, обыкновенно принимаютъ для удвоенныхъ новыхъ паевъ знаки Ɵ = 16, Ȼ = 12, Ꞩ = 32 и проч. Тогда формулы, наприм. этилена, уксусной кислоты будутъ:

$$Ȼ_2H_4 = C_4H_4 \text{ и}$$

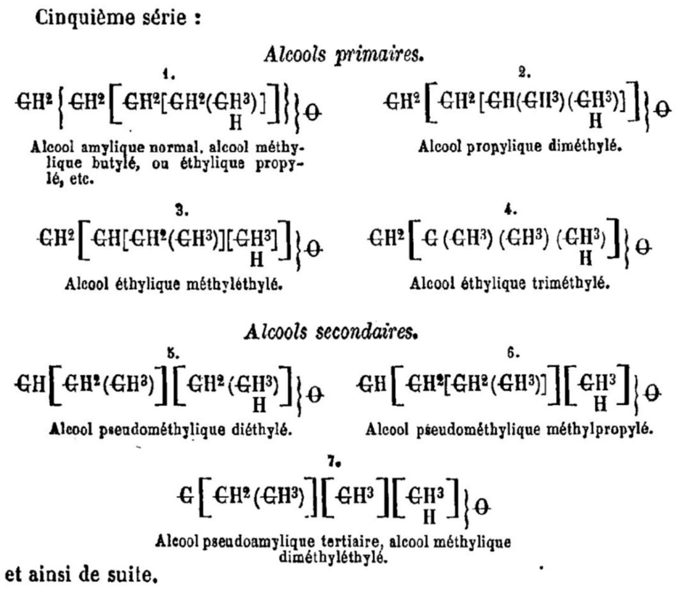
$$Ȼ_2H_4Ɵ_2 = C_4H_4O_4$$

Такъ какъ Ɵ = 8 ед. по вѣсу занимаетъ вдвое меньше пространства, чѣмъ H = 1 ед.

***Figure 11**. Notes from Butlerov's lectures for 1859-1860, taken by Markovnikov (top), and for 1862-1863, taken by Bukhvostov (bottom). Note the modern atomic weights used in 1862. Images courtesy of the Lobachevskii Scientific Library of Kazan University.*

which was much closer to that of Couper than Kekulé. The notes from this class (30), recorded by his student, Ivan Bukhvostov in 1862-1863 (Figure 11, bottom row), are still extant.

There is another critical document that has a bearing on the question of the timing of Butlerov's conversion from a Type Theorist to a Structuralist. In September 1861, Butlerov attended the 36th Assembly of German natural scientists and medical practitioners in Speyer. Here, in what has become known as "the Speyer paper," he presented his version of structural theory. Emil Erlenmeyer had been in the audience, and pressed Butlerov to publish the paper in his journal, the *Zeitschrift für Chemie und Pharmacie* (31).



Cinquième série :

Alcools primaires.

1.

$$CH^2\left\{CH^2\left[CH^2[CH^2(\underset{H}{CH^3})]\right]\right\}\Big\}O$$

Alcool amylique normal, alcool méthylique butylé, ou éthylique propylé, etc.

2.

$$CH^2\left[CH^2[CH(CH^3)(\underset{H}{CH^3})]\right]\Big\}O$$

Alcool propylique diméthylé.

3.

$$CH^2\left[CH[CH^2(CH^3)][\underset{H}{CH^3}]\right]\Big\}O$$

Alcool éthylique méthyléthylé.

4.

$$CH^2\left[C(CH^3)(CH^3)(\underset{H}{CH^3})\right]\Big\}O$$

Alcool éthylique triméthylé.

Alcools secondaires.

5.

$$CH\left[CH^2(CH^3)\right]\left[CH^2(\underset{H}{CH^3})\right]\Big\}O$$

Alcool pseudométhylique diéthylé.

6.

$$CH\left[CH^2[CH^2(CH^3)]\right]\left[\underset{H}{CH^3}\right]\Big\}O$$

Alcool pseudométhylique méthylpropylé.

7.

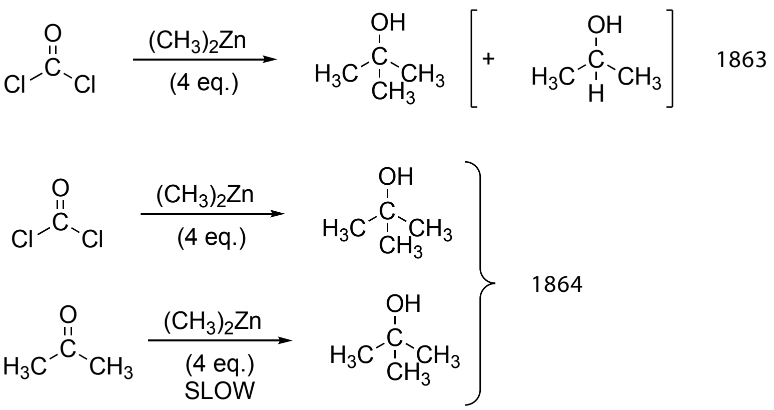
$$C\left[CH^2(CH^3)\right]\left[CH^3\right]\left[\underset{H}{CH^3}\right]\Big\}O$$

Alcool pseudoamylique tertiaire, alcool méthylique diméthyléthylé.

et ainsi de suite.

***Figure 12**. The isomers of amyl alcohol predicted by Butlerov.*

In this paper, Butlerov 1) set out his version of Structural Theory, which was now similar to Couper's version; 2) proposed the term, *chemical structure*; and 3) set the limitation that each compound be represented by a single structure, and that a structure represent a single compound. He was, however, careful to point out in the same paper that the *chemical* structure was distinct from *physical* structure, and that it did not imply anything about the location of atoms in the molecule. Even so, it is worth noting that, just three years later, he did suggest that it might be possible at some time in the future to locate the physical atoms in a molecule (32).



***Scheme 1**. Butlerov's syntheses of tert-butyl alcohol, and evidence that acetone may not be an intermediate stage in the reaction.*

Butlerov showed how his theory could be used to predict the existence of new isomers of known compounds (e.g., the amyl alcohols, Figure 12), and he then confirmed those predictions by preparing the compounds themselves. The first of Butlerov's syntheses was the synthesis of *tert*-butyl alcohol, which he reported twice (Scheme 1). In 1863, he reported (33) that the reaction between phosgene and dimethylzinc afforded a mixture of isopropyl alcohol and *tert*-butyl alcohol. The following year, he reported (34) that acetyl chloride and dimethylzinc gave only *tert*-butyl alcohol, and provided evidence that acetone may not be involved as an intermediate stage in the reaction because the direct reaction between acetone and dimethylzinc was exceptionally slow. From a modern perspective, it is probable that the addition to acetone may have been catalyzed by the zinc chloride generated during the first reaction, making the reaction autocatalytic, but because the concept of autocatalysis did not emerge until the 20th century, Butlerov did not know to explore this possibility. The same year, he began publication of his textbook of organic chemistry (35), the first based entirely on Structural Theory, with none of the trappings of Type Theory.

The first decade of predicting new compounds and confirming their existence by synthesis was instrumental in firmly establishing Structural Theory, but the theory would have stagnated were it not for another brilliant chemist to emerge from Kazan: Butlerov's student, Vladimir Vasil'evich Markovnikov (1838-1904, Figure 13) (36). Markovnikov was the first to apply Structural Theory to the study not only of chemical structure, but also chemical reactivity. It was Markovnikov who moved from simple prediction of isomers to studying the isomer ratios of the products of reactions, what today we would call, "regiochemistry." This application of Structural Theory to reactions was the first of its kind in this author's experience.

***Figure 13**. Vladimir Vasil'evich Markovnikov (1838-1904). Image courtesy of the Butlerov Museum of the Kazan Chemistry School.*

Markovnikov was born near Nizhny Novgorod, and entered Kazan University in 1856 as a student in economic science. At the time, Russia was seeking to introduce the Cameral system for educating bureaucrats, so Markovnikov was required to take two years of chemistry as part of his degree. After hearing Kittary, the young Markovnikov had decided to pursue study in technology, but Kittary's departure for Moscow led to him coming under the influence of Butlerov. Butlerov had just returned from western Europe and was slowly developing his own version of structural theory.

Markovnikov took the fourth course in organic chemistry from 1 October 1859 to 1 April 1860, and during this year, Butlerov taught Type Theory. However, Markovnikov was ill at the end of the year, so he could not take his final examinations. Butlerov allowed him to take the final examination late. Markovnikov arrived at Butlerov's home and the two men went to the park. There, Butlerov gave him an oral examination. The question that he posed was simple, and suggestive: "What is your opinion of mechanical types?" (37).

Buterov had marked Markovnikov as a candidate for the Professorship, so immediately after he had taken his *Diplom* in Economic Science, Markovnikov began research for the degree of *kandidat* under Butlerov's direction. This degree, which was, at the time, basically equivalent to the B.Sc.(Hons.) degree in the British system or an M.S. degree in the U.S., was the first step up the academic ladder. Markovnikov submitted his dissertation (Figure 14), "On Aldehydes and their Relationship to Alcohols and Ketones," (38) on October 7, 1860. It was based on Type Theory and equivalent weights.

Thus, it seems clear that Butlerov was not yet a Structuralist at the end of October, 1860. Had he been, it would have been extremely unlikely that he would not have brought his favorite student into the Structuralist camp. Regardless, everything had changed by September 1861. That month, Butlerov presented a paper at the *Versammlung deutscher Naturforscher und Ärzte zu Speyer*. At the urging of Erlenmeyer, he published this paper in the *Zeitschrift für Chemie und Pharmacie* (Figure 15) (31).

This paper essentially restates Couper's theory, but in much clearer and more useful terms. In it, he stated:

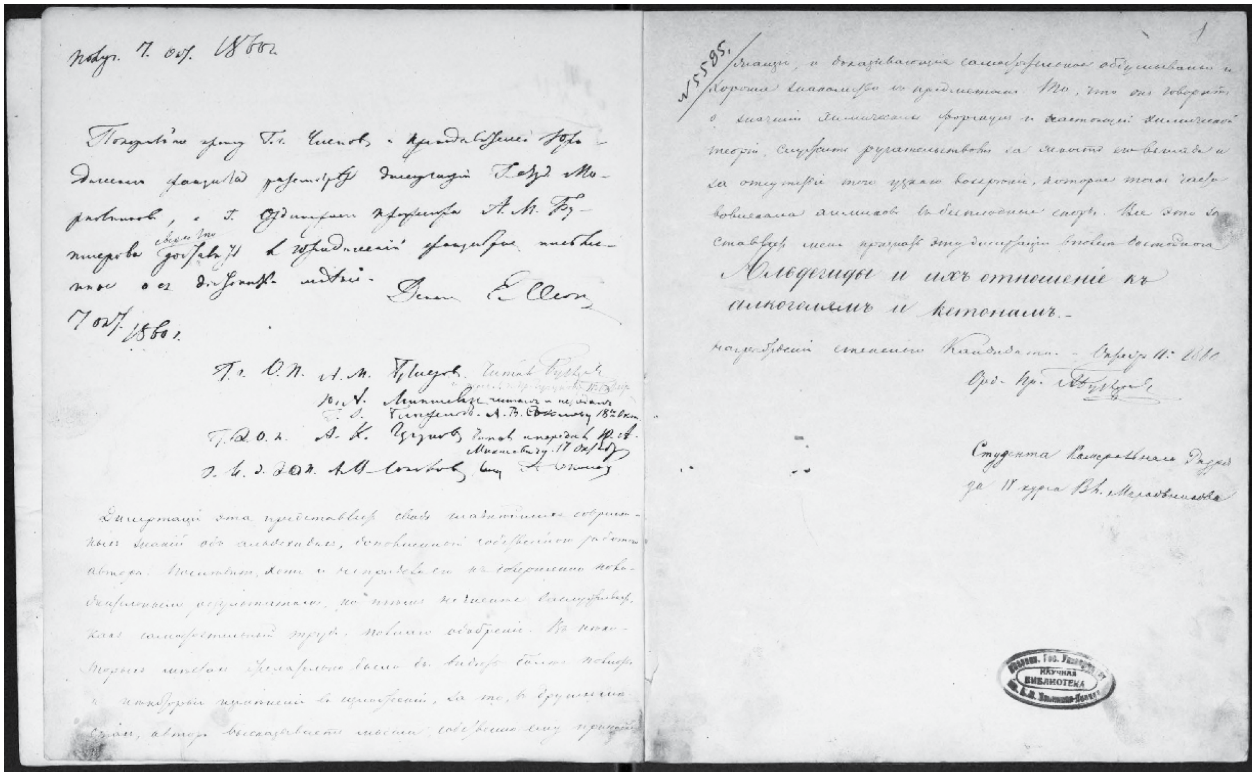
> The well-known rule that says that the nature of compound molecules depends on the nature, the quantity, and the arrangement of its elementary constituents can for the present be changed as follows: the chemical nature of a compound molecule depends on the nature and quantity of its elementary constituents and on its chemical structure.

Although Butlerov had criticized Couper's structures in 1859, at the end of his Speyer lecture in 1861 he made the following telling comment:

> I am even obliged to remark that the theory and formulas of Couper—whose too absolute and exclusive conclusions I disputed at that time—contained similar thinking. It was, however, neither clearly enough perceived nor expressed.

So what happened to cause this complete reversal of Butlerov's position in the space of less than a year?

It seems reasonable to suggest that something in late 1860 may have been the triggering event. I posit that the trigger may have been Markovnikov because this period coincides with the time that Markovnikov began to work closely with Butlerov. The two men rapidly became more friends and colleagues than mentor and student. One must



Альдегиды и ихъ отношенiе къ алкоголямъ и кетонамъ.-

Студента Камеральнаго Разряда IV курса Вл. Марковникова

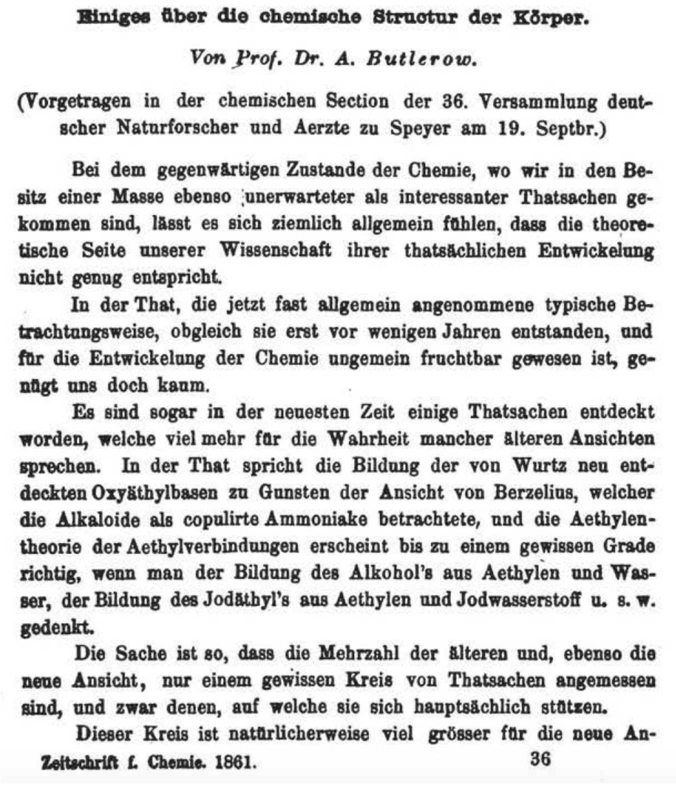
***Figure 14**. The title page of Markovnikov's dissertation for the degree of kandidat. This page also carries the Examiners' report, which accounts for its messy appearance. Image courtesy of the Lobachevskii Scientific Library of Kazan University.*

ask oneself, "Is it coincidental that Butlerov's conversion to committed Structuralist coincides with when he began to work closely with the most brilliant young theorist of his generation?" It is my contention that this is exactly what happened. Between them, they made a formidable intellectual team. The last page of Markovnikov's *kandidat* dissertation contains the following statement:

> The similarity of the properties of aldehydes with their [enol] isomers is explained by the similarity of the methods of their formation: aldehydes can be obtained by the method of Piria and Limpricht by the dry distillation of salts. *Obviously, such similarity of properties makes one assume that in these bodies there is an almost identical arrangement of their atoms*.

[Insertion and italics mine—DEL] This certainly appears to presage one of the foundational tenets of Butlerov's version of Structural Theory.

We know that up to his return to Russia in 1859, Butlerov had resisted Structural Theory despite being in Paris, where he was present as Couper developed his version of structural theory and despite meeting Kekulé during the gestation of his. The first course he taught following his return to Russia was based not on



Einiges über die chemische Structur der Körper.

Von Prof. Dr. A. Butlerow.

(Vorgetragen in der chemischen Section der 36. Versammlung deutscher Naturforscher und Aerzte zu Speyer am 19. Septbr.)

Bei dem gegenwärtigen Zustande der Chemie, wo wir in den Besitz einer Masse ebenso unerwarteter als interessanter Thatsachen gekommen sind, lässt es sich ziemlich allgemein fühlen, dass die theoretische Seite unserer Wissenschaft ihrer thatsächlichen Entwickelung nicht genug entspricht.

In der That, die jetzt fast allgemein angenommene typische Betrachtungsweise, obgleich sie erst vor wenigen Jahren entstanden, und für die Entwickelung der Chemie ungemein fruchtbar gewesen ist, genügt uns doch kaum.

Es sind sogar in der neuesten Zeit einige Thatsachen entdeckt worden, welche viel mehr für die Wahrheit mancher älteren Ansichten sprechen. In der That spricht die Bildung der von Wurtz neu entdeckten Oxyäthylbasen zu Gunsten der Ansicht von Berzelius, welcher die Alkaloide als copulirte Ammoniake betrachtete, und die Aethylentheorie der Aethylverbindungen erscheint bis zu einem gewissen Grade richtig, wenn man der Bildung des Alkohol's aus Aethylen und Wasser, der Bildung des Jodäthyl's aus Aethylen und Jodwasserstoff u. s. w. gedenkt.

Die Sache ist so, dass die Mehrzahl der älteren und, ebenso die neue Ansicht, nur einem gewissen Kreis von Thatsachen angemessen sind, und zwar denen, auf welche sie sich hauptsächlich stützen.

Dieser Kreis ist natürlicherweise viel grösser für die neue An-

Zeitschrift f. Chemie. 1861. 36

***Figure 15**. The beginning of Butlerov's "Speyer paper" (Ref. 31).*

Structural Theory, but on Type Theory; he seemed to be trapped by an inertia that inhibited his embrace of new ideas. Markovnikov, on the other hand, was a firebrand with the intellect of a true genius, but his mercurial tendencies needed moderating. Butlerov, the steadier of the two, was the ideal moderating influence over his younger colleague. The two built a team, like a charioteer and a horse, that allowed them to popularize Structural Theory so effectively that within a decade, it was the conventional wisdom.

I have always found it a coincidence, which I have heretofore ignored, that Butlerov's conversion from Type Theorist to Structural Theorist coincided with the beginning of Markovnikov's studies for the degree of *M. Khim*., in January, 1860. In retrospect, I now find this coincidence much harder to ignore—it is too facile an action to dismiss it entirely. Unfortunately, there is not yet any documentary evidence to provide direct support for this hypothesis.

Nevertheless, I do hypothesize that the characters of the two men, and their closeness as friends, are entirely consistent with Markovnikov feeling comfortable about broaching ideas similar to those that Butlerov had dismissed in Couper's paper as over-reach. In these discussions between the two men, it may be that Butlerov re-evaluated Couper's version of Structural Theory, and realized what it *could* be. In the end, it was Butlerov who was responsible for taking these ideas and forming them into a cohesive whole. Obviously, this question will require substantial further research, the first step of which will be the transcription and translation of the two sets of lecture notes (29, 30) to find an acceptable answer. This work is underway.

Acknowledgments

Nobody gets an award like the HIST Award without the direct or indirect help of a support network, to all of whom I express my very real gratitude. My network consists of the members of HIST, who have read my work; the *Bulletin* and its Editors (Carmen Giunta and the late Paul Jones), who have published my work; my peers, who have reviewed my work; my students, who have made the work fun to pass down to the next generation; and—especially—my wife, Debbie (Figure 16), who has stood with me through it all.

***Figure 16**. (l-r): Our interpreter, Academician Aleksandr Ivanovich Konovalov, David E. Lewis, Mrs. Deborah Lewis, Professor Igor Sergeevich Antipin and Ms. Gul'nar Mel'nikova in the Butlerov auditorium of the Butlerov Museum of the Kazan School of Chemistry (November 2013). Author's photograph.*

References and Notes

1. Presented at the 256th National Meeting of the American Chemical Society, Boston, MA, Aug. 21, 2018, HIST 33 in the HIST Award Symposium Honoring David Lewis.
2. (a) [F.] Wöhler and [J.] Liebig, "Untersuchungen über das Radikal der Benzoesäure," *Ann. Chem. Pharm*., **1832**, *3*, 249-282.
3. (a) [F.] Wöhler and [J.] Liebig, "Untersuchungen über das Radikal des Benzoesäure," *Pogg. Ann. Phys. Chem*., **1832**, *26[2]*, 325-343. (b) [F.] Wöhler and [J.] Liebig, "Untersuchungen über das Radikal des Benzoesäure," *Pogg. Ann. Phys. Chem*., **1832**, *26[2]*, 465-479. (c) [F.] Wöhler and [J.] Liebig, "Untersuchungen über das Radikal der Benzoesäure," *Ann. Phys.*, **1832**, *102*, 465-485.
4. (a) [J.] Liebig, "Extrait d'une lettre de M. Liebig à M. Gay-Lussac sur le radical de l'acide benzoïque," *Ann. Chim. Phys*., **1832**, *50*, 334-335. (b) [F.] Wöhler and [J.] Liebig, "Recherches sur le radical de l'acide benzoïque," *Ann. Chim. Phys*., **1832**, *51*, 273-314. (c) [F.] Wohler and [J.] Liebig, "Sur le radical de l'acide benzoïque," *J. Pharm. Sci. Access*., **1833**, *19[2]*, 117-143.
5. F. Wöhler, letter to J. J. Berzelius (28 Jan. 1835). Cited in A. L. Mackay, *A Dictionary of Scientific Quotations*, CRC Press, Boca Raton, FL, 1991, p 267.
6. (a) J. B. A. Dumas, "Recherches de chimie organique," *Ann. Chim. Phys.,* **1834**, *56[2]*, 113-115. (b) A. Laurent, "Théorie des combinaisons organiques," *Ann. Chim. Phys.*, **1836**, *61[2]*, 125-146. (c) C. Gerhardt, "Sur la constitution des sels organiques à acides complexes, et

leurs rapports avec les sels ammoniacaux," *Ann. Chim. Phys.*, **1839**, *72[2]*, 184-214. (d) J. Dumas, "Mémoire sur la constitution de quelques corps organiques et sur la théorie des substitutions," *C. R. Séances Acad. Sci.*, **1839**, *8*, 609-622. (e) J. Dumas, "Ueber die Chloressigsäure, die Constitution einiger organischer Körper und über die Substitutionstheorie," *Ann. Chem. Pharm.*, **1839**, *32*, 101-119. (f) J. Dumas, "Ueber die Constitution der Essigsäure und Chloressigsäure," *Ann. Chem. Pharm.*, **1840**, *33*, 179-182.

7. S. C. H. Windler [F. Wöhler], "Ueber das Substitutionsgesetz und die Theorie der Typen," *Ann. Chem. Pharm.*, **1840**, *33*, 308-310.

8. (a) J. Dumas, *Ann. Chem. Pharm.*, "Ueber das Gesetz der Substitutionen und die Theorie der Typen," **1840**, *33*, 259-300. (b) J. Dumas, "Premier Mémoire sur les Types Chimiques," *Ann. Chim. Phys.*, **1840**, *73[2]*, 73-100.

9. (a) A. W. Williamson, "Theory of Ætherification," *Phil. Mag.,* **1850**, *37[iii]*, 350-356. (b) A. W. Williamson, "Suggestions for the Dynamics of Chemistry Derived from the theory of Ætherification," *Chem. Gaz.*, **1851**, *9*, 294-298. (c) A. W. Williamson, "On the Constitution of Salts," *Chem. Gaz.*, **1851**, *9*, 334-339; this was also reproduced as: A. W. Williamson, "On the Constitution of Salts," in "Notices of Papers Contained in British and Foreign Journals," *Quart. J. Chem. Soc.*, **1852**, *4*, 350-355. (d) A. W. Williamson, "On Etherification," *Quart. J. Chem. Soc.*, **1852**, *4*, 229-239.

10. (a) A. W. Hofmann, "Researches on the Volatile Bases. I. On the Action of Cyanogen on Aniline, Toluidine and Cumidine," *Quart. J. Chem. Soc.,* **1849**, *1*, 159-173. (b) A. W. Hofmann, "Researches on the Volatile Organic Bases. II. On the Action of Iodine on Aniline," *Quart. J. Chem. Soc.,* **1849**, *1*, 269-281. (c) A. W. Hofmann, "Researches on the Volatile Organic Bases. III. Action of Chloride, Bromide and Iodide of Cyanogen on Aniline. Melaniline, a New Conjugated Alkaloid," *Quart. J. Chem. Soc.,* **1849**, *1*, 285-317. (d) A. W. Hofmann, "Researches on the Volatile Organic Bases. IV. Anilides," *Quart. J. Chem. Soc.,* **1850**, *2*, 36-51. (e) A. W. Hofmann, "Researches on the Volatile Organic Bases. V. On the Action of Acids and Bases upon Cyaniline," *Quart. J. Chem. Soc.,* **1850**, *2*, 300-335. (f) A. W. Hofmann, "Researches on the Volatile Organic Bases. VIII. On the Behaviour of Aniline and the Alcohol-Bases with Nitrous Acid," *Quart. J. Chem. Soc.,* **1851**, *3*, 231-240.

11. (a) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen Basen. I. Ueber die Einwirkung des Cyans auf Anilin, Toluidin und Cumidin," *Ann. Chem. Pharm.,* **1848**, *66*, 129-149. (b) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen organischen Basen II. Ueber die Einwirkung des Jods auf Anilin," *Ann. Chem. Pharm.,* **1848**, *67*, 61-78 (c) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen organischen Basen. III. Einwirkung des Chlorcyans, Bromcyans und Jodcyans auf Anilin. Melanilin, eine neue gepaarte Base," *Ann. Chem. Pharm.,* **1848**, *67*, 129-173. (d) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen organischen Basen. IV. Anilide" *Ann. Chem. Pharm.,* **1849**, *70*, 129-149. (e) A. W. Hofmann, "Ueber zwei neue Reihen flüchtiger organischer Basen," *Ann. Chem. Pharm.,* **1850**, *73*, 91-92. (f) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen organischen Basen. V. Ueber das Verhalten des Cyananilins gegen Säuren und Basen," *Ann. Chem. Pharm.,* **1850**, *73*, 180-189. (g) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen organischen Basen. VI. Metamorphosen des Dicyanomelanilins. Bildung das der Cyansäure entsprechenden Gliedes der Anilinreihe," *Ann. Chem. Pharm.,* **1850**, *74*, 1-33. (h) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen organischen Basen. VIII. Constitution dieser Körper, Verhalten des Anilins und Ammoniaks zu den Bromüren des Methyls, Aethyls und Amyls," *Ann. Chem. Pharm.,* **1850**, *74*, 117-177. (i) A. W. Hofmann, "Beiträge zur Kenntniss der flüchtigen organischen Basen. IX. Notiz über das Verhalten des Anilins und der Alkohol-Basen gegen salpetrige Säure," *Ann. Chem. Pharm.,* **1850**, *75*, 356-368.

12. C. Gerhardt, "Recherches sur les acides organiques anhydres," *Ann. Chim. Phys.,* **1853**, *37[3]*, 285-342.

13. A. Kekulé, "Ueber die s. g. gepaarten Verbindungen und die Theorie der mehratomigen Radicale," *Ann. Chem. Pharm.,* **1857**, *104*, 129-150.

14. J. Jacques, "Boutlerov, Couper et la Société Chimique de Paris. (Notes pour servir à l'histoire des théories de la structure chimique)," *Bull. Soc. Chim. Fr.*, **1953**, 528-530.

15. A. J. Rocke, *Chemical Atomism in the Nineteenth Century*, Ohio State University Press, Columbus, 1984.

16. A. Kekulé, "Ueber die Constitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," *Justus Liebigs Ann. Chem.,* **1858**, *106*, 129-159.This paper has also appeared in English translation: O. T. Benfey, T. In Benfey, O.T., Ed. *Classics in the Theory of Chemical Combination* (Dover: New York, 1963), pp. 109-131.

17. (a) A. S. Couper, "Sur une nouvelle théorie chimique," *C. R. Séances Acad. Sci.*, **1858**, *46*, 1157-1160; "Sur une nouvelle théorie chimique," *Ann. Chim. Phys.*, **1858**, *53[3]*, 469-489; (b) A. S. Couper, "On a New Chemical Theory," *Phil. Mag.*, **1858**, *16*, 104-116; "Ueber eine neue chemische Theorie," *Justus Liebigs Ann. Chem.*, **1859**, *110*, 46-51.

18. A. J. Rocke, *Nationalizing Science. Adolphe Wurtz and the Battle for French Chemistry*, MIT Press, Cambridge, MA, 2001, pp. 205-211 contains an account of the development of Wurtz' views on atomic and molecular structure, and his dispute with Couper.

19. A. J. Rocke, personal communication, August 2018.

20. A. Kekulé, *Lehrbuch der organischen Chemie*, Ferdinand

Enke, Erlangen, 1859-1861, 1864-1866. This work appeared as six fascicles over the seven-year period.

21. Butlerov's response is typical of the reaction at the time: A. Butlerow, "Bemerkungen über A. S. Couper's neue chemische Theorie," *Justus Liebigs Ann. Chem*., **1859**, *110*, 51-66.

22. For a lucid discussion of Kolbe's opposition to the movement towards the Structural Theory, see A. J. Rocke, *The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry*, University of California Press, Berkeley, 1993, Ch. 6, pp. 134-155.

23. H. Kolbe, "Zeichen der Zeit," *J. prakt. Chem.,* **1877**, *15[2]*, 473-477.

24. For biographies and biographical sketches of Butlerov in Russian, see: "Pamyati Aleksandra Mikhailovicha Butlerova [Remembrances of Aleksandr Mikhailovich Butlerov], a 96-page, special section at the beginning of vol. 19 of the *Zh. Russ. Fiz.-Khim. O-va.* (1887), which contains the following papers: (a) N. Menshutkin, "Vospominanie ob Aleksandre Mikhailoviche Butlerove [Reminiscences of Aleksandr Mikhailovich Butlerov]," pp 3-12. (b) A. Zaitsev, "Aleksandr Mikhailovich Butlerov (materialy dlya bibliografii i ocherk experimental'nykx rabot) [Aleksandr Mikhailovich Butlerov (materials for a bibliography and essay on his experimental work)]," pp 13-57. (c) G. Gustavson, "Aleksandr Mikhailovich Butlerov, kak predstavitel shkoly [Aleksandr Mikhailovich Butlerov as the founder of a school]," pp 58-68. (d) V. V. Markovnikov, "Vospominaniya i cherty ot zhizni i deyatel'nosti A. M. Butlerova [A memoire and features of the life and activities of A. M. Butlerov]," pp 69-96. (e) *A. M. Butlerov. 1828-1928*, Akademiya Nauk SSSR, Leningrad, 1929. This publication on the centenary of Butlerov's birth contains chapters by V. E. Tishchenko, D. I. Konovalov, A. E. Favorskii, I. A. Kablukov, I. A. Gorbov, and A. E. Chichibabin. (f) G. F. Valitova, *Alexander Butlerov*, "Zhein" Press, Kazan, Tatarstan, Russia, 2014.

    For biographies in English, see: (g) H. M. Leicester, "Alexander Mikhaïlovich Butlerov," *J. Chem. Educ*., **1940**, *17*, 203-209. (h) G. V. Bykov, "Butlerov, Aleksandr Mikhailovich," in C. C. Gillespie, Ed., *Dictionary of Scientific Biography*, , Charles Scribners and Sons, New York, 1970, Vol. 2, p. 620. (i) N. M. Brooks, "Butlerov, Aleksandr Mikhailovich," *Complete Dictionary of Scientific Biography*, Vol. 19, Scribner's Sons, Detroit, 2008, pp 465-468. (j) D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer Verlag, Heidelberg, 2012, pp 47-50.

25. A. M. Butlerov, "Dnevnye babochki volgo-ural'skoi fauni [Diurnal butterflies of the Volga-Ural fauna]," Kand. diss., Kazan, 1849.

26. (a) A. Butlerov, "Ob okislenii organicheskikh soedinenii [On the oxidation of organic compounds]," M. Khim. diss., Kazan, 1851. (b) A. Buttlerow, "Ueber die oxydierende Wirkung der Osmiumsäure auf organische Körper," *Bull. Classe phys.-math. Acad. Sci. St.-Pétersbourg*, **1852**, *10*, 177-187, abstracted in *J. prakt. Chem.*, **1852**, *56*, 271-283, and as A. Buttlerow, "Ueber die Einwirkung der Osmiumsäure auf organische Substanzen," *Ann. Chem. Pharm.,* **1852**, *84*, 278-280. (c) A. Buttlerow, "Osmiumsaure," *Jahresb.*, **1852**, 429-430. (d) A. Butlerov "Ob okislyayushchiem deistvii osmievoi kisloty na organicheskie veshchestva [On the oxidizing action of osmic acid on organic matter]," in A. M. Butlerov, *Sochichenie*, vol. 1, pp 13-20.

27. (a) A. Butlerov, "Ob efirnykh maslakh [On ethereal oils]," Dr. Khim. diss., Moscow, 1854. (b) A. Buttlerow, "Ueber das Oel des *Pulegium micranthum Claus*," *Bull. Classe phys.-math. Acad. Sci. St.-Pétersbourg*, **1854**, *12*, 241-246. (c) A. Buttlerow, "Oel von *Pulegium micranthum*," *Jahresb.* **1854**, 594-595. (d) A. Butlerov, "O masle iz *Pulegium micranthum* Claus [On the oil from *Pulegium micranthum* Claus]," *Sochichenie*, vol. 1, pp 21-25.

28. A. V. Zakharov, Kazanskii universitet. Khronologiya stanovleniya khimicheskoi laboratorii i Kazanskoi khimicheskoi shkoly. Chast I, 1806-1872. [Kazan University: Chronology of the Formation and Development of the Chemical Laboratory and the Kazan School of Chemistry. Part I. 1806-1872], Kazan University, 2011, p 602.

29. Organicheskaya khimiya, sostavlennaya po lektsiyam ord. prof. A. M. Butlerova stud. Vl. Morkovnikovym [Organic chemistry compiled from the lectures of Ord. Prof. A. M. Butlerov by student V. Morkovnikov]; Kazan lit., 1859-1860 (166 pp).

30. Organicheskaya khimiya, sostavlennaya po lektsiyam ord. prof. A. M. Butlerova stud. Iv. Bukhvostovym [Organic chemistry compiled from the lectures of Ord. Prof. A. M. Butlerov by student I. Bukhvostov]; Kazan lit., 1862-1863 (298 pp).

31. A. Butlerow, "Einiges über die chemische Structur der Körper," *Zeit. Chem. Pharm*. **1861**, *4*, 549-560. This paper is available in English translation: F. F. Kluge and D. F. Larder, "A. M. Butlerov. On the Chemical Structure of Substances," *J. Chem. Educ*., **1971**, *48*, 289-291.

32. A. Boutlerow, "Sur les explications différentes de quelques cas d'isomérie," *Bull. Soc. Chim. Paris*, **1864**, *1[N.S.]*, 100-128. This paper is available in English translation: "Primary Documents: On the Different Explanations of Certain Cases of Isomerism," [D. E. Lewis, Trans.], *Bull. Hist. Chem*., **2015**, *40*, 13-28.

33. A. Boutlerow, "Sur quelques composés organiques simples," *Bull. Soc. chim. Paris*, **1863**, *5*, 582-594.

34. A. Boutlerow, "Sur l'alcool pseudobutylique tertiaire ou alcool méthylique triméthylé," *Bull. Soc. chim. Paris*, **1864**, *2[N.S.]*, 106-116.

35. A. Butlerov, *Vvedenie polnomu izucheniiu organicheskoi*

khimii [Introduction to the Complete Study of Organic Chemistry], Kazan, 1864-1866. The book later appeared in German translation: A. Butlerow, *Lehrbuch der organischen Chemie: zur Einführung in das specielle Studium derselben*, Quandt & Händel, Leipzig, 1867-1868.

36. For biographies and biographical sketches of Markovnikov in Russian, see: (a) V. V. Markovnikov, "Markovnikov, Vladimir Vasil'evich," in N. P. Zagoskin, Ed., *Biografichskii slovar professorov i prepodavatelei Imperatskogo Kazanskogo universiteta: Za sto let (1804-1904) [Biographical Dictionary of the Professors and Instructors of Imperial Kazan University: To 100 years (1804-1904)],* Tipo-lit. Imp. un-ta, Kazan, 1904, Part 1, 424-428. (b) A. A. Yakovkin, "Pamyati V. V. Markovnikova," *Zh. Russ. Fiz.-Khim. O-va.*, **1904**, *36*, 181-183. (c) P. S. Grigorovich, "Markovnikov (Vladimir Vasil'evich)," *Entsiklopedicheskoi slovar Brokhauza i Yefrona [Brockhaus and Efron Encyclopedic Dictionary]*, St. Petersburg, 1906, vol XVIIIa, 656-657. (d) I. A. Kablukov, "Vladimir Vasil'evich Markovnikov (biograficheskaya svedeniya i kratkii ocherk nauchnykh rabot) [Vladimir Vasil'evich Markovnikov (biographical information and a brief sketch of his scientific work)]," *Zh. Russ. Fiz.-Khim. O-va.*, **1905**, *37*, 247-303. (e) A. F. Platé, G. V. Bykov and M. S. Eventova, *Vladimir Vasil'evich Markovnikov: Ocherk zhizni i deyatel'nosti, 1838-1904 [Vladimir Vasil'evich Markovnikov: A Sketch of his Life and Work, 1838-1904],* Izd-vo Akad. Nauk SSSR, Moscow, 1962. (f) Ref. 24(f), pp 68-73.

37. Ref. 36(e), p 10.

38. V. Markovnikov, "O al'degidakh i ikh otnosheniyakh k alkogol'am i ketonam [On Aldehydes and their Relationship to Alcohols and Ketones." Kand. diss., Kazan, 1860.

About the Author

About the Author. David E. Lewis is Professor of Chemistry at the University of Wisconsin-Eau Claire. He holds B.Sc., Ph.D. and D.Sc. degrees from the University of Adelaide in South Australia. He is the recipient of the 2018 HIST Award and the 2019 V. V. Markovnikov Diploma and Medal. Lewis is the author of over 90 papers and book chapters, and 6 books. His research interests are in organic synthesis and the history of organic chemistry in Russia. His most recent book, *The Wolff-Kishner Reduction and Related Reactions. Discovery and Development* (Elsevier: Amsterdam, 2019; ISBN 9780128157275) was released in July 2019.

Call for Nominations for the 2020 HIST Award

The Division of History of Chemistry (HIST) of the American Chemical Society (ACS) solicits nominations for the 2020 HIST Award for Outstanding Achievement in the History of Chemistry. This award, formerly known as the Dexter Award and then the Edelstein Award, continues a tradition started in 1956. The award is sponsored by and administered by the Division of the History of Chemistry (HIST). It is international in scope, and nominations are welcome from anywhere in the world. Previous winners of the Dexter and Edelstein Awards include chemists and historians from the United States, Canada, Germany, France, the Netherlands, Hungary, and the United Kingdom.

Each nomination should consist of

- a complete curriculum vitae for the nominee, including biographical data, educational background, awards, honors, list of publications, and other service to the profession;
- a letter of nomination summarizing the nominee's achievements in the field of the history of chemistry and citing unique contributions that merit a major award; and
- at least two seconding letters.

All nomination materials should be submitted (either as e-copy or as hard-copy in triplicate) to the Division of the History of Chemistry, for arrival no later than December 31, 2019. Send e-copy to Vera V. Mainz at mainz@illinois.edu OR alternatively send three (3) hard-copy sets to:

Vera V. Mainz, HIST Sec/Treas
2709 Holcomb Drive
Urbana, IL 61802
USA

THE KAZAN SCHOOL OF CHEMISTRY: A RE-INTERPRETATION (1)

Nathan M. Brooks, New Mexico State University, Las Cruces, New Mexico, USA; nbrooks@nmsu.edu

Introduction

One of the most remarkable aspects of chemistry in nineteenth-century Russia was the emergence of a succession of chemists who worked at the isolated and remote Kazan University and produced path-breaking research over the course of most of that century. As early as the 1860s, contemporary Russian chemists began to term their colleagues there as belonging to the "Kazan School." This concept of the Kazan School of Chemistry has become well-entrenched in the historiography of Russian chemistry up to the present day and is normally cited without further reflection or consideration. However, in this paper I would like to take a closer look at the idea of a series of chemists in Kazan forming an unbroken school of chemistry in the nineteenth century. In particular, I would like to examine what most scholars see as the early years of this school, from the 1830s through the 1860s. I aim to argue that instead of a succession of chemists forming a Kazan School of chemistry, we should more properly see chemistry in Kazan as forming several successive schools, beginning with A. M. Butlerov in the late 1850s.

What we usually take as the canonical description of the Kazan School of Chemistry was laid down by one of its members—A. E. Arbuzov—in a 1940 popular science article that was reprinted and revised many times in the ensuing decades (2). Arbuzov had a long-standing interest in the history of chemistry that spanned his entire career. He saw the Kazan School of Chemistry as an apostolic succession of chemists who taught at Kazan beginning with N. N. Zinin in the 1830s and continuing up through the time of Arbuzov himself, from Imperial times extending well into the Soviet era. Zinin—and Karl Klaus who arrived at Kazan around the time of Zinin—taught A. M. Butlerov. Butlerov took over the teaching of chemistry after, first, Zinin left Kazan to go to St. Petersburg in 1848, and then completely after Klaus as well departed Kazan for Dorpat in 1852. Butlerov trained many prominent chemists, including A. N. Popov, M. D. L'vov, V. V. Markovnikov and A. M. Zaitsev, the last two of whom succeeded Butlerov at Kazan after their mentor moved to St. Petersburg in 1868. Markovnikov—as was his wont—soon had a falling out with the administration and some other faculty members at Kazan University and moved to Novorossiisk University in Odessa in 1871, but quickly received a call to Moscow University where he established his own flourishing school of chemistry, beginning in 1873. Zaitsev, however, remained at Kazan until his death in 1910, teaching E. E. Vagner, S. N. Reformatskii, A. N. Reformatskii, A. A. Al'bitskii, and A. E. Arbuzov, among many others. A number of these chemists taught for a short time at Kazan but most soon moved on to other higher educational institutions in Russia. When Zaitsev died, he was succeeded in the chair of chemistry by Arbuzov in 1911, who taught at Kazan until his death in 1968. Arbuzov had many students of his own, who became chemistry professors during the Soviet era, including his two sons and one daughter. Arbuzov's eldest son, B. A. Arbuzov, became a chemistry professor at Kazan, as well as a member of the Academy of

Sciences of the USSR, the highest honor for a scientist in the Soviet Union.

This is a convenient and appealing story. Many historians of chemistry have written about it. I have written about it—and our distinguished award winner David Lewis has as well, which is why I selected this topic for my paper.

This is a convenient and appealing story. But it is wrong.

Let me briefly explain briefly. My argument is that we should not see an unbroken apostolic succession of chemists constituting a Kazan School of Chemistry. Only using the loosest definition for a School of Chemistry can we see a Kazan School of Chemistry running from Zinin through to B. A. Arbuzov. Instead, I will argue that what we have in Kazan is the **Butlerov** School of Chemistry beginning in the late 1850s, perhaps followed by the Zaitsev School or later by the Arbuzov School. Zinin and Klaus did not found a School of Chemistry. That only happened later with Butlerov, and then, not until after Butlerov's first trip abroad at the end of the 1850s.

One more thing before I get into the meat of the discussion. I will focus in this paper on the biographies of the chemists involved. I believe that it is through presenting specific biographical details that we can discern the contours of what defines these research schools (3). Most treatments of the Kazan School of Chemistry that I am aware of have been relatively general in scope, so they miss the finer, granular details that can reveal patterns about the research school. It is like we are viewing a part of the Milky Way Galaxy with a telescope. At first you can see a blurry continuous image, but if you increase the power of the telescope you are then able to see more individual stars and notice the gaps between them.

That is what I want to do in this paper. I want to give a fine-grained analysis that will show **why** we need to re-evaluate our ideas about the Kazan School of Chemistry. Viewed in a wider perspective, the traditional view of the Kazan School of Chemistry seems reasonable. But when we look closer—in a more fine-grained analysis—the gaps reveal problems with the traditional view.

However, I would first like to briefly summarize some of my guiding ideas for considering the idea of a scientific research school. While scientists often used the term "school" in the nineteenth century and after, historians of science have generally settled on the term "research school" to describe "small groups of mature scientists pursuing a reasonably coherent programme of research side-by-side with advanced students in the same institutional context and engaging in direct, continuous social and intellectual interactions" (4). J. B. Morrell published one of the most influential discussions of the concept of a research school in 1972 (5). In this work, Morrell contrasted the research schools of J. Liebig and Thomas Thompson, which allowed him to point out some of the most important factors contributing to the success (or lack of success) of a research school. While these factors should not be taken as a rigid model, they are useful as a point of departure for examining research schools as a unit of analysis (6). Morrell emphasized that the director played the key role in the success of the research school. The director offered a program of work for his students to follow and conduct, as well as a body of techniques that students could learn without undue difficulty. A successful director needed to be sufficiently charismatic to attract a sufficient number of students on a continual basis for the school to flourish. In addition, the director should have an outlet for publishing his work and that of his students, if the research school was to garner more than a local recognition. Furthermore, a successful director should have sufficient institutional power and support to maintain the school on an ongoing basis.

In the years since Morrell analysis appeared, there have been many studies of research schools that have refined and contested the factors he presented (7). For the purposes of this paper, however, I will use Morrell's factors as a general lens through which to analyze the Kazan School of Chemistry.

Chemistry at Kazan

Kazan University was founded in 1804 as one of the building blocks of the new Russian university system being developed during the early years of the nineteenth century. Located about 500 miles east of Moscow along the Volga River, the university in Kazan was designed to provide education for those from Siberia and the eastern regions of the Russian Empire. The first chemistry professors engaged to teach at Kazan University were foreigners who had difficulty speaking in Russian, as was the case for many university professors at other Russian universities at this time (8). However, the relative isolation of Kazan from the more populated centers in Russia made it difficult for the university administrators there to engage qualified professors, especially those who could speak Russian. Eventually, Russian education officials turned to solve this problem by grooming their own promising students as future faculty members or hiring the few Russian-speaking graduates from other Russian higher educational institutions. Thus, the Curator of the Kazan Educational District in 1811 requested to hire I. I. Dunaev, a recent graduate of the Main Pedagogical Institute in St. Petersburg. Dunaev was one of the first generation of native Russian professors at the universities during the nineteenth century (9). However, Dunaev was undistinguished as a teacher or scholar and conducted no laboratory research or even laboratory instruction for his students.

During Dunaev's time at Kazan University, the institution was rocked by considerable controversies, especially those connected with the Curatorship of M. Magnitskii, an extreme reactionary who severely weakened the university by persecuting various professors, succeeding in purging some of them (10). Magnitskii also disrupted teaching at the university by hiring multiple instructors for some subjects, like chemistry, who had no training in the field or who could not even speak Russian. In 1826, Magnitskii was replaced by Count M. N. Musin-Pushkin, a wealthy and high-ranking military officer from a prominent noble family near Kazan. Musin-Pushkin would begin to bring order to the university and improve its academic quality. Chemistry would benefit from Curator Musin-Pushkin's efforts, with the construction and extensive equipping of a new laboratory and the solidification of instruction by engaging N. N. Zinin (1812-1880) and K. K. Klaus (1796-1864) as professors.

Zinin was born in 1812 into a lower-ranking military officer family. He was orphaned at an early age and was raised by a relative not too far from Kazan. He was able to obtain a solid education and was intending on studying at a state institute in St. Petersburg after graduation, but then his relative died, forcing him to attend Kazan University instead, beginning in 1830. Zinin studied in the physics-mathematics faculty, likely influenced by another relative who was an astronomy professor at the time. At Russian universities at this time, students did not "major" in a specific field but rather took a wide range of courses offered in their faculty. The main way to show a specialization was by working on a thesis in the third and fourth years as a student. Zinin wrote a *kandidat* thesis about the motion of the planets, showing that he was mainly interested in mathematics and physics. Writing a *kandidat* thesis gave Zinin the qualifications to continue on for further education at a university and after graduation in 1833 Zinin began to teach courses in physics and mathematics at Kazan while studying for a master's degree. Obviously, Zinin was being groomed to become a professor of physics or mathematics. But then, as it were, fate intervened.

These years in the 1830s were an era of transition at Russian universities, and particularly at Kazan University, as Russian education officials, especially the Curator Musin-Pushkin, were trying to upgrade the quality of the teaching staff as well as to replace with Russians as many as possible of the foreign professors currently teaching at Russian higher educational institutions. The position of Curator was an immensely powerful one, having direct control over all of the educational institutions sponsored by the Ministry of Education in one of the six educational districts of the empire, each of which had a university at its apex (11). Magnitskii had attempted to curry favor with Tsar Alexander I and his entourage following their turn towards mysticism and nationalism after the victory over Napoleon, coming very close to actually shutting down Kazan University. The chemistry professor at Kazan during these years was the undistinguished Russian Dunaev, who had been educated in Russia but had also studied at a European university for a year. He had fallen into disfavor with Magnitskii but was able to regain his standing by giving several public lectures, including one entitled "The use and misuse of the natural sciences and the need for them to be based on Christian piety." Magnitskii eventually was replaced as Curator in 1826 by Musin-Pushkin. While Musin-Pushkin is usually described as an ignorant, crude, and overbearing official, he seems in actuality to have been quite sincere and dedicated to improving conditions at Kazan University. One of Musin-Pushkin's tasks was to upgrade the teaching staff and when in he made a list of professors to be replaced in conjunction with the new University Statutes in 1835, Dunaev's name headed the list. But who could replace Dunaev? There was only a very tiny pool of possible candidates in Russia at this time and the earlier typical solution of hiring someone from a foreign country was frowned upon now. So Russian higher educational institutions looked inward and began grooming their own students to become professors. This could prove to be difficult as it often was tricky to precisely predict when a chair (*kafedra*) would become available for the Russian student. And this type of complication happened for Zinin. Curator Musin-Pushkin evidently began to see Zinin as the replacement for Dunaev (12). In 1835, Zinin was transferred to teaching in support of Dunaev and given a topic in chemistry for his master's thesis, which he received in 1836. The next year, he was given a fellowship to study abroad. The plan outlined for this trip was to attend lectures at various universities in Berlin and other places in Germany, as well as with Berzelius in

Sweden. No research or laboratory work was envisioned, and at this time at Russian universities no experimental research was necessary to receive a doctorate. However, once Zinin was abroad, he evidently heard about Liebig at Giessen and went there to attend lectures and eventually gained a spot in Liebig's laboratory where he conducted some original research on a topic of interest to Liebig. Thus, everything seemed to be proceeding according to plan, even if it wasn't the exact one outlined for Zinin before his departure. But then a big snag happened.

Karl Klaus, a Baltic German pharmacist educated in Russia, moved to Kazan to open a pharmacist's shop (13). He became popular with the local citizens of the town and evidently decided in about 1838 that he wanted to become a chemistry professor at Kazan. This was not an outrageous plan, although it was not a common one at Russian universities, as pharmacists usually became laboratory assistants there, not professors. Indeed, Kazan University had another Baltic German serving as laboratory assistant at this time. Therefore, it was a logical decision to have Klaus become the chemistry professor and it would be a good fit. But what to do about Zinin, who was currently abroad, and intending on returning to become the chemistry professor? Curator Musin-Pushkin decided that since the chair of technology also was vacant, Zinin could take an extra year of study abroad to expand his knowledge of technology and then return to Kazan as the professor of technology. It seems that Zinin was not thrilled with this change in plans, but he accepted it in part because it provided him with an extra year of state support for study abroad. With Zinin's acceptance of this change in direction, things seemed to be working out with the plans for chemistry and technology at Kazan. Curator Musin-Pushkin assisted Klaus to obtain a doctorate in chemistry which would give him the formal qualifications to be named as professor of chemistry, while Zinin returned from abroad, wrote his doctoral thesis in St. Petersburg and then returned to Kazan as professor of technology. While in St. Petersburg, Zinin did attempt to gain the appointment as professor of chemistry at Kharkov University, but Curator Musin-Pushkin intervened to squelch that idea.

Zinin remained at Kazan University from 1841 until 1848, when he was appointed professor at the St. Petersburg Medical-Surgical Institute (14). Since the Institute was under the auspices of the Minister of War, the Curator of the Kazan Educational District could not block the appointment as the university was controlled by a different Ministry, the Ministry of Education. While in Kazan, Zinin continued the research he had initiated as a student at Giessen under Liebig, although it proved difficult to obtain the compounds he wanted to work with in Russia. It was during this time that Zinin discovered his method for the reduction of nitrobenzene to produce aniline. This was the work that gained Zinin great renown some years later, with A. W. Hoffmann stating that this work will be written in golden letters in history (15).

Klaus also did famous research work during these years on the platinum-group metals. He discovered and isolated the new element ruthenium, announced in a publication in 1843, and continued work on other platinum-group metals until he left Kazan in 1852 to move back to his native Dorpat, in Estonia, then part of the Russian Empire, but which was culturally German at that time.

Both Zinin and Klaus worked in home laboratories, not in the university laboratory. This is an important point because it limited the amount of time and attention either of them could give to any students working in the university chemistry laboratory. Thus, when A. M. Butlerov was an undergraduate student at Kazan from 1844 until his graduation in 1849, he most likely would have had only scant opportunities to do original laboratory work with Zinin or Klaus (16). Instead, while Butlerov took the usual chemistry courses for students in the physics-mathematics faculty, he seemed to be more interested in botany and other natural sciences rather than chemistry. In fact, Butlerov wrote his *kandidat* thesis in 1849 on "The diurnal butterflies of Volga-Ural fauna." Similar to the situation with Zinin, it appears that Butlerov was interested in becoming a university science professor, but not in chemistry. However, soon after Butlerov graduated with his *kandidat* degree in 1849, Klaus's health declined significantly and he needed help teaching chemistry. Butlerov turned out to be the only possible choice readily available. So soon Butlerov was unofficially assisting Klaus in his chemistry classes and by 1851 was appointed adjunct in chemistry, having received his master's degree in chemistry the year before. It was clear that Butlerov was viewed as Klaus's successor as chemistry professor once he had obtained the necessary doctoral degree. Butlerov did do some experimental work on osmium compounds under Klaus's direction, which formed part of his master's thesis, but these experiments were quite minimal in scope and Butlerov did not continue them after he was awarded his degree.

I am arguing here that Butlerov was not influenced in his subsequent research by either Zinin or Klaus. Historians often use a quote written by Butlerov from an 1880 obituary of Zinin (17) to indicate Zinin's influence on Butlerov. But I believe this quote does not prove what these historians seem to imply.

> I attracted [Zinin's] attention and soon he acquainted me with the course of his work and with the various subjects of the benzoyl and naphthalene series, with which he was then working. Little by little I began to work primarily under his direction, who did not limit himself to his personal investigations, but also was interested in repeating experiments of others. Assigning these in part to his students, he would undertake the major part himself. Thus, together with him we completed a whole series of many well-known experiments…

Yes, this quote shows that Zinin introduced the young Butlerov to chemistry experimentation, but the influence on Butlerov was limited. There is nothing subsequent in Butlerov's career to show that he ever conducted organic chemistry research along the lines of Zinin's work, even in the years immediately after Zinin's departure from Kazan.

There is another example from Butlerov's life which we might say helps prove the rule. In 1854, Butlerov was attempting to defend his doctoral thesis, a literature review of some essential oils. However, Butlerov's thesis was rejected at Kazan University, likely mainly due to personal jealousy from a faculty member who was one of the official evaluators of the thesis but possibly partly due to its lack of scientific rigor (18). Butlerov asked Klaus, who was now a professor of pharmacy at Dorpat University, for help. Klaus believed that it would be very difficult for Butlerov to defend the thesis at Dorpat (because the thesis and the defense would need to be conducted in German and Klaus was in the medical faculty not the physics-mathematics faculty where the defense would be conducted), but suggested Butlerov try Moscow or St. Petersburg. Also, Klaus recommended a few experiments for Butlerov to add to the thesis. We have many letters sent by Klaus to Butlerov which indicate how much Butlerov relied on Klaus's advice (19). But the information in these letters, plus Butlerov's actions in the 1850s, indicate that Klaus's research had no impact on Butlerov's research career. Klaus had personal influence on Butlerov, but no influence on Butlerov's scientific choices. Indeed, it did not appear at that time that Butlerov had any intention of pursuing experimental chemistry research.

Furthermore, Soviet and Russian historians of chemistry often point to a visit Butlerov had with Zinin in 1854 when Butlerov was in St. Petersburg contemplating where to defend his doctoral thesis (20). Again, in Butlerov's obituary of Zinin, Butlerov mentions this visit and commented that Zinin recommended that he become acquainted with the work of Laurent and Gerhardt (17). Soviet and Russian historians of chemistry use this incident to help forge another link between Zinin and Butlerov, strengthening the idea of an unbroken Kazan School of Chemistry transmitted from Zinin to Butlerov. This conclusion is quite weak, in my view. While Butlerov does appear to have adopted the ideas of the French chemists or to have become receptive to them, this meeting with Zinin did not influence Butlerov's experimental work. Perhaps the strongest evidence, however, for the limited influence of Zinin on Butlerov at this time is simply the fact that there are no extant letters from Zinin to Butlerov from this time. Butlerov seems to have saved most, if not all, of the letters he received and they have been published. Also, I have checked the original letters located in Butlerov's archive at the Academy of Sciences in St. Petersburg and no letters from Zinin are found there for these years.

After he defended his doctoral thesis, Butlerov devoted little effort to laboratory work in chemistry. He published three short articles, in effect three abstracts, on widely varied subjects. One concerned a study of mineral water and another examined the monochloride of turpentine oil or "artificial camphor," in Butlerov's term. There was no apparent scientific connection between these works, and Butlerov seemed to be casting around for a suitable subject for detailed investigation (21). Clearly, these investigations done by Butlerov show no influence from Zinin and the type of research studies he was conducting up to this time.

At the same time, however, as Butlerov was dabbling with these chemical researches, he was devoting a great deal of effort to activities quite distant from the study of chemistry. During 1853-1857, Butlerov published far more articles in journals of botany and agriculture than he did in chemistry journals. He published more than 27 articles and reviews in the local Kazan economic society journal, ranging from the cultivation of certain seeds to notes for lovers of fruit gardens. As I have argued elsewhere, these publications show that during these years, Butlerov's outlook was oriented toward local concerns (21). Also, Butlerov gave a series of public lectures on chemistry and technical chemistry designed for the townspeople of Kazan. In addition, he made a futile foray into producing an egg soap for sale to the local community as well as an attempt to produce phosphorous matches (22).

Thus, considering all of these activities of Butlerov, I argue that there was no scientific continuity from Zinin and Klaus to Butlerov. There is no reason to posit any kind of Kazan School of Chemistry beginning with Zinin and Klaus that was transmitted through Butlerov.

However, we **can** discern a specific **Butlerov** School of Chemistry at Kazan that began in the late 1850s. Butlerov's life and career changed dramatically in the aftermath of the Crimean War and the death of Tsar Nicholas I in 1855. Among the series of Great Reforms that the new Tsar Alexander II initiated, some of the most important concerned education, since it was widely believed that learning and science were necessary for Russia to achieve parity with the other European powers. The first important reform concerning education was the re-establishment of the right to travel and study abroad (23). The consequences of these reforms for Butlerov—and for all of Russian chemistry—were profound as many young Russian chemists began to travel and study abroad, bringing back to Russia new ideas and laboratory experiences from Europe. These young Russian chemists helped professionalize the study of chemistry in Russia in the next decades (24).

Although Butlerov was not as young as most other Russian chemists who went abroad at this time, the impact of his travel abroad in 1857-1858 was highly consequential for him. However, judging from Butlerov's plans for his trip, he originally conceived of it more as a vacation rather than undertaking serious scholarly activities, and his wife would accompany him on the travels. The original itinerary included many sites of no particular scientific interest, but which were prime vacation areas. After only a few weeks, though, Butlerov's plans completely changed. He had arranged some visits with Kekulé and Erlenmeyer, who both apparently affected him greatly. From this time, Butlerov began to be drawn into the current theoretical controversies in organic chemistry, especially concerning structural theory, and he was gradually beginning to develop his own views. Butlerov had felt isolated in Kazan, but his travels in Europe gave him the opportunity to establish personal contacts that would last for many years.

Butlerov eventually changed his plans for the trip and spent an extended period of time in Paris, working in the laboratory of Wurtz as well as attending lectures and participating in sessions of the Paris Chemical Society (25). The work Butlerov performed in Wurtz's laboratory was his first significant experimental research. He began working on methylene and its derivatives, continuing this work for more than four years and publishing the results in various French and German journals. One important aspect about this work was that it was a **series** of investigations, not just some individual and isolated experiments. From this time forward, a characteristic of Butlerov's research would be a systematic approach to his subject, often to prove a theoretical point, as in his later work on the structural theory.

When Butlerov returned to Russia in July 1858, his attitude toward his teaching and research had changed dramatically. Butlerov's experiences induced him to shift his intellectual focus from concerns that were important to the local community in Kazan to a concentration on issues that were important to the international community of chemists.

It was at this time that Butlerov also began to lay the foundations of what we can term the **Butlerov** School of Chemistry. Butlerov began a concerted effort to improve the chemistry laboratory at Kazan University and have every chemistry student conduct laboratory exercises, with advanced students even pursuing original research work that was associated with his own studies. For example, in one petition to the Kazan University authorities, Butlerov stated: "All foreign laboratories have significantly more resources than our laboratory, including space, equipment, glassware, and materials" (26). He kept up these petitions, and even when he succeeded in wrenching additional resources for the laboratory, he kept asking for more. In addition, Butlerov shed many of his extra duties, like teaching extra classes for additional salary that he had eagerly sought in years past, and began to devote all of his time to his core chemistry teaching and to his research (27).

Butlerov gradually began to construct a career path for his students—one with specific fellowships and positions that would support them until they could receive the degrees that would allow them to become professors in their own right. Butlerov's two most famous students were V. V. Markovnikov (1837-1904) and A. M. Zaitsev (1841-1910), who both became professors at Kazan University following Butlerov's move to St. Petersburg University in 1868. Markovnikov soon (1871) left Kazan University for Novorossiisk University in Odessa following a dispute with other faculty members at Kazan, but then quickly obtained a professorship at Moscow University (1873), where he established his own flourishing research school. Zaitsev remained at Kazan University for the rest of his career and trained a generation of chemists who continued Butlerov's excellence in organic chemistry. For example, A. N. Popov (1840-1881) established Warsaw University as a center of organic chemistry research and was succeeded after his premature death by another Kazan University graduate, E. E. Vagner (1849-1903) (28). In addition to these students who became chemistry professors, the graduates of Kazan University obtained positions at nearly every higher educational institution in the Russian Empire in the first few decades after Butlerov first established his research school. Thus, Butlerov's influence as a chemist extended far beyond the confines of Kazan University and had a lasting impact on chemistry throughout Russia.

Conclusion: The Research School under Butlerov

Finally, I would like to conclude with a consideration of what a Research School of Chemistry at Kazan was around the time Butlerov was teaching at Kazan.

If we use the characteristics of a Research School outlined by Morrell and Geison, we can see that the Butlerov School fits quite nicely into this model. We have a charismatic leader—Butlerov—who was rapidly gaining an international research reputation through his work on developing the structural theory of organic chemistry. He conducted his own experimental work in direct view of his students and thus could serve as an example and model for his students. He was able to gain institutional resources and attract students to do research under his direction. He had a focused research program that could provide students with a variety of suitable paths for experimentation. Moreover, with the founding of the Russian Chemistry Society in 1868, chemistry students had a suitable place to publish the fruits of their research and they took ample advantage of this publication outlet (29). With their experience in Butlerov's laboratory, his students were well prepared to compete for positions at other higher educational institutions in Russia. The overwhelming success of Kazan students in gaining employment elsewhere in Russia testified to the strong foundations instilled in them while at Kazan University. All of these—and more—added up to make Butlerov's laboratory and students a productive Research School.

Perhaps the key aspect in the formation of the Butlerov School of Chemistry at Kazan University was Butlerov's adoption of the structural theory of organic chemistry and making it the central focus of research. The fruits of this choice can be seen in Markovnikov's research while at Kazan University during the 1860s. Markovnikov contributed key research on the structural theory that helped establish its essential theoretical foundations.

Seen in this light, perhaps we should not consider Zaitsev as a direct successor to Butlerov and as a member of Butlerov's research school. Zaitsev had a rather unusual background and had spent some of his early years working in Marburg with Kolbe, who influenced him greatly (30). Upon his return to Kazan, Zaitsev presented a dissertation to Butlerov, based on the work done in Kolbe's laboratory. Butlerov angrily rejected this study, as Zaitsev—perhaps naively—parroted Kolbe's theoretical ideas which were fundamentally opposed to those of Butlerov himself. Zaitsev did revise this work and eventually regained the good graces of Butlerov. Still, Zaitsev's research never seemed to reflect the degree of influence from the structural theory of organic chemistry that was shown by the work of Markovnikov and other young chemists at Kazan University. Therefore, perhaps we should not consider Zaitsev as a direct successor to Butlerov and his research school. Zaitsev seemed to have a different research agenda than did Butlerov and Markovnikov. While Zaitsev's research agenda was based on the structural theory, the essence of his work was in a different direction than the work of Butlerov or Markovnikov. In a similar vein, Arbuzov's work did not evolve out of Zaitsev's work and so he should not be considered a direct successor to Zaitsev, as predicated by the unified Kazan School of Chemistry approach.

References and Notes

1. Presented at the 256th National Meeting of the American Chemical Society, Boston, MA, Aug. 21, 2018, HIST 32 in the HIST Award Symposium Honoring David Lewis.
2. A. E. Arbuzov, "Kazanskaia shkola khimikov," *Uspekhi khimii*, **1940**, *9*, 1378-1394. This is reprinted in A. E. Arbuzov, *Izbrannye raboty po istorii khimii*, Nauka, Moscow, 1975, pp 109-131.
3. On this point, also see John W. Servos, "Research Schools and Their Histories," *Osiris*, **1993**, *8*, 2-15.
4. G. L. Geison, "Scientific Change, Emerging Specialties, and Research Schools," *Hist. Sci.*, **1981**, *19*, 20-40.
5. J. B. Morrell, "The Chemist Breeders: The Research Schools of Liebig and Thomas Thompson," *Ambix*, **1972**, *19*, 1-46.
6. See G. L. Geison, "Research Schools and New Directions in the Historiography of Science," *Osiris*, **1993**, *8*, 226-238.
7. For example, see the articles in G. L. Geison and F. L. Holmes, Eds., "Research Schools. Historical Reappraisals," *Osiris*, **1993**, *8*, 1-248; L. Klosterman, "A Research School of Chemistry in the Nineteenth Century: Jean Baptiste Dumas and His Research Students," *Ann. Sci.*, **1985**, *42*, 41-80; and M. P. Crosland, "Research Schools

of Chemistry from Lavoisier to Wurtz," *Br. J. Hist. Sci.*, **2003**, *36*, 333-361.

8. For a more detailed discussion of chemistry at Kazan University, see: N. M. Brooks, The Formation of a Community of Chemists in Russia: 1700-1870. Ph.D. dissertation, Columbia University, 1989, pp 198-291; A. Al'bitskii, "Kafedra khimii I khimicheskaia laboratoriia imp. Kazanskogo universiteta v ikh proshlom I nastoiaschchem," in *Lomonosovskii sbornik. Materialy dlia istorii razvitiia khimii v Rossii*, Moscow, 1901; and D. E. Lewis, "The University of Kazan—Provincial Cradle of Russian Organic Chemistry. Part I: Nikolai Zinin and the Butlerov School. Part II: Aleksandr Zeitsev and his Students," *J. Chem. Educ.*, **1994**, *71*, 39-42, 93-97.

9. For information about Dunaev, see Al'bitskii, Ref. 8, pp 8-10; and N. P. Zagoskin, Ed., *Biograficheskii slovar' professorov I prepodavatelei imp. Kazanskogo universiteta za sto let (1804-1904)*, vol. 2, Kazan', 1904, p 317.

10. For information about Magnitskii, see J. T. Flynn, "Magnitskii's Purge of Kazan University: A Case Study in the Uses of Reaction in Nineteenth-Century Russia," *J. Mod. Hist.*, **1971**, *43*, 1971, 598-614; and C. H. Whittaker, *The Origins of Modern Russian Education: An Intellectual Biography of Count Sergei Uvarov, 1786-1855*, Northern Illinois University Press, DeKalb, 1984.

11. Other Ministries had control of different types of higher educational institutions besides the universities. For example, the Russian Orthodox Church controlled the seminaries, while various technical institutes were under the direction of the corresponding ministries. Thus, the Ministry of War controlled the Military Medical-Surgical Institute.

12. For details, see N. M. Brooks, "Nikolai Zinin at Kazan University," *Ambix*, **1995**, *42*, 129-142.

13. For information about Klaus, see N. N. Ushakova, *Karl Karlovich Klaus, 1796-1864*, Nauka, Moscow, 1972.

14. See Ref. 12 for details about Zinin's study and career at Kazan.

15. See N. M. Brooks, "Nikolai Zinin and Synthetic Dyes: The Road Not Taken," *Bull. Hist. Chem.*, **2002**, *27*, 26-36.

16. For information about Butlerov, see G. V. Bykov, *Aleksandr Mikhailovich Butlerov*, Nauka, Moscow, 1961; and N. M. Brooks, "Alexander Butlerov and the Professionalization of Chemistry in Russia," *Russ. Rev.*, **1998**, *57*, 10-24.

17. A. P. Borodin and A. M. Butlerov, "Nikolai Nikolaevich Zinin. Vospominaniia o nem I biograficheskii ocherk," *Zhurnal Russkogo Fiziko-Khimichekogo Obshchestva*, **1880**, *12*, 215-252.

18. G. V. Bykov, Ed., *Pis'ma russkikh khimikov k A. M. Butlerovu. Nauchnoe nasledstvo. 4*, Akademiia Nauk SSSR, Moscow, 1961, 161. Letter of Klaus to Butlerov dated 12 May 1854.

19. G. V. Bykov, ed., Pis'ma russkikh khimikov (Ref. 18).

20. Ref. 16 (Bykov), p 57.

21. Ref. 16 (Brooks).

22. S. F. Glinka, "Aleksandr Mikhailovich Butlerov v chastnoi I domashnei zhizni (Po lichnym vospominaniiam)," *Trudy Institut Istorii Estestvoznaniia i Tekhniki*, **1956**, *12*, 182-199.

23. For a good overview of the Great Reforms, see W. B. Lincoln, *The Great Reforms: Autocracy, Bureaucracy, and the Politics of Political Change in Imperial Russia*, Northern Illinois University Press, DeKalb, 1990.

24. For a discussion of this professionalization process, see N. M. Brooks, Ph.D. dissertation (Ref. 8).

25. For information about Wurtz and his laboratory, see A. J. Rocke, *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry*, MIT Press, Cambridge, 2001.

26. A. M. Butlerov, *Sochineniia*, t. 3 Akademiia Nauk SSSR, Moscow, 1958, pp 71-72.

27. For example, see Butlerov's petition in 1859 asking that his teaching load not be increased: A. M. Butlerov, *Nauchnaia i pedagogicheskaia deiatel'nost'*, Akademiia Nauk SSSR, Moscow, 1961, p 26.

28. For details about these chemists, see D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer, Heidelberg, 2012.

29. For information about the Russian Chemical Society, see N. M. Brooks, M. Kaji, and E. Zaitseva, "Russia: The Formation of the Russian Chemical Society and its History until 1914," in Anita Kildebaek Nielsen and Soňa Štrbáňová, Eds., *Creating Networks in Chemistry: The Founding and Early History of Chemical Societies in Europe*, Royal Society of Chemistry, Cambridge, UK, 2008, pp 281-304.

30. For information about Zaitsev, see A. S. Kliuchevich and G. V. Bykov, *Aleksandr Mikhailovic Zaitsev, 1841-1910*, Nauka, Moscow, 1980. For an excellent description of Kolbe, see A. J. Rocke, *The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry*, University of California Press, Berkeley, 1993.

About the Author

Nathan M. Brooks is an Associate Professor in the Department of History at New Mexico State University, Las Cruces, New Mexico, where he teaches a wide range of courses in Russian history, the history of science, and Global history, including the history of Central Asia. His research focuses on the history of science and technology in Russia and the Soviet Union, with a focus on chemistry and chemical technology.

MENDELEEV, MEYER, AND ATOMIC VOLUMES: AN INTRODUCTION TO AN ENGLISH TRANSLATION OF MENDELEEV'S 1869 ARTICLE "ON THE ATOMIC VOLUME OF SIMPLE BODIES" (1)

Gregory S. Girolami and Vera V. Mainz, School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, IL 61802, USA; ggirolam@illinois.edu; mainz@illinois.edu

Supplemental material

Introduction

The German chemist Julius Lothar Meyer (1830-1895) is well known for having pointed out that the atomic volumes of the chemical elements vary in a regular way as a function of increasing atomic weight, in a paper submitted in December 1869 and published in March 1870 (2). In this paper, Meyer summarized this correlation in a graph that quickly became known as Meyer's curve (3). This visual display of the data, which made it easy to see the rise and fall of the atomic volume of the elements with increasing atomic weight (Figure 1), remains today an iconic representation of an important scientific correlation (4).

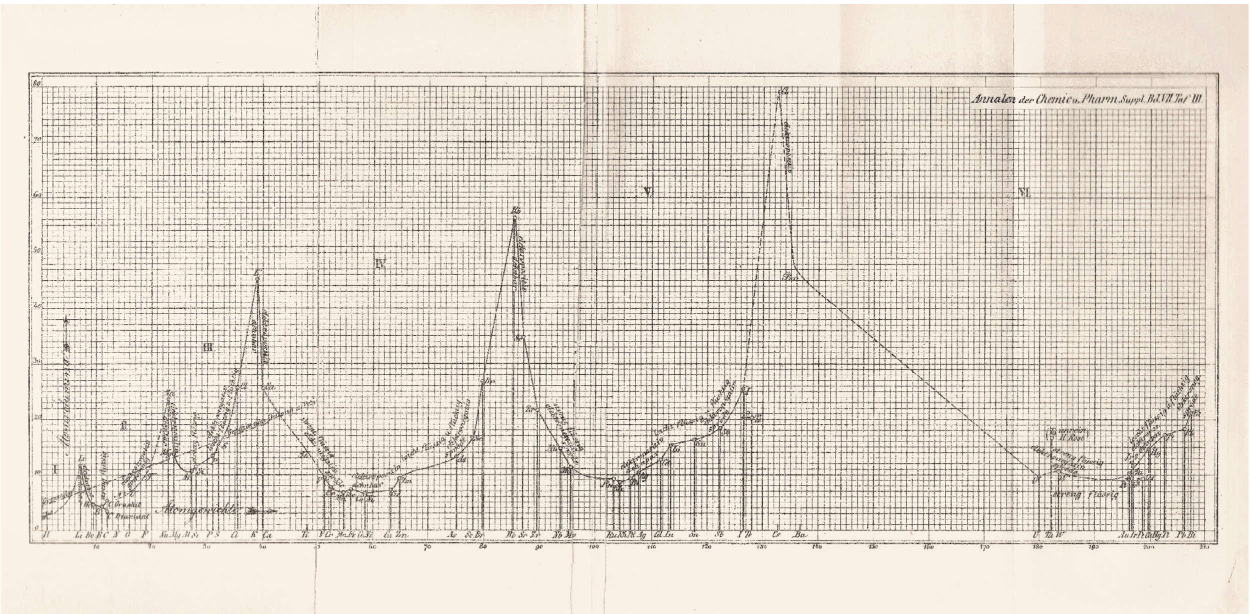


Figure 1. Meyer's curve, from Ref. (2). Although this chart has often been reproduced, the resolution is invariably poor. This figure has been constructed from new scans of the original journal publication. A high-resolution digital image is included in the supplemental material.

Meyer had been prompted to submit his paper in response to a brief abstract in German of the periodic system that Dmitri Ivanovich Mendeleev (1834-1907) had submitted in March 1869 (5) to the *Zhurnal Russkogo Khimicheskogo Obshchestva* (*Journal of the Russian Chemical Society*) (6). Because neither Mendeleev's first journal publication nor his 1869 book *Osnovy Khimii* (7) contained a detailed discussion of the dependence of atomic volumes on atomic weight, it is often assumed that Meyer was the first to reveal this relationship (8).

But on the 23rd of August 1869 (O.S.; 4 Sep 1869 N. S.), a few months after having published his announcement of the periodic system, and several months before Meyer's paper was submitted, Mendeleev presented his second full paper on his periodic system to the chemical section of the Second Congress of Russian Scientists and Physicians, held in Moscow. A short abstract of the paper Mendeleev read was published at the time of the Congress (9); the full paper did not appear until the Congress proceedings was printed in early 1870 (10).

In part because this 1869 Congress paper has never been translated in its entirety from the original Russian into English or German (11, 12), it has often been ignored in discussions of Meyer's curve and the early history of the periodic system. To be sure, a few scholars have discussed it briefly, as we will mention below, but this paper deserves greater attention for at least three reasons: (a) as the second full paper that Mendeleev wrote on his periodic system it gives valuable insights into his early thinking, (b) it contain Mendeleev's first detailed predictions of the properties of undiscovered elements, and (c) it shows that Mendeleev had anticipated Lothar Meyer's 1870 paper on the periodic relationship of atomic volume to atomic weight.

Historical Context of Mendeleev's 1869 Congress article

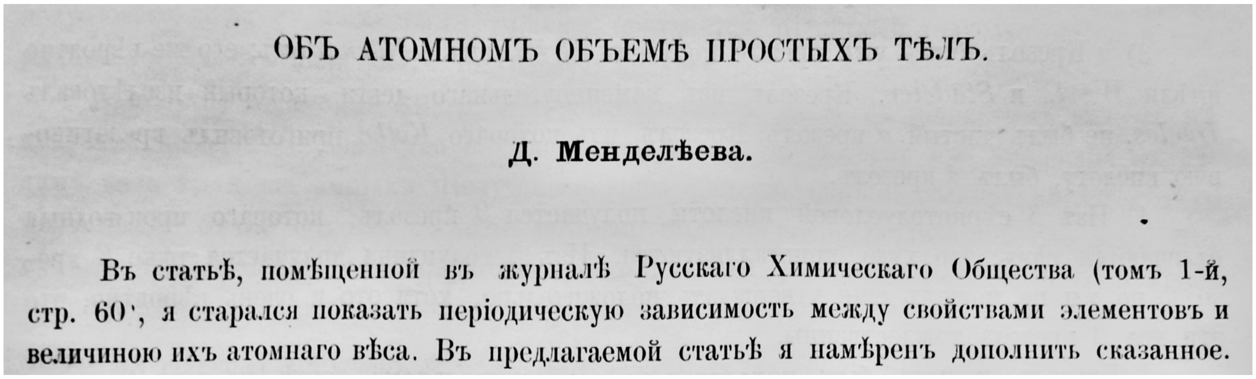
In order to better understand the historical context of Mendeleev's 1869 Congress paper "On the Atomic Volume of Simple Bodies," we present a short history of the relevant science of the time. Atomic volumes (and the related concept of molar volumes) are easily calculated by dividing the atomic or molecular weight (g/mol) of a substance by the density (g/cm^3), earlier called the specific weight, of a solid sample of the substance. Before the mole was named or formally defined, atomic and molar volumes were reported as unitless quantities; today, they are reported in units of cubic centimeters per mole. Atomic volumes played an important role in the development of chemistry in the 19th century (13).

The concept of atomic volume had been devised in 1821 (14) by the French chemists Auguste Le Royer (1793-1863) and his student Jean Baptiste André Dumas (1800-1884). The main part of Le Royer and Dumas's paper was devoted to descriptions of their studies of the densities of various inorganic substances, such as silica, boric acid, chalk, alumina, gypsum, and the oxides of copper, bismuth, lead, and mercury. They then used these measured densities to compute the molar volumes of these substances, and found that many of them (but not all) were integer multiples of the molar volume of ice. Similarly, turning to a group of twenty solid elements, they found once again that the atomic volumes were in simple whole number ratios to one another. To some extent, the attempt by Le Royer and Dumas to find regularities in the atomic volumes of the chemical elements resembles Prout's similar effort six years previously (15) to find regularities in the atomic weights of the elements.

All of the numerical relationships in Le Royer and Dumas's paper, unfortunately, were the result of overinterpretation of a limited body of data. Many of their atomic volumes do not match modern values, because they depend on the atomic weight assigned to the element. Some of their atomic weights (and thus atomic volumes) were correct, but quite a few were not (as was common in those pre-Cannizzaro days). The importance of Le Royer and Dumas's paper lies not so much in its results and analysis, but rather in its definition of a new physical property—atomic volume—and its role in stimulating other chemists to investigate this property.

About ten years later, in 1830, the French chemist Polydore Boullay (1806-1835) wrote his doctoral thesis on the subject of atomic volumes (16). In it, Boullay reported that he had been unsuccessful in finding what he had initially sought: a law relating the atomic volume of an element in the uncombined state to that of its volume after combination. But he went on to suggest another kind of relationship: that the atomic volumes of the elements were correlated with their cohesive ability. Boullay noted that the greatest cohesion is found for elements with the smallest atomic volume (such as carbon), and the weakest for elements with the largest volume (such as sodium and potassium). Just as for Le Royer and Dumas, however, Boullay's correlation was based in part on flawed data: for example, his atomic volume for carbon was two times too small because he assigned to this element an atomic weight of six that was commonly used at the time, but which in actuality was half of the correct value.

In 1843, in a lecture to the Turin Academy of Sciences, the Italian chemist Amedeo Avogadro (1776-1856) discussed a topic closely related to his famous hypothesis of 1811. Whereas his earlier paper concerned the molar volumes of gases, in this later paper Avogadro studied the molar volumes of solids and liquids (17). Avogadro summarized his goals as follows: "I sought to establish that the atomic volumes of simple bodies in the solid state . . . depended on their electro-chemical quality, being so much more electro-positive or less electro-negative" (18). In particular, of the elements that are either solids or liquids (or could be rendered such by cooling), Avogadro found that the smallest atoms (such as oxygen and chlorine) were the most electronegative whereas the largest (such as sodium and potassium) were the most electropositive (19).



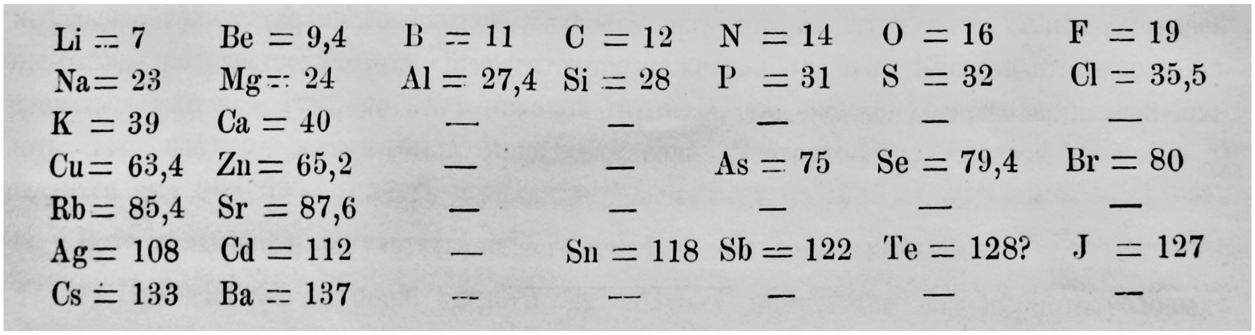
ОБЪ АТОМНОМЪ ОБЪЕМѢ ПРОСТЫХЪ ТѢЛЪ.

Д. Менделѣева.

Въ статьѣ, помѣщенной въ журналѣ Русскаго Химическаго Общества (томъ 1-й, стр. 60), я старался показать періодическую зависимость между свойствами элементовъ и величиною ихъ атомнаго вѣса. Въ предлагаемой статьѣ я намѣренъ дополнить сказанное.

***Figure 2**. Mendeleev, D. I., "On the Atomic Volume of Simple Bodies" Proceedings of the 2nd Congress of Russian Scientists, chemistry section (1869), p 62.*

Atomic and molar volumes formed an important role in Mendeleev's own chemical education: his master's thesis of 1856 (20), which was exclusively devoted to the topic, showed that molar volumes exhibited consistent mathematical regularities. He pointed out, for example, that the molar volume of potassium hydroxide is approximately equal to the average of the molar volumes of potassium oxide and water. Moreover, the tables in his master's thesis often list the elements according to what eventually would be groups in the periodic table: for example, the alkali metals Li, Na, and K are listed in that order, and are immediately followed by the alkaline earths Be, Mg, Ca, Sr, and Ba.



Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 27,4	Si = 28	P = 31	S = 32	Cl = 35,5
K = 39	Ca = 40	—	—	—	—	—
Cu = 63,4	Zn = 65,2	—	—	As = 75	Se = 79,4	Br = 80
Rb = 85,4	Sr = 87,6	—	—	—	—	—
Ag = 108	Cd = 112	—	Sn = 118	Sb = 122	Te = 128?	J = 127
Cs = 133	Ba = 137	—	—	—	—	—

***Figure 3**. "Attached example" (table) from Mendeleev's Congress paper, (Ref. 10).*

The Translation and Content of Mendeleev's 1869 Congress Paper

Mendeleev's paper "On the Atomic Volume of Simple Bodies" was presented at the Second Congress of Russian Scientists, held in Moscow in the autumn of 1869 (10). The proceedings of the Congress, which were published early in 1870, contain Mendeleev's paper along with contributions from other Russian scientists, including the chemists Friedrich Konrad Beilstein (1838-1906), Alexander Mikhailovich Zaitsev (1841-1910), and Alexander Mikhailovich Butlerov (1828-1886). As far as we can determine, no hard copy of these proceedings exists in any library outside of Russia, and no electronic copy of them is available online as of 2019. The full text of Mendeleev's paper in the original Russian, however, can be found in the set of his collected works

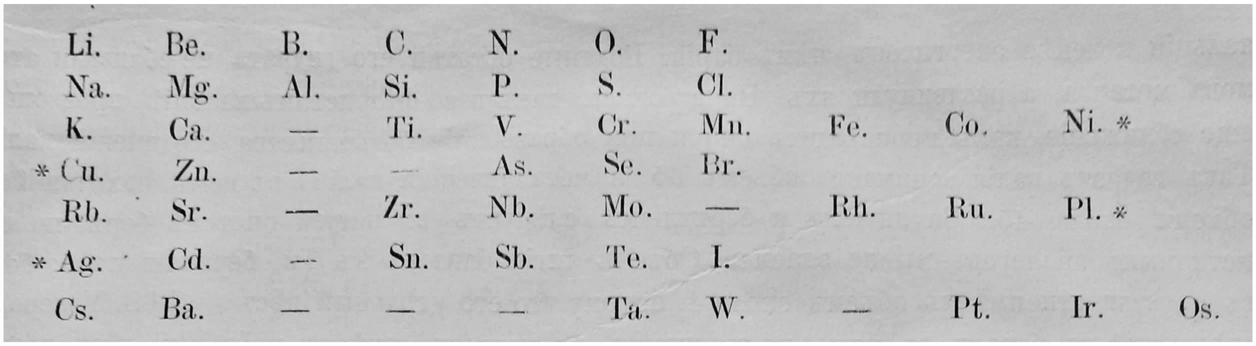
(21). Even so, this paper has largely been unrecognized and undiscussed.

At the end of the present paper, we give a translation of Mendeleev's 1869 Congress article into English; here we wish to make a few remarks about its contents and significance. As has been noted by others (22), there are challenges associated with the translation of pre-Soviet Russian into English. A literal (or close to literal) translation of Mendeleev's text can sound ponderous and stilted. We have tried to be faithful to the original text, but in a few places we have made some stylistic changes and insertions (indicated with square brackets) to make the whole more readable.

The opening text of Mendeleev's 10 page paper (Figure 2) refers to the March article in which he announced his periodic system, and states the purpose of this follow-up paper:

> In an article published in the Journal of the Russian Chemical Society (Volume 1, page 60), I tried to show the periodic relationship between the properties of the elements and the magnitude of their atomic weight. In the present article I intend to supplement what has been previously said.

Mendeleev's paper starts by stating that "similar elements" can be classified into two kinds of groups: those in which the elements exhibit significant differences in atomic weight, and those in which the elements have similar atomic weights. The former groups "can be distributed in terms of the atomic weight into completely symmetrical groups, clearly showing the periodic dependence of the properties on the atomic weight, as can be seen from the attached example." The "attached example" is the short-form (here, a seven column) table in which, for example, the alkali metals and the coinage metals are placed in the same column (Figure 3). Mendeleev comments that, in this arrangement, the column number corresponds to the "atomicity" (= valency) of the elements, so that "the elements of the first column are monatomic, the second, third, and fourth represent di-, tri-, and tetraatomic elements; the elements of the fifth column are triatomic, sixth diatomic, and the seventh monatomic," where Mendeleev is using the term "monatomic" to mean "having a combining power of 1," etc. He further comments that elements with similar properties are placed close together and elements most diverse in chemical properties are farthest apart, so that metals and metalloids are on opposite sides of the table.



Li.	Be.	B.	C.	N.	O.	F.				
Na.	Mg.	Al.	Si.	P.	S.	Cl.				
K.	Ca.	—	Ti.	V.	Cr.	Mn.	Fe.	Co.	Ni. *	
* Cu.	Zn.	—	—	As.	Se.	Br.				
Rb.	Sr.	—	Zr.	Nb.	Mo.	—	Rh.	Ru.	Pl. *	
* Ag.	Cd.	—	Sn.	Sb.	Te.	I.				
Cs.	Ba.	—	—	—	Ta.	W.	—	Pt.	Ir.	Os.

***Figure 4**. Table from Mendeleev's Congress paper (Ref. 10, p 65) including similar elements with similar atomic weights. Mendeleev does not comment on the meaning of the asterisks, but a logical guess is that they are to emphasize that Ni and Cu have similar properties and so do Pl (palladium) and Ag.*

Mendeleev then continues by considering the second category of groups of similar elements, those that have similar atomic weights. He identifies four such groups: the cerium metals (cerium, lanthanum and didymium); metals of the iron group (chromium, manganese, iron, cobalt and nickel, and also including titanium and vanadium), metals similar to palladium whose atomic weight is 104-106 (palladium, rhodium, ruthenium), and metals of the platinum group (platinum, iridium and osmium, and gold). He points out that many of these metals can be inserted into the table by taking advantage of chemical similarities (Figure 4).

Before we turn our attention to the main subject of Mendeleev's paper, atomic volumes, we point out that this Congress paper contains a notable advance in the prediction of properties of undiscovered elements (12). In the table Mendeleev included in his long March paper (6) there several gaps, three of which were filled with the entries, ? = 45, ? = 68, and ? = 70. But in reference to these entries, Mendeleev had said only the following: "We should still expect to discover many unknown simple bodies; for example, those similar to Al and Si, elements with atomic weights of 65 to 75." In the Congress paper, Mendeleev goes further (p 67):

> …it is possible to say that the two elements which are not yet in the system should show similarity to aluminum and silicon and have atomic weights of about 70. They will have atomic volumes of about 10 or 15, i.e., they will have specific weights of about 6, and thus will occupy just the middle ground, in all respects, or they will constitute a transition in properties from zinc to arsenic.

Several people had made correct predictions of the atomic weights of unknown elements before 1869 (23), but Mendeleev's 1869 Congress paper was the first to make clear-cut predictions about *other* properties of unknown elements. Meyer's 1864 periodic table can be seen in hindsight to have predicted the valencies of the two then-unknown elements gallium and germanium, but Meyer himself did not make such a prediction (24).

This 1869 Congress paper also contains Mendeleev's first suggestion that indium belongs in the aluminum series (25). Mendeleev had used an atomic weight of 75.6 for indium in his March 1869 paper (6), whereas one of the missing elements in the aluminum series, as he pointed out, should have an atomic weight of about 70. Mendeleev says (p 67),

> It may be that indium occupies a place in the aluminum series if, in determining the weight of an atom, it is possible to admit an error that might occur from incomplete purification from metals heavier than it (maybe cadmium).

In other words, he is proposing that indium's true atomic weight should be about 70. Late the next year (26), Mendeleev came up with the right explanation by recognizing that the atomic weight of 75.6 had been assigned assuming that indium was divalent. By assuming instead that indium is trivalent, its atomic weight of 113 indeed fits in the aluminum group, but one row below that of the element, gallium, that eventually was to fill the place with an atomic weight of 70.

We now turn to Mendeleev's discussion of atomic volumes, which occupies the bulk of the paper. He starts by stating (p 65):

> In order to clearly establish the dependence that exists between atomic weights and the specific volumes of various groups of elements, we shall first compare them in vertical and then in horizontal rows of the table. It has long been known that such homologous elements as potassium, rubidium, cesium, or calcium, strontium, barium, or phosphorus, arsenic, antimony, etc., display a gradual change in specific volumes with a change in atomic weight.

Mendeleev mentions in the latter context the work of Le Royer and Dumas.

Mendeleev goes on to list atomic volumes for all the other elements known at the time (p 65):

> Here are some examples of this: lithium has a specific weight of 0.594, and hence its volume = 11.2; potassium has an atomic volume equal to 44.8; rubidium 56.1; beryllium, corresponding to lithium in the series of alkaline earth metals, has a specific weight of 2.1, and therefore its volume is 4.5; it is less than the volume of lithium, just like the volumes of calcium and strontium are less than the atomic volumes of potassium and rubidium. Indeed, the specific weight of calcium = 1.58, and its volume = 25.5; the volume of strontium = 35.5, and barium about 30.

In tracing the change in atomic volume down a group, Mendeleev is here repeating analyses that had previously been done by others. But then he considers a problem never before discussed: how do the volumes change across a period? Here is how he introduces this issue (p 66):

> The volume of lithium is close to 12, beryllium 5; boron has a volume of about 4, because its specific weight is 2.68. Carbon, which follows boron in the series of elements above, has a specific weight that varies much, depending on the modification [i.e., allotrope]. Only in the form of diamond, whose specific weight = 3.54, is the volume of carbon less than that of boron; in the form of graphite, it is already greater, viz. = 5.7, because the specific weight of graphite is close to 2.1; in the form of coal, the volume of the carbon atom is even greater. Therefore, it is not possible to say with certainty whether the volume will increase or decrease when we pass along the first row of elements from carbon to nitrogen, oxygen and fluorine. By analogy with other rows, however, it is more likely to exhibit an increase, for example, similar to the one that exists in the transition from Si to P, S and Cl, or from Sn to Sb, Te and I.

What follows in the paper is a lengthy and detailed discussion of atomic volumes for elements in the later periods of the periodic table. This discussion includes several generalizing statements of which the following is one (p 66): "in horizontal rows corresponding to Li, K, Rb, Cs as the atomic weight increases, at first the volume decreases rapidly, and then remains almost constant." Here, Mendeleev is referring to periods beginning Li, beginning with K, etc.; in the short form of the periodic table, these rows end in the "group 8" transition elements. The intervening rows, starting with Cu and Ag in the short-form table, show different behavior (p 67):

> For [the silver] row, therefore, with an increase in the atom weight, the specific volume also increases, despite the difference in chemical character; . . . It is

> obvious that the regularity that is so obvious in the silver series, is less apparent [in the copper row], although there is still a continuous increase in the specific volume with an increase in the weight of the atom.

Mendeleev mentions that the allotropy of carbon, phosphorus, and sulfur makes it more difficult to draw conclusions about the trends in atomic volumes across the relevant periods, because the different allotropes have different densities and thus different (and quite distinct) calculated atomic volumes.

The last part of Mendeleev's paper returns to the changes in atomic volumes within individual vertical groups, paying special attention to the relationships between elements that we now classify as "main group elements" and "transition metals." Thus, Mendeleev compares the atomic volumes (and other chemical properties) of chromium and sulfur, and manganese and chlorine, among others.

Mendeleev concludes his paper with a short discussion of how the molar volumes of compounds cannot be calculated from the atomic or molar volumes of their constituents. Mendeleev does not cite Boullay in this context, but instead credits his earlier master's thesis on specific volumes, published in 1856 (20).

Who Gets the Credit?

In his 1869 paper in the *Proceedings of the Second Congress of Russian Scientists*, Mendeleev discussed in great detail the variation of atomic volumes as a function of increasing atomic weight (i.e., across the rows of the short form of his periodic table). Mendeleev states that the atomic volumes of the elements, when arranged in order of increasing atomic weight, show the following behavior across the periods of the short form of the periodic table: starting with the alkali metals, the volumes initially *decrease* and then stay relatively constant, whereas starting with the coinage metals, they *increase*. Although Mendeleev did not explicitly state that the volumes fall, stay constant, and then rise between one alkali metal and the next (i.e., as viewed in terms of a long-form view of the periodic table) it is clear that Mendeleev's discussion embodies the same trend. In other words, Mendeleev's 1869 Congress article codifies textually what Meyer's chart shows visually.

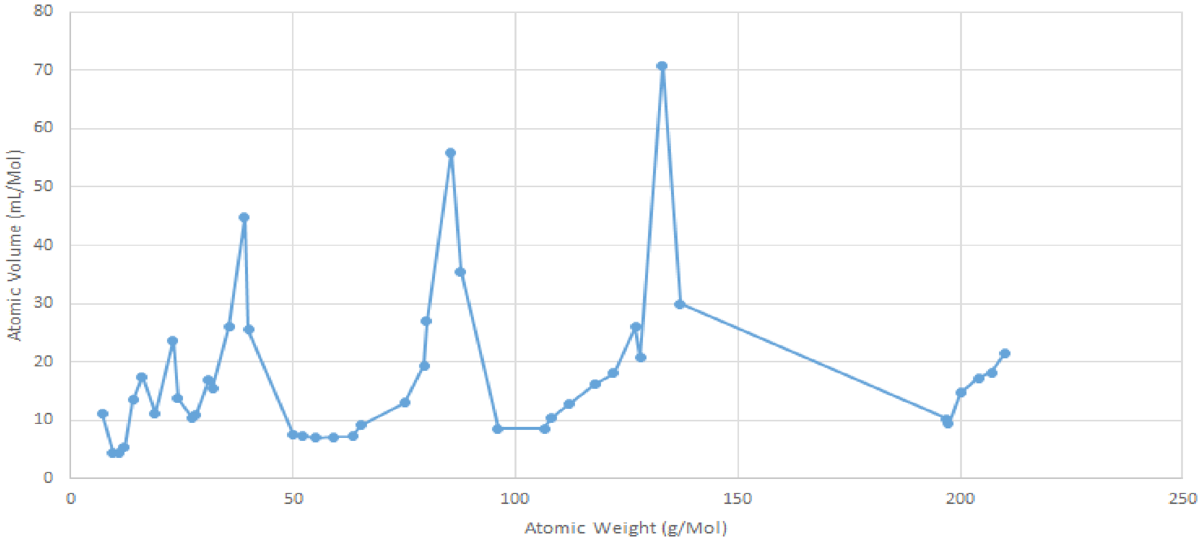


***Figure 5**. Plot of atomic volume vs. atomic weight taken from data in Mendeleev's Congress paper (Ref. 10, pp 62-71).*

In the course of his Congress paper, Mendeleev gave values for the atomic volumes of essentially every element known at the time. Mendeleev did not convert these data into a chart, but instead described the trends he saw in words. We can take the data in Mendeleev's paper, however, and do what he did not do: construct a chart of atomic volume vs. atomic weight; the result is shown in Figure 5. It is no surprise that the plot replicates Meyer's almost exactly, because they both had the same raw data in hand. Of course, Mendeleev takes 10 pages of dense text to describe what Meyer's curve shows in a single glance.

Mendeleev's paper is followed by a note added in proof, written after he had seen Meyer's 1870 paper. In this note, Mendeleev gives Meyer credit for devising a way to increase the clarity of the relationship between atomic volume and atomic weight, while making the point that the Congress paper contained all the essential ideas (p 71):

> **Note**. The foregoing was communicated by me at the Congress in August 1869. In 1870, in *Liebig's Annalen* (after this article was sent by me for printing), an article by Lothar Meyer appeared, dealing with the same subject. Mr. Meyer's conclusions are based on the assumption of the system of elements proposed by me and agree with those that I have made with respect to the volumes of atoms. He also pays special attention to the descending and ascending series of elements and to the sequence of volume changes. But the conclusions were increased in clarity by the graphic image attached to the article. By putting this postscript I have no desire to raise the issue of scientific priority, (in my opinion, these questions do not often have any academic interest), and I only want to point to the table attached to Mr. Meyer's article as a means of capturing and explaining those complex relations, which are indicated in the previous text.

Much has been written about the priority conflict between Mendeleev and Meyer (27 -29). Both Mendeleev and Meyer came to be recognized as independent discoverers of the periodic table. For example, they were jointly awarded the Davy Medal from the Royal Society in 1882, "For their discovery of the periodic relations of the atomic weights" (30). The content of Mendeleev's 1869 Congress paper supports and extends the conclusion that the two men independently devised many of the important ideas behind the periodic system. Although credit for the graphic representation of the periodic dependence of atomic volumes on atomic weight is Meyer's alone, it is clear that in August 1869 Mendeleev wrote about this dependence in great detail, analyzing the change in atomic volumes across periods of the periodic table, several months before Meyer—in December of that year—submitted his paper on the same topic.

Supplemental Material

The following can be found in the Supplemental Material for the *Bulletin for the History of Chemistry* at the journal's website, http://acshist.scs.illinois.edu/bulletin/index.php:

1. An image of the original article,

2. A transliteration of the original article (omitting the Russian characters eliminated in 1918) side-by-side with the English translation, and

3. A high resolution image of Meyer's curve (Figure 1) from Ref. (2).

Acknowledgment

We wish to thank Andrei Rykhlevskii for transcribing the Russian text into electronic format, and Dr. Taras Porogolev for his help in improving the translations of idiomatic words and phrases into English. We also gratefully thank Prof. David E. Lewis for his detailed critique of the translation and Prof. Michael Gordin for several helpful suggestions.

References and Notes

1. Presented at the 256th National Meeting of the American Chemical Society, Boston, MA, Aug. 21, 2018, HIST 26 in the HIST Award Symposium Honoring David Lewis.
2. J. L. Meyer, "Die Natur der chemischen Elemente als Function ihrer Atomgewichte [The Nature of the Chemical Elements as a Function of their Atomic Weights]," *Ann. Chem Suppl.*, **1870**, *7*, 354-364.
3. C. T. Blanshard, "The Position and Character of Mercury and Copper, Founded upon their Atomic Weights," *Chem. News*, **1875**, *32*, 151-152.
4. E. Tufte, *The Visual Display of Quantitative Information*, Graphics Press, Cheshire, CT, 1997.
5. For a timeline of Mendeleev's early publications on the periodic system, see M. Kaji, "Mendeleev's Discovery of the Periodic Law: The Origin and the Reception," *Found. Chem.*, **2003**, *5*, 189-214.
6. D. I. Mendeleev, "Sootnoshenie svoistv s atomnyn vesom elementov [The Correlation of Properties with the Atomic Weights of the Elements]," *Zh. Russ. Khim. Obshch.*, **1869**, *1*, 60-77. Most non-Russian chemists (including Meyer) learned of Mendeleev's work through the abstract of this paper, translated into German and printed in D. Mendelejeff, "Über die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente [On the Relation of the Properties to the Atomic Weights of the Elements]," *Z. Chem.*, **1869**, *12*, 405-406. Mendeleev's formulation of the periodic law was also briefly noted in *Ber. Deut. Chem. Ges.,* **1869**, *2*, 553-555 as part of a letter written by Victor von Richter. For a translation of the full article in *Zh. Russ. Kim. Obshch*., see W. B. Jensen, *Mendeleev on The Periodic Law: Selected Writings, 1869-1905,* Dover, Mineola, NY, 2005, pp 18-37.
7. D. I. Mendeleev, *Osnovy Khimii [Principles of Chemistry*], Tovarishchestvo 'Obshchestvennaia Pol'za', St. Petersburg, 1869, Vol. 1.
8. For example, Partington cites Mendeleev's August 1869 Congress paper (i.e., the subject of the present article) but

says only that it contains a periodic table in the modern form. Partington then discusses Meyer's first publication on the periodic properties of the elements, and credits him for "the well-known atomic volume curve showing maxima and minima with increasing atomic weights." J. R. Partington, *A History of Chemistry*, vol. 4, Macmillan and Co. Ltd., London, pp 895-896. Ihde makes no mention of Mendeleev's August 1869 Congress paper at all, but prominently describes Meyer's paper, which "included the curve resulting when Meyer plotted atomic weights against atomic volumes; he observed that similar elements appeared at similar places on the curve; non-metals are on the ascending sides, and metals on the descending sides and in the valleys." A. J. Ihde, *The Development of Modern Chemistry*, Harper & Row, New York, NY, 1964, p 251.

9. Mendeleev's paper is briefly abstracted in an anonymous summary of the chemical papers given at the 1869 Congress in *Zh. Russ. Khim. Obshch.*, **1869**, *1*, 229-230. This short abstract says very little about Mendeleev's ideas about atomic volumes:

> D.I. Mendeleev reported on the periodicity of the atomic weights of the elements and the system of elements proposed on this basis by him in the current year (*Journal of the Russian Chemical Society*, vol. 1. p. 60 and his work *Osnovy Khimii*). The [system] based on the values of the atomic weights not only 1) expresses their chemical similarity, but also 2) conforms to the division of elements into metals and metalloids, 3) distinguishes [elements according to] their atomicity, 4) juxtaposes similar elements of different groups (e.g., B, C, Si, Al, Ti), 5) explains the similar homology of corresponding elements which many chemists have pointed out, 6) distinguishes hydrogen from the typical elements as modern science recognizes, 7) groups together in one place common elements that are mutually accompanying in nature, 8) show the insufficiency of Prout's hypothesis, and 9) even indicates the relation of elements according to their mutual affinity. Moreover, 10) a comparison of the atomic volumes and atomic weights of elements belonging to different rows shows to some extent the naturalness of the system as well. So for example the silver row displays the following weights:

Atomic weights					
Ag-108	Cd-112	Sn-118	Sb-122	Te-128	J-127
Atomic volumes					
10.5	8.6	7.3	6.7	6.2	5.0

> Therefore, the development of further results from the concept of the periodicity of the properties of the elements set in rows in terms of atomic weights is considered by Mendeleev to be able to lead to important consequences in connection with the nature of the elementary bodies of chemistry.

10. D. I. Mendeleev, "Ob atomnom ob'eme prostykh tel [On the Atomic Volume of Simple Bodies]," in *Trudy Vtorogo S'ezda Russkikh Estestvoispytatelei v Moskve 20-30 Avgusta 1869* [*Proceedings of the Second Congress of Russian Scientists in Moscow 20-30 August 1869*], **1870**, Chemistry section, pp 62-71.

11. The footnote Mendeleev added in proof to his 1869 Congress paper, and one other paragraph, was translated into German in D. Mendeleev, "Zur Geschichte des periodischen Gesetzes [On the History of the Periodic Law]," *Ber. Deut. Chem. Ges*., **1880**, *13*, 1796-1804; the footnote was translated from German into English in J. W. van Spronsen, "The Priority Conflict Between Mendeleev and Meyer," *J. Chem. Educ*., **1969**, *46*, 136-139. The footnote, and several other short passages, were translated from the original Russian into English in J. R. Smith, "Persistence and Periodicity: a Study of Mendeleev's Contribution to the Foundations of Chemistry," Ph.D. thesis, Chelsea College (University of London), 1976, p 171 et passim; Smith's thesis can be accessed at https://kclpure.kcl.ac.uk/portal/files/2925773/473179.pdf (accessed Oct. 25, 2019).

12. A translation into English of a brief portion of Mendeleev's 1869 Congress paper, on the prediction of the atomic volumes of ekasilicon and ekaaluminum, appears on p 352 of Smith's 1976 thesis (see Ref. 11 above) and more fully in M. D. Gordin, *A Well-Ordered Thing: Dmitrii Mendeleev and the Shadow of the Periodic Table*; Basic Books, New York, 2004, p 34.

13. T. M. Cole Jr., "Early Atomic Speculations of Marc Antoine Gaudin: Avogadro's Hypothesis and the Periodic System," *Isis,* **1975**, *66*, 334-360.

14. A. Le Royer and J.-A. Dumas, "Essai sur le volume de l'atome des corps [Essay on the Volume of the Atom of Substances]," *Phys. Chim. Hist. Nat.*, **1821**, *92*, 401-411.

15. Anon. [W. Prout] "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," *Ann. Phil.*, **1815**, *6*, 321-330; W. Prout, "Correction of a Mistake in the Essay on the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," *Ann. Phil.*, **1816**, *7*, 111-113.

16. P. Boullay, *Dissertation sur le volume des atomes et sur les modifications qu'il subit dans les combinaisons chimiques* [*Dissertation on the Volume of Atoms and on the Modifications that they Undergo in Chemical Combination*], Paris, V[euv]e Thuau, 1830.

17. A. Avogadro, "Mémoire sur les volumes atomiques et sur leur relation avec le rang que les corps occupent dans la série électro-chimique [Memoir on Atomic Volumes and their Relationship with the Rank that Bodies Occupy in the Electrochemical Series]," *Memorie della Reale Accademia delle Scienze di Torino*, **1846**, *8*, 129-194.

18. A. Avogadro, "On the Atomic Volumes of Bodies," *The Chemist*, **1850**, *1*, 492-494.
19. W. B. Jensen, "Electronegativity from Avogadro to Pauling: Part 1: Origins of the Electronegativity Concept," *J. Chem. Educ*., **1996**, *73*, 11-20.
20. D. I. Mendeleev, *Udelnye obyemy* [*Specific volumes*], Tip. Departamenta vneshnei torgovli, St. Petersburg, Russia, 1856.
21. D. I. Mendeleev, *Sochineniia* [*Works*], vol. 2, A. N. Bach, B. N. Vyropaev, (and others), Eds., Leningrad: Khimteoret, 1934, pp. 20-29; *Periodicheskiy zakon khimicheskikh elementov* [*Periodic Law of Chemical Elements*], M. N. Dukelsy, V. A. Rakovsky, Eds., Leningrad, Izd. Akad. Nauk SSSR, 1934, pp 22-34.
22. V. Suntsov & D. E. Lewis, "Introduction to an English Translation (Abridged) of Kizhner's Pioneering Papers on Deoxygenation," *Bull. Hist. Chem*., **2015**, *40(2)*, 61-64.
23. Among those who had made specific predictions about the atomic weights of unknown elements were Lenssen (1851), Lea (1860), Meyer (1864), and Newlands (1863-1865). See J. W. van Spronsen, *The Periodic System of Chemical Elements. A History of the First Hundred Years*, Elsevier, New York, 1969.
24. J. L. Meyer, *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik [The Modern Theory of Chemistry and its Meaning for Chemical Statics]*, Maruschke & Berendt, Breslau, Germany, 1864.
25. I. S. Dmitriev, "Problema razmeshcheniia indiia v periodicheskoi sisteme elementov [The Problem of the Placement of Indium in the Periodic System of Elements]," *Voprosy Istoriia Estestvoznaniia I Tekhniki*, **1984**, *2*, 3-14.
26. D. I. Mendeleev, "Über die Stellung des Ceriums im System der Elemente [On the Position of Cerium in the System of Elements]," *Bull. Acad. Imp. Sci. St. Petersbourg*, **1871**, *16*, 45-51.
27. Van Spronsen (Ref. 11).
28. M. D. Gordin, "The Textbook Case of a Priority Dispute: D. I. Mendeleev, Lothar Meyer, and the Periodic System," in M. Biagioli and J. Riskin, Eds., *Nature Engaged: Science in Practice from the Renaissance to the Present*, Palgrave Macmillan, New York, 2012, pp 59-82.
29. M. D. Gordin, "The Table and the Word: Translation, Priority, and the Periodic System of Chemical Elements," *Ab Imperio*, **2013**, no. 3, 53-82.
30. "The Davy Medal to D. Mendelejeff and Lothar Meyer," *Phil. Trans. Roy. Soc. London*, **1883**, *173*, iii.

About the Authors

Gregory S. Girolami is the William H. and Janet G. Lycan Professor of Chemistry at the University of Illinois at Urbana-Champaign. He received his B.S. degrees in chemistry and physics from the University of Texas at Austin and his Ph.D. degree from the University of California at Berkeley. Thereafter, he was a NATO postdoctoral fellow with Sir Geoffrey Wilkinson at Imperial College of Science and Technology, and joined the Illinois faculty in 1983. His research interests are primarily the synthesis, properties, and reactivity of new inorganic, organometallic, and solid state species, especially as relates to mechanistic studies of organometallic reactions such as the activation of alkanes, the synthesis of new "molecule-based" magnetic materials, the chemical vapor deposition of thin films from "designed" molecular precursors, and the design of an artificial photosynthetic center.

Vera V. Mainz is retired from her position as the Director of the NMR Laboratory in the School of Chemical Sciences at the University of Illinois at Urbana-Champaign. She received her B.S. degrees in chemistry and mathematics from Kansas Newman University and her Ph.D. degree from the University of California at Berkeley working with Prof. Richard A. Andersen. She has been the Secretary/Treasurer of HIST since 1995.

PRIMARY DOCUMENTS

ON THE ATOMIC VOLUME OF SIMPLE BODIES

D. I. Mendeleev

“Ob atomnom ob’eme prostykh tel [On the Atomic Volume of Simple Bodies],” *Trudy Vtorogo S’ezda Russkikh Estestvoispytatelei v Moskve 20-30 Avgusta 1869 [Proceedings of the Second Congress of Russian Scientists in Moscow 20-30 August 1869],* **1870**, Chemistry section, pp 62-71

Translated by Gregory S. Girolami and Vera V. Mainz.

In an article published in the *Journal of the Russian Chemical Society* (Volume 1, page 60), I tried to show the periodic relationship between the properties of the elements and the magnitude of their atomic weight. In the present article I intend to supplement what has been previously said.

All groups of similar elements can be divided into two main categories: in one of the categories, similar elements exhibit a significant difference in atomic weight; most simple bodies belong here and they can be distributed in terms of the atomic weight into completely symmetrical groups, clearly showing the periodic dependence of the properties on the atomic weight, as can be seen from the attached example.

Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 27.4	Si = 28	P = 31	S = 32	Cl = 35.5
K = 39	Ca = 40	—	—	—	—	—
Cu = 63.4	Zn = 65.2	—	—	As = 75	Se = 79.4	Br = 80
Rb = 85.4	Sr = 87.6	—	—	—	—	—
Ag = 108	Cd = 112	—	Sn = 118	Sb = 122	Te = 128?	J = 127
Cs = 133	Ba = 137	—	—	—	—	—

These groups could be considered as homologous if there were no terms in them that break the sequence in changing properties. So, in the first group with alkali metals, copper and silver are placed between potassium, rubidium, and cesium. It is not possible to doubt that this placement accounts for much chemical data. Thus, it is known that silver in its oxidized state has many similarities with sodium: silver nitrate cannot be separated by crystallization from sodium nitrate. Isomorphism is also manifested between the compounds cuprous oxide and silver oxide; cuprous chloride, like silver chloride and sodium chloride, crystallizes in cubes. We note that the relationship between zinc and cadmium and the alkaline earth metals is exactly the same as that between copper and silver on the one hand and the alkali metals on the other. They [zinc and cadmium] also have to be placed between calcium, strontium, and barium, although they have a better resemblance to magnesium, like copper and silver do with sodium. If we could distinguish these two groups of elements from [those in] the first two rows, then we would have to significantly complicate the classification, without, at the same time, achieving any particular simplicity. With its specific features, however, the above comparison already furnishes a considerable number of benefits. They consist mainly of the following: 1) based on the magnitude of the atomic weight, such a system clearly expresses the chemical similarity and determines the degree of combining with oxygen (1); 2) it corresponds to the separation of elements into metals and metalloids, because on the one side the first classes of simple bodies [metals] are mainly grouped, with the other class [metalloids] on the other side; 3) it corresponds to the atomicity of the elements in the form in which it is usually recognized; indeed, the elements of the first column are monatomic, the second, third, and fourth represent di-, tri-, and tetraatomic elements; the elements of the fifth column are triatomic, sixth diatomic, and the seventh monatomic; 4) at the same time this system brings together similar elements of different groups, such as, for example, boron, carbon, silicon and aluminum; 5) to some extent, it clarifies the homology that has long been noted in the magnitude of atomic weights for the bodies of one particular group; 6) the elements most diverse in chemical character are also the most remote in this system.

Another category of groups of similar elements is composed of those that have close atomic weights. Between them, four groups are best known: 1) the cerium metals: cerium, lanthanum and didymium, mass 92-95; 2) metals of the iron group: chromium, manganese, iron, cobalt and nickel, having an atomic weight from 51 to 59; 3) metals similar to palladium, the atomic weight of which is 104-106, and 4) metals of the platinum group, to which—apart from platinum, iridium and osmium—it is fair to include gold, which is similar to them not only in terms of atomic weight (197-199), but also in most basic properties. These groups of metals have in the above-mentioned system a completely definite position based on their atomic weight and partly on the chemical nature of the compounds formed by them. The iron group is the transition from the missing members of the last columns to copper. Chromium can be conveniently placed in line with oxygen, between sulfur and selenium, just as copper is between potassium and rubidium. In fact, chromium in the form of chromic acid presents a remarkable resemblance to sulfuric acid, as is well known to everyone, which is particularly pronounced in the significant similarity that SO_2Cl_2 and CrO_2Cl_2 have. The closest analog to chromium in the iron group is manganese. Its atomic weight is greater than chromium, and it can be placed in the series of halogens. Manganese presents with them [the halogens] the same similarity in its highest degree of oxidation as chromium does with sulfur. Indeed, the manganate potassium salt $KMnO_4$ is known to be isomorphic and extremely similar, even in specific weight, to the chlorate potassium salt $KClO_4$. Manganese is followed by iron, cobalt, and nickel, representing, in both atomic weight and chemical properties, as well as the ability to form different degrees of oxidation, a clear transition to copper. The iron group is adjoined on the chromium side by two other elements, vanadium and titanium, the striking similarity of whose compounds with those of phosphorus and silicon is not subject to the slightest doubt.

The zirconium (90), niobium (96) and molybdenum (94) series exactly corresponds to that of titanium, vanadium and chromium and must be located in appropriate places below the named metals; and for rhodium, ruthenium and palladium one can hardly deny the analogy with iron, cobalt and nickel. By the magnitude of their atomic weights, these elements constitute a transition to silver, as elements of the iron group do to copper. Platinum, osmium, iridium and gold must be placed in the same position below these metals. The similarity is expressed not only in the similarity of their degrees of oxidation (RO, R_2O_3, RO_2), but also in such traits as the ability to produce ammonium compounds, characterized by well-known traits belonging in the same measure to ammonia-cobalt, ammonia-ruthenium, and ammonia-platinum compounds.

It is very important to pay attention to the location that the groups of similar elements mentioned here acquire; It is absolutely determined in a number of groups of the first category. Therefore, there is no doubt that in principle the distribution of elements in terms of their atomic weights embodies the true guiding principle when studying the basic natures of the elements. In my treatise, entitled *Fundamentals of Chemistry*, I attach the described system to an elementary exposition of chemistry and present evidence of the similarities in the groups defined by the above-mentioned method, and therefore I do not cover this subject here. Now I will draw attention to the fact that the comparison of elements according to the principles mentioned here finds some confirmation in the comparison of the physical properties of simple bodies taken separately, and even more so in their respective chemical compounds. In this article I will focus exclusively on the comparison of specific weights and specific volumes, especially since the comparison of other physical properties at present, due to lack of information, is almost impossible. As proof of the naturalness of the system proposed by me in relation to other properties, one can cite from the remarkable investigations of Wiedemann (*Pogg. Ann.* 1865 and 1869) that the elements of the group of cerium and the group of iron are magnetic in their compounds, and their atomic magnetism changes smoothly when going from one analogue to another. It would be most interesting to now investigate, in this respect, the elements of the platinum group and their compounds most similar in chemical characteristics to ceric and iron compounds.

As before, here is a table of elements, in which are inserted the bodies possessing similar atomic weights from the series of iron and platinum.

Li.	Be.	B.	C.	N.	O.	F.			
Na.	Mg.	Al.	Si.	P.	S.	Cl.			
K.	Ca.	—	Ti.	V.	Cr.	Mn.	Fe.	Co.	Ni.*
*Cu.	Zn.	—	—	As.	Se.	Br.			
Rb.	Sr.	—	Zr.	Nb.	Mo.	—	Rh.	Ru.	Pl.*
*Ag.	Cd.	—	Sn.	Sb.	Te.	I.			
Cs.	Ba.	—	—	—	Ta.	W.	—	Pt.	Ir.

In order to clearly establish the dependence that exists between atomic weights and the specific volumes of various groups of elements, we shall first compare them in vertical and then in horizontal rows of the table. It has long been known that such homologous elements as potassium, rubidium, cesium,—or calcium, strontium, barium,—or phosphorus, arsenic, antimony, etc.,—display a gradual change in specific volumes with a change in atomic weight. This was exhibited for the first time, if we are not mistaken, [by] Dumas and Le Royer; they argued, justifiably in many cases, that similar elements and compounds display either closely related specific volumes or volumes that constantly increase with increasing atomic weight, which allows one to compare the last category of similar bodies with homologs for which the last kind of relation exists. Here are some examples of this: lithium has a specific weight of 0.594, and hence its volume = 11.2; potassium has an atomic volume equal to 44.8; rubidium 56.1; beryllium, corresponding to lithium in the series of alkaline earth metals, has a specific weight of 2.1, and therefore its volume is 4.5; it is less than the volume of lithium, just like the volumes of calcium and strontium are less than the atomic volumes of potassium and rubidium. In fact, the specific weight of calcium = 1.58, and its volume = 25.5; the volume of strontium = 35.5, and barium about 30.

Here we notice that the increase in atomic volume is not so rapid as in the series of alkali metals. But as the atomic weight increases for both the first and the second [groups], the atomic volume and the energy [i.e., reactivity] of the element also increase. This latter [reactivity] is explained by the significant changes in their atomic distances as their atomic weights increase. Barium atoms, although they are heavier than calcium atoms, are, however, more distant [from other atoms] than the latter. The influence of the distances on the course of reactions, if I am not mistaken, was first pointed out by Avogadro. It manifests itself in the formation of the corresponding compounds of the two named elements. Thus, aqueous barium oxide (specific weight 4.5, and volume = 30) has a smaller volume than metallic barium itself, i.e., the two water residues, in joining the barium, not only did not move its atoms apart, but made them even closer. Hence, there was enough space between the barium atoms to place these elements. Calcium atoms have a much smaller volume and its aqueous oxide occupies a larger volume (34, because the specific weight is 2.2) than the metal itself, because calcium is less energetic than barium. The water components of its hydrate did not bring the metal atoms together, but pushed them apart. But in [potassium] oxide, as in calcium fluoride, there was still a contraction, as occurs with the formation of most potassium compounds. So potassium hydrate takes up a volume of 35, and metallic potassium, which is in it, has a volume of about 45. Lithium and beryllium are followed by boron in our system, but we do not know its true analogs. The volume of lithium is close to 12, beryllium 5; boron has a volume of about 4, because its specific weight is 2.68. Carbon, which follows boron in the series of elements above, has a specific weight that varies much, depending on the modification [i.e., allotrope]. Only in the form of diamond, whose specific weight = 3.54, is the volume of carbon less than that of boron; in the form of graphite, it is already greater, viz. = 5.7, because the specific weight of graphite is close to 2.1; in the form of coal, the volume of the carbon atom is even greater. Therefore, it is not possible to say with certainty whether the volume will increase or decrease when we pass along the first row of elements from carbon to nitrogen, oxygen and fluorine. By analogy with other rows, however, it is more likely to exhibit an increase, for example, similar to the one that exists in the transition from Si to P, S and Cl, or from Sn to Sb, Te and I.

The second series, or more correctly, the second row of elements, which contains sodium and chlorine, displays a special phenomenon, which we will consider next. Now we mention that in the horizontal rows to which potassium, rubidium and cesium belong, we know few reliable examples. But if we take the potassium row, we will find in it potassium, whose volume is close to 45, calcium, whose volume = 25, titanium, whose specific weight 5.3 indicates an atomic volume of about 7.5; then chromium, whose volume is about 7.4 and manganese, whose volume = 7.0, because the specific weight is about 8.0. This shows that in the potassium row, with an increase in the atom [i.e., atomic weight], the volume decreases, as we saw in the lithium series; but the reduction here is even faster than for the lithium row. In the rubidium row, this decrease is even more noticeable because rubidium has a volume of 56, strontium 34, molybdenum 8.5. Palladium is about the same. Thus, for the vertical series corresponding to lithium (Li, K, Rb, Cs; Be, Ca, Sr, Ba; Cr, Mo, W; Ni, Pl, Os), we notice an increase in volume with increasing atomic weight, and in horizontal rows corresponding to Li, K, Rb, Cs as the atomic weight increases, at first the volume decreases rapidly, and then remains almost constant. Special phenomena are seen for sodium and elements similar to it that stand in the same horizontal row.

The volume of sodium = 23.7 because the specific weight = 0.97; the volume of copper = 7.2, silver 10.3. The volume of magnesium = 13.7, [which is] much less than the volume of sodium. So far, the phenomena are the same as for the preceding, but there is further distinction. Zinc has an atomic volume of 9.1, i.e. greater than copper, just as cadmium, having a volume of 12.8, is greater than silver. In the silver row we notice the greatest density and moreover regularity in the following, namely: palladium, ruthenium and rhodium all having a similar volume of 9.1; silver 10.3; cadmium 12.8; tin, which, without a doubt, belongs to this series, as an analog of silicon, has a volume of 16.2; antimony from the phosphorus series has a volume of 18.1; tellurium from the sulfur series 20.7 and iodine from the chlorine series has a volume of 26, because its specific weight is 4.93. For this row, therefore, with an increase in the atom weight, the specific volume also increases, despite the difference in chemical character; hence here the change along the horizontal rows is different than what we noticed in the rows above the elements examined. This is even clearer in the row of heavy metals not listed in the table, viz: volume Pt = 197/21 = 9.4; Au = 197/19.3 = 10.2; Hg = 200/13.6 = 14.7; Tl = 204/11.89 = 17.2; Pb = 207/11.35 = 18.2; Bi = 210/9.8 = 21.4, that is with the increase in atomic weight along the horizontal row, the volume increases, and does not decrease or remain constant, as we saw for the horizontal rows corresponding to potassium, rubidium, [and] cesium.

For elements of the same category from the rows corresponding to copper and sodium, we see however the transition to the property of the rows corresponding to K, Rb, Cs. So for the elements that correspond to copper we do not notice a previous rapid increase, namely we see the following: iron, cobalt and nickel have close volumes, about 7.1; copper 7.2; zinc 9.1; we do not know the analogs of aluminum and silicon in this series, but from the phosphorus series we have arsenic, whose volume = 13 or 16, depending on whether we take the crystalline or amorphous state of arsenic. In any case, the volume is significantly increased. Selenium in the same row has an even larger volume—19.4, bromine is even greater—27, and therefore we first see an extremely slow increase in volume, and then an extremely rapid increase. For the series of silver we notice a continuous and regular decrease in the specific weight, starting from palladium to iodine. In fact, the specific weight of Pl = 11.7, Ag = 10.5, Cd = 8.6, Sn = 7.3, Sb = 6.7, Te = 6.2, I = 5.0, whereas in the copper series, a phenomenon of a different kind is seen: first, the specific weight increases, and then decreases; Fe has a specific weight of 7.8; Co = 8.6; Ni = 8.5; Cu = 8.8; Zu = 7.1; As = 5.7; Se = 4.3; Br = 3.0. It is obvious that the regularity that is so obvious in the silver series, is less apparent here, although there is still a continuous increase in the specific volume with an increase in the weight of the atom. Therefore, it is possible to say that the two elements which are not yet in the system should show similarity to aluminum and silicon and have atomic weights of about 70. They will have atomic volumes of about 10 or 15, i.e., they will have specific weights of about 6, and thus will occupy just the middle ground, in all respects, or they will constitute a transition in properties from zinc to arsenic.

It may be that indium occupies a place in the aluminum series, if, in determining the weight of an atom, it is possible to admit an error that might occur from incomplete purification from metals heavier than it (maybe cadmium). After what has been said, it will be clear that in the sodium row we encounter a phenomenon completely different from the previous ones. Indeed, sodium represents a volume of 24, magnesium 13.7, aluminum 10.3, i.e., up to now the volume of the atom decreases with increasing atomic weight, and the specific weight increases. Going further, we encounter a complication: silicon has a volume of a little more than aluminum, namely about 11; phosphorus in its two forms [i.e., allotropes] displays a specific weight [of] 1.96 for red phosphorus and 1.83 for white phosphorus, i.e., atomic volumes of 15.8 and 17.0. The proportions of sulfur in its two modifications are almost the same as for the two modifications of phosphorus: prismatic sulfur has a specific weight of 1.96, and ordinary sulfur is 2.06, i.e., the volumes of the sulfur atoms in the two states = 15.5 and 16.3. For chlorine, which follows sulfur in this series, the volume of the atom is close to 26, because liquid chlorine has a specific weight close to 1.3.

So, starting from sodium to aluminum, we have a decrease in volume, and then an increase; but there is no real consistency. The latter is partly explained by the difference in the physical state that exists for the elements in this series, and which can not be assumed for the elements in the two preceding series, at least to as large an extent as here. Sodium and magnesium, at least the latter, probably contain one atom each in their particle; the analogy with cadmium, and [their] volatility, can confirm this. One could hardly doubt that a particle of silicon, like a carbon particle, contains a significant number of atoms; this explains the deviation that carbon and silicon exhibit from the law of Dulong and Petit, as I will try to prove in a special article (2).

Phosphorus in its particle contains at least 4 atoms; the red form is probably even more complex than the white; its atoms are even closer, the polymer state is even more complex. The same thing should be noted about sulfur. Prismatic sulfur is simpler than rhombic, but in the former there are at least 6 atoms in the particle, as can be seen from the density of sulfur vapor observed at a temperature of about 600°. Chlorine, in the same series, contains only 2 atoms in its particle. If sulfur were known in liquid form and in the same polymer [i.e., dimer] state as chlorine is known, it would probably exhibit a much larger atomic volume. Thus, elements that have very different numbers of atoms in their particles are grouped in the sodium-chlorine row. Therefore it is not surprising that we notice here a lack of the harmony that is characteristic of the other rows examined by us. If we take the extreme members of the rows examined by us, we note the following: silver has a volume significantly different from the volume of iodine; the volume of copper is even more different from the volume of bromine, but the volume of sodium differs little from the volume of chlorine. Does this not depend on the fact that the particles of sodium and copper are composed in different ways? Looking at the series of elements just described along vertical series, we note the following feature that clearly distinguishes these series from the series of lithium, potassium, rubidium, cesium and similar ones, previously considered. There we saw an increase in both specific weight and atomic volume, coupled with an increase in atomic weight and chemical energy. Here, the opposite is seen: with increasing atomic weight, sodium, copper and silver exhibit a decrease in chemical energy, just like in the transition from magnesium to zinc and cadmium. The volume of the magnesium atom, 13.7, is greater than the volume of [both] zinc (9.1) and cadmium (12.8), just as the volume of sodium is larger than the volume of [both] copper and silver. Moreover, copper and zinc display a smaller volume than silver and cadmium, exactly as in the corresponding rows of the right side of the table. Phosphorus in both its modifications displays a larger volume than arsenic; but the volume of antimony is greater than the volume of arsenic, just as the volumes of cadmium and silver are greater than the volumes of zinc and copper. However, the volume of selenium is greater than [that of] sulfur, and [the volume] of tellurium is even greater than [that of] selenium. The volumes of the atoms of chlorine, bromine and iodine are known to be close to one another.

From what has been said, it is clear that there is some regularity in the change in the specific weights and atomic volumes in the series of elements distributed in a general system according to the magnitude of [their] atomic weights. But this regularity is upset by the changes in the physical and chemical nature of the elements: the number of their atoms in the particle and the quality of the atoms, or their ability to join [together in] chemical compounds, all depend on this. For example, if we turn our attention to the first series of elements, which include alkali metals, copper and silver, then we find the following numbers: Li = 11.8; Na = 23.7; K = 44.8; Cu = 7.2; Rb = 56.1; Ag = 10.3; .... Tl = 17.2, i.e. we see no regularity in the changes in the volumes of the atom. But, paying attention to the close similarity existing between lithium, potassium, rubidium and cesium on the one hand, and sodium, copper and silver on the other, we already see some regularity, absolutely clear in the first row but not visible in the second, that copper has the smallest volume; for elements below and above [copper], the volume of the atom is greater than for copper. This is completely parallel to the fact that in the series of magnesium, zinc and cadmium the volume of zinc is much less than that of magnesium, and even less than cadmium. Lead is larger than thallium, just as zinc is larger than copper, and [it is] more like cadmium than silver. Magnesium, however, has a volume less than sodium. In the phosphorus series, the volume of arsenic is less than that of phosphorus and less than the volumes of antimony and bismuth; the volume of bismuth is greater than that of lead, just as the volume of antimony is greater than that of cadmium. These complex relations acquire a special meaning when we compare the properties of elements with the properties of their compounds and especially with the reactions in which they participate. These relations are set out by me in the second volume of my book *Fundamentals of Chemistry* and are not included in the purpose of the present article. But in order to supplement what was said above by pointing out the variety of relations that are observed in this case, I will add a few fragmentary remarks concerning the specific weight and volume of analogous compounds belonging to the series considered earlier.

The specific weight of potassium compounds is always slightly less than that of the corresponding sodium compounds; for example. potassium chloride has a specific weight of 1.9, and sodium chloride has a specific weight of 2.1; potassium nitrate 2.1, and sodium nitrate 2.2; caustic potassium 2.0, and caustic soda 2.1; potassium oxide 2.7, and sodium oxide 2.8; metallic potassium 0.87, and sodium 0.95. The relationship between magnesium and calcium is exactly the same: magnesium compounds are usually somewhat denser than calcium compounds. For example. calcium oxide has a specific weight of 3.2, and magnesium oxide is 3.7; slaked lime 2.2, and milk of magnesia 2.3; calcium chloride 2.1, and magnesium chloride 2.2 (3); calcium carbonate in the form of [Iceland] spar has a specific weight of 2.72, and magnesium carbonate in the form of spar 2.95; calcium has a specific weight of 1.58, and magnesium has a specific weight of 1.74. Thus, calcium compounds relate to magnesium compounds in exactly the same way as potassium compounds relate to sodium compounds; so with an increase in the [atomic] weight there will be an increase in volume. But if we go further, we note again a decrease in volumes; so analogous compounds of copper and sodium are close in volume. For example, sodium oxide Na_2O has a particle volume of 22, and cuprous oxide Cu_2O of 25; the volume of sodium chloride particles is 28, and of copper chloride corresponding to table salt, is also 28, because the specific weight is 3.5. This is despite sodium and copper in a free state displaying, as we have seen, a very significant difference in volumes; the specific gravities of copper and sodium compounds are very different.

Similarly, zinc in its compounds has a volume slightly smaller than calcium, namely, close to magnesium; zinc oxide has a volume of 45, because the specific weight is 5.6 and magnesium oxide has a volume of 11. Zinc chloride exhibits a volume of 48, and magnesium chloride of 43; [that of] the sulfate salt of zinc in the anhydrous state is 43, and the sulfate salt of magnesium is 44. Therefore, the transition from sodium to copper (in the lower oxide salts) and from magnesium to zinc in the corresponding compounds does not entail a significant change in the volumes, despite the considerable difference in the volumes and in the energy of the free metals. The silver compounds in the oxide salts have almost the same volume as the copper compounds in the lower oxide salts, hence, the same as the sodium compounds. It is sufficient, for example, to indicate that silver nitrate has a partial volume of 39.0 (specific weight 4.34), whereas the cuprous nitrate salt has a partial volume of 37.9 and a specific weight of 2.24 [typo for 3.24]; copper chloride has a volume of 28.0, and silver chloride is 26.3. It is also remarkable that copper, in the salts of the oxide [CuO], is isomorphous with the salts of magnesia, and shares with them a proximity in the magnitude of specific volumes. So, for example, anhydrous sulfate of magnesium has a volume of 44, and anhydrous sulfate of copper, 45. This is similar to the fact that the chromium [i.e., chromate, CrO_4] salt has a volume [of] 72, the sulfate salt of potassium [has a volume of] 66, and the potassium manganate salt $KMnO_4$ has a volume of 58.3, a little more than the potassium chlorate salt, $KClO_3$, whose volume = 54.6. The volume of chromium and manganese salts is greater here than the corresponding salts containing sulfur and chlorine, although the volume of chlorine and sulfur is much greater than that of chromium and manganese. It is clear from this that in compounds made analogously, one often observes the similarity in the magnitude of volumes and the volume ratio that is not at all anticipated and in no way agrees with the volumes that the participating elements have in a separate [i.e., free] state. From this it becomes clear that, in the system we have applied, based on the magnitude of the atomic weights and similarity in the chemical nature, the above deviations from the simple order are [actually] what one would expect. Atomic weights, like [chemical] analogies, are determined not by the properties of individual elements, but by the properties and composition of the compounds.

The remarks given above can serve as new evidence of the law which I defended in my article "specific volumes" and which can be formulated as follows: the volume of compounds can not be judged from the volume of their constituents. That is why it is necessary to treat with very great caution those systems of specific volumes, which are based on the assumption of the opposite statement.

Note. The foregoing was communicated by me at the Congress in August 1869. In 1870, in *Liebig's Annalen* (after this article was sent by me for printing), an article by Lothar Meyer appeared, dealing with the same subject. Mr. Meyer's conclusions are based on the assumption of the system of elements proposed by me and agree with those that I have made with respect to the volumes of atoms. He also pays special attention to the descending and ascending series of elements and to the sequence of volume changes. But the conclusions were increased in clarity by the graphic image attached to the article. By putting this postscript I have no desire to raise the issue of scientific priority, (in my opinion, these questions do not often have any academic interest), and I only want to point to the table attached to Mr. Meyer's article as a means of capturing and explaining those complex relations, which are indicated in the previous text.

References and Notes

1. After the Congress, I made a special report on this subject in *J. Russ. Chem Soc.* **1870**. *№1.*
2. This article is already in the *J. Russ. Chem. Soc.* **1870**, vol. 2.
3. The sulfate salt of lime has a specific weight of 2.95, and the anhydrous sulfate salt of magnesium is 2.65. This apparent deviation depends, in my opinion, on the fact that the sulfate salt of lime in the anhydrous state is in two aggregated states. In the form obtained by calcining gypsum, it is able to combine with water and then probably has a smaller specific weight; it must be assumed that it will be about 2.5. In the form of anhydrite, the sulfate salt of lime does not have the ability to combine with water, and in this form it does not display an aggregated state like that in which it is found in alabaster, and in no way is analogous to an anhydrous sulfate salt of magnesium. However, the latter, after strong calcination, dissolves very slowly in water, which may depend on the molecular change occurring at the same time.

2020 Conferences in History and Philosophy of Chemistry

- International Society for the Philosophy of Chemistry: 24th annual meeting. July 21-23 in Buenos Aires, Argentina (http://www.filoexactas.exactas.uba.ar/ispc2020/)
- ACS Division of the History of Chemistry at the Spring 2020 National Meeting of ACS, Philadelphia, Pennsylvania, March 22-26 (www.acs.org/content/acs/en/meetings/national-meeting.html).
- European Society for the History of Science (ESHS): 9th International Conference, hosted by the Centre for the History of Universities and Science at the University of Bologna (CIS) and by the Italian Society for the History of Science (SISS), will take place in Bologna, Italy, August 31-September 3, 2020 (https://sites.google.com/view/eshsbologna2020)
- ACS Division of the History of Chemistry at the Fall 2020 National Meeting of ACS, San Francisco, California, August 16-20
- History of Science Society, October 7-11 in New Orleans, Louisiana, USA

TERPENE TRANSFORMATIONS AND FAMILY RELATIONS: VLADIMIR IPATIEFF (1)

Christopher P. Nicholas, Exploratory Catalysis and Materials Research, Honeywell UOP,
Des Plaines, IL, USA; Christopher.Nicholas@UOP.com

Introduction

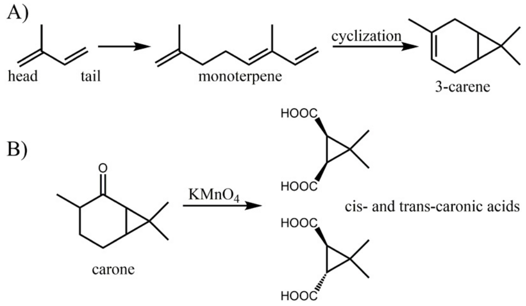
At the Fall 2018 American Chemical Society (ACS) Meeting in Boston in the Symposium in honor of David Lewis, I presented on the Russian chemist Vladimir Nikolaevich Ipatieff's contributions to the development of catalytic chemistry both before and after emigrating to the United States. From some of that work, a basic biographic sketch and an account of Ipatieff's most important catalytic discoveries was recently published in *ACS Catalysis* (2) and highlighted in *Chemical & Engineering News* (3). Ipatieff is a major figure in the Russian chemical diaspora and much has been previously written about him (4, 5, 6). Here, I expand on Ipatieff's work at Northwestern University, particularly in the field of terpene chemistry, and his relationship with family members, including his wife Barbara and half-brother Lev Chugaev.

Russian Life and Early Terpene Experiences

Born in Moscow November 21, 1867, the son of the architect Nikolai Alekseevich Ipatieff, and schooled at the Mikhail Artillery Academy in St. Petersburg, Vladimir Ipatieff graduated in 1892 before returning to Moscow to marry Barbara Dmitrievna Ermakova, who would be partnered with him until their deaths in late 1952 (4).

After teaching near Moscow for a year, Ipatieff returned to St. Petersburg to research with A. E. Favorsky at the University of St. Petersburg before receiving a scholarship from the Russian government to study abroad in Germany with the group of Adolph von Baeyer. This experience set the tone for much of Ipatieff's future work due to the people he became acquainted with and the science pursued.

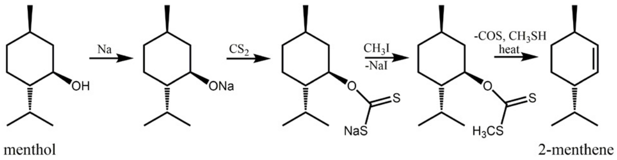
The project assigned in Munich was to determine the structure of carone, a monoterpene ketone derivative. Monoterpenes have the formula $C_{10}H_{16}$ and are biosynthetically prepared via head to tail polymerization of isoprene (Scheme 1) (7). Significant questions for investigation often involved structure, reactivity, and location of oxygenate functional groups and were of interest to investigate transformations of organic molecules throughout the length of Ipatieff's career.



***Scheme 1**. Terpene biosynthesis is shown in part A and the oxidation of carone to caronic acids in part B.*

While von Baeyer had been working with carone (8), and Wagner had previously suggested a structure (9), it was Ipatieff's work utilizing oxidation to caronic acids with $KMnO_4$ that proved the structure (10). The *cis*- and *trans*-caronic acids could be separated, with the ratio of *cis*- to *trans*- corresponding to the stereochemistry of the original carone, while also allowing confirmation of the presence of a cyclopropane ring in carone. Following the conclusion of his fellowship with von Baeyer in late 1896, Ipatieff returned to Russia to begin a very successful career researching in St. Petersburg.

One of Ipatieff's acquaintances from Moscow was Lev Chugaev, also a chemist (11). While Chugaev is best known as an originator of coordination chemistry for his work on platinum complexes, he worked in many fields (12, 13). Just prior to 1900, Chugaev worked on reacting deprotonated terpene alcohols with CS_2 to form xanthogens which could be distilled to form a single hydrocarbon compound, (Scheme 2) thereby greatly enhancing terpene structural understanding.



Scheme 2. *Conversion of menthol to 2-menthene via the xanthenogen route pioneered by Chugaev.*

As the two famous chemists talked during Chugaev's move from Moscow to St. Petersburg University in 1908, he and Ipatieff discovered they were half-brothers, children of Anna Aleksandrovna Gliki six years apart (14). Anna had fallen for the science teacher Aleksandr Fomich Chugaev at the girls school she attended, but was not allowed to marry him for economic reasons. Instead, she married Nikolai Ipatieff. About 5 years after Vladimir's birth, Anna left the family to join A. F. Chugaev with whom she had Lev Chugaev. Shortly thereafter, she returned to live with the Ipatieffs before dying of tuberculosis in 1880, just before Vladimir turned 13. Both Chugaev and Ipatieff wrote warmly of their mother and it is amazing she is the parent of two well-regarded chemists (15).

Like many Russians of the time, Ipatieff had a beard throughout his life in Russia, usually of quite impressive character. Early in his career, Ipatieff spilled a few drops of isobutyric acid into his beard, an event which kept Barbara at a distance for days (16a). Perhaps due to this, the beard shortened over the years, and upon leaving Russia permanently, Ipatieff shaved his beard as a new start to life, and was clean-shaven thereafter (17, 18a).

Figure 1. *Photographs of Vladimir Ipatieff over the course of his career. A) 1897 during his stint with von Baeyer. B) as General Lieutenant in 1914. C) Pre-1917, but likely 1916 upon election as an ordinary academician. D) Early 1930s while at UOP. E) in 1942, shown with his wife Barbara. Photos D and E are reproduced with permission from the ACS from references 2 and 19, respectively.*

Travel to USA and Work with UOP

At the 1930 World Power Congress in Berlin, Ipatieff was introduced to the head of Universal Oil Products (UOP) research, Gustav "Gasoline Gus" Egloff by Hans Tropsch. Egloff was seeking to start a catalytic research program at UOP and Ipatieff agreed to visit. At the age of 63, Ipatieff left Barbara in Berlin for the summer and traveled by ship from Cherbourg, France, to New York City in the last second-class berth available on the Bremen IV (18b).

After meeting with Hiram Halle, the President of UOP, in New York, Ipatieff came to Chicago to see the operation. Chicago was, in 1930, a booming place: the second largest city in the United States and the 6th largest in the world with a population of 3,376,438 at the census time (20). The UOP Chicago office was then located in the middle of it all on the 21st floor of the Straus Building, a Graham, Anderson, Probst & White designed structure that was one of the first two Chicago buildings over 260 ft in height (Figure 2).

***Figure 2**. The Straus Building, located at 310 S. Michigan Avenue, Chicago, IL (corner of Jackson and Michigan). Photograph from the Art Institute of Chicago's Ryerson & Burnham Historical Archival Image Collection.*

While the drafting, sales and CEO offices were in downtown Chicago (the CEO's office was in the northeast corner looking out onto Grant Park and Lake Michigan), the newly constructed $500,000 research facility (21) was located southwest of Chicago in the suburb of Riverside on what at that time was Route 66. It had three buildings on the corner of the lot with trees to approximate a quiet college campus and was co-located with a small independent oil refinery to serve as the demonstration location for newly developed technology. Ipatieff was driven out to Riverside for discussions about leading research at UOP, reporting in his memoir (18c):

> I saw at once that no real scientific work was being done here and that before us was a virgin laboratory, unfertilized by chemical thought and unadapted to work on catalysis and high pressures.

At an age when most would have considered retirement, lacking knowledge of English, and given these comments, Ipatieff surprisingly agreed to return the next summer to lead research programs at UOP. Between the difficulty of acquiring a US visa for a Russian in the period between the two World Wars, tension in Germany, and the significant compensation offered (22), the prospect of building catalysis at UOP while lecturing part-time at Northwestern was a good offer.

Returning to Europe in the fall of 1930, Ipatieff continued previously contracted work for Bayerische Stickstoff Werke. With the help of Ward Evans, Chair of Chemistry at Northwestern University, Ipatieff was afforded a work visa in exchange for delivering a lec-

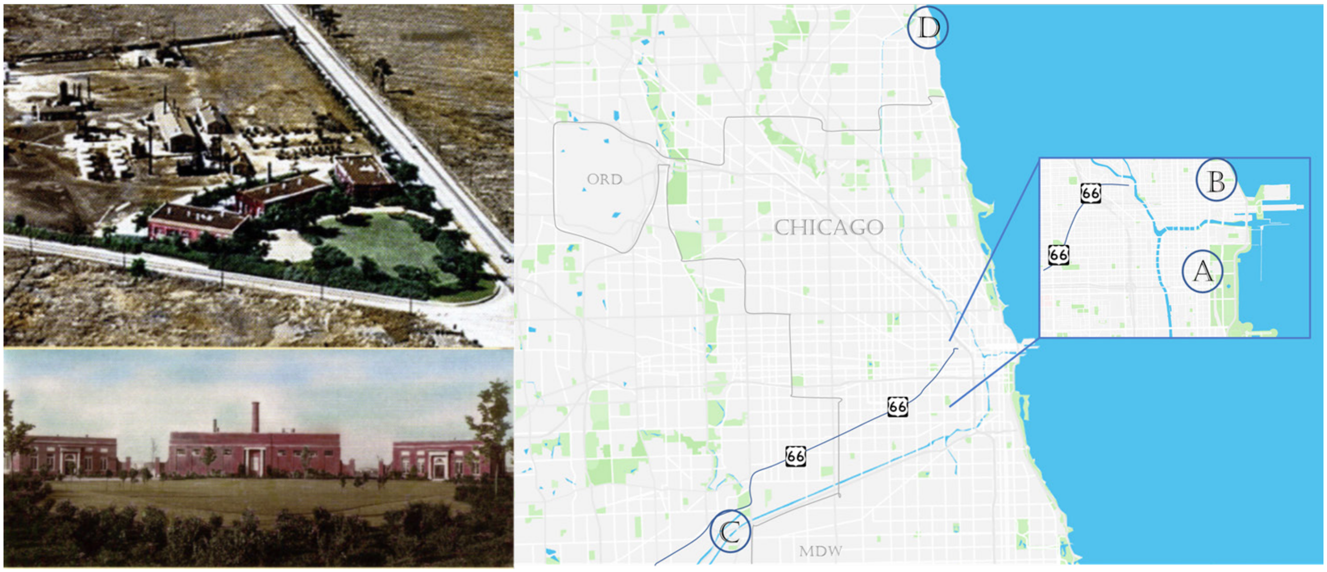


***Figure 3**. The upper left shows an aerial view of the Riverside facility showing the "university campus" in the foreground and the refining development area behind. The bottom left shows the "three imposing buildings" comprising the research facility. The right side shows a map of Chicagoland and an inset of downtown marked with the locations of A) the UOP Chicago office, B) the Pearson Hotel, where the Ipatieffs lived, C) the UOP Riverside facility, and D) Northwestern University (25). Left images courtesy of UOP and the Chicago Aerial Survey.*

ture series at Northwestern in 1931-32. In the spring of 1931, he, Barbara, and another woman, Alexandra "Shura" Seldowitsch sailed from Berlin to New York City in a first-class cabin on the S. S. Columbus (18d, 23).

After arriving in Chicago, the three took a two-bedroom suite in the Pearson Hotel, the women in one bedroom and Ipatieff in the other (24). The Pearson was located on the north side of downtown at Chicago and Michigan Avenues, now the site of Water Tower Place. From the Pearson Hotel, Ipatieff had easy access to Route 66 via Chicago Avenue and was driven out to Riverside daily until named Research Professor at Northwestern University in 1937, when he split time by commuting 2-3 times a week north to the Evanston campus to teach and research there. (Figure 3).

While the true nature of the relationship between the Ipatieffs and Seldowitsch will never be known, this did not stop the Hearst papers from putting out headlines in November of 1932 entitled "Northwestern Professor in Love Tangle" after Ipatieff was sued in US court by Gregory Seldowitsch for "loss of affection" (26).

The legal dispute was quickly thrown out and appears not have hindered the scientific output of Ipatieff or significantly shaken his relationship with Barbara. The discoveries that he, Herman Pines, and Vladimir Haensel made were of importance to UOP and to the USA, generating 8,790 US and foreign patents from 1921-1955. For this productivity, the Riverside facility (Figure 2) was named a National Historical Chemical Landmark in 1995 (21).

Among the discoveries Ipatieff participated in were three previously highlighted acid-catalyzed reactions: oligomerization, aromatic alkylation, and paraffin alkylation, all three of which were used to make 100 octane fuel during World War II (2, 6).

Meanwhile, Ipatieff researched and taught at Northwestern from 1937, the same year he and Barbara became US citizens, shortly after having their Soviet citizenship revoked (4). To start the Northwestern lab, Ipatieff personally funded much of the laboratory equipment while UOP paid salaries. The early years were fraught with every manner of dispute between university and corporation (16b), but were solved in 1942 when the laboratory moved from University Hall to the newly built Technological Institute (Figure 4) and was inaugurated as the Ipatieff Teaching Laboratory. To distinguish work carried out at Northwestern from that at UOP, Ipatieff often worked with molecules not present in crude oil fractions. Significant among these were the terpenes Ipatieff first encountered in Germany.

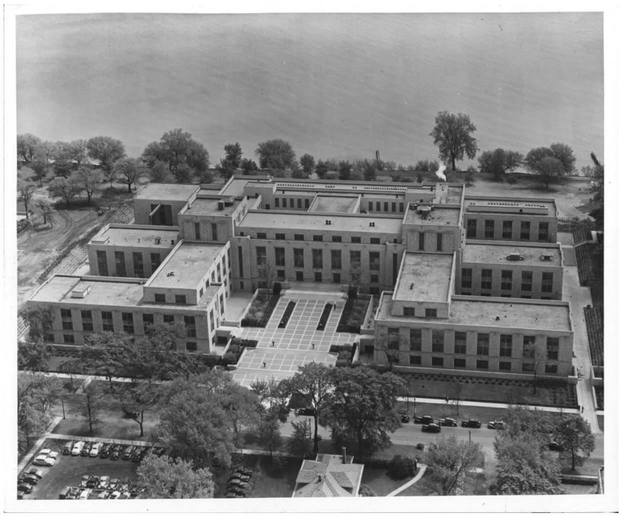


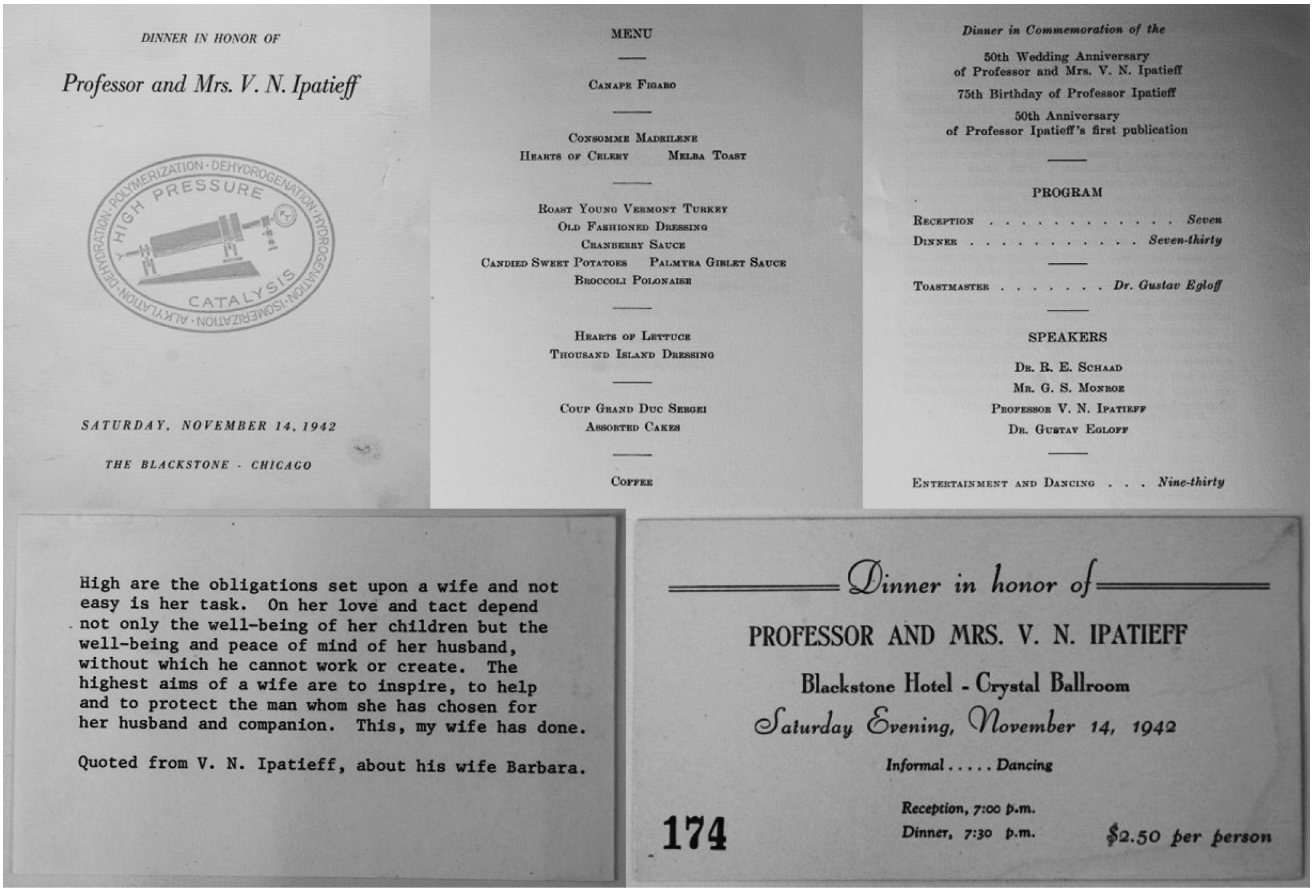
***Figure 4**. Exterior aerial view of Northwestern Technological Institute in 1942. Photo courtesy of the Northwestern University Archives.*

He and Herman Pines started their terpene work by studying the dehydration of alcohols to alkenes (27). From this initial 1944 publication until Ipatieff's death in 1952, the pair collaborated on twenty papers covering reactivity patterns of the terpenes, with Pines extending the series until 1959. While Ipatieff's initial work in terpenes was largely structural in character, he now focused primarily on reactivity patterns.

The dehydration work was designed to probe C–H reactivity by understanding the location of double bonds formed, though this led to a study of carbocation stability once Ipatieff and Pines determined that alkyl shifts also occurred during catalysis (28, 29).

Among other interesting discoveries were a method for determining ring structure and size for an unknown terpene. Ipatieff and Pines heated terpenes including cyclofenchene, isocamphane, and isobornylane in the presence of 1-2% aqueous $MgCl_2$ to learn which size rings were most susceptible to cleavage.

From this work, they concluded that cyclopropanes such as that found in the carene or cyclofenchene structures ring-opened most readily, and that six-membered rings were most stable. Other size rings opened at intermediate temperatures. This knowledge was used to predict, and helped confirm, the structure of 2,6-dimethylbicyclo[3.2.1]-2-octene, a new terpene that Ipatieff had observed during solid phosphoric acid (SPA) catalyzed isomerization of limonene (30, 31). SPA was invented



DINNER IN HONOR OF

Professor and Mrs. V. N. Ipatieff

SATURDAY, NOVEMBER 14, 1942

THE BLACKSTONE · CHICAGO

MENU

CANAPE FIGARO

CONSOMME MADRILENE
HEARTS OF CELERY MELBA TOAST

ROAST YOUNG VERMONT TURKEY
OLD FASHIONED DRESSING
CRANBERRY SAUCE
CANDIED SWEET POTATOES PALMYRA GIBLET SAUCE
BROCCOLI POLONAISE

HEARTS OF LETTUCE
THOUSAND ISLAND DRESSING

COUP GRAND DUC SERGEI
ASSORTED CAKES

COFFEE

Dinner in Commemoration of the

50th Wedding Anniversary
of Professor and Mrs. V. N. Ipatieff

75th Birthday of Professor Ipatieff

50th Anniversary
of Professor Ipatieff's first publication

PROGRAM

RECEPTION . . . . *Seven*
DINNER . . . . *Seven-thirty*

TOASTMASTER . . . . *Dr. Gustav Egloff*

SPEAKERS

DR. R. E. SCHAAD
MR. G. S. MONROE
PROFESSOR V. N. IPATIEFF
DR. GUSTAV EGLOFF

ENTERTAINMENT AND DANCING . . . *Nine-thirty*

High are the obligations set upon a wife and not easy is her task. On her love and tact depend not only the well-being of her children but the well-being and peace of mind of her husband, without which he cannot work or create. The highest aims of a wife are to inspire, to help and to protect the man whom she has chosen for her husband and companion. This, my wife has done.

Quoted from V. N. Ipatieff, about his wife Barbara.

Dinner in honor of

PROFESSOR AND MRS. V. N. IPATIEFF

Blackstone Hotel - Crystal Ballroom

Saturday Evening, November 14, 1942

Informal . . . . . Dancing

Reception, 7:00 p.m.
Dinner, 7:30 p.m.

174

$2.50 per person

Figure 5. *The invitation, menu, and program from the November 14th, 1942, dinner in honor of Professor and Mrs. Barbara Ipatieff. At the bottom of the composite are two inserts into the invitation: a quote from Ipatieff about his wife Barbara and the invitation card (35).*

by Ipatieff by combining a silica source with H_3PO_4 and extruding the mixture and is still produced commercially today for acid catalyzed reactions (32). He was even able to propose a mechanism for the formation of the new terpene which depended on the concentration of limonene in the reaction.

Hydrogenation was also frequently studied using the high-pressure autoclaves that Ipatieff had previously developed (33). He utilized particular steels to fabricate autoclaves where thin Cu metal seals were held between knife edges on the top and bottom of the autoclave. These autoclaves were the first apparatus to allow reactions at pressures up to 1300 atm to be investigated.

With discoveries of historic importance, patents, and papers from this US work adding up, in addition to accomplishments in Russia, accolades arrived, including election to the National Academy of Sciences in 1939 (4). One such accolade for Ipatieff was a dinner (Figure 5) in late 1942 hosted by UOP to commemorate the 50th wedding anniversary of him and Barbara, his 75th birthday, and the 50th anniversary of his first paper (34).

Interestingly, a card was inserted into the menu / program describing the respect Ipatieff had for Barbara and her ability to ensure life was taken care of so that he could continue discovering new science. Ipatieff appears to have consistently consulted Barbara about life decisions. As they left Russia in 1930, he reports a conversation wherein they discuss returning to Russia, but both suspect it may not be their fate to return (18e).

Later, on Christmas Eve 1936, the Ipatieffs received a cable from their two children remaining in Russia noting that the Ipatieffs must return to Russia immediately, or the children would not be responsible for the consequences. Ipatieff gave Barbara the ultimate decision in whether they would return. They chose not to, with Barbara reasoning that to do so would mean a death sentence for Ipatieff and that the children would be worse off, likely sent to a distant place (18f). As Paul Haensel wrote (5):

> For him and his wife, in their private life, emigration was a cruel experience, however. The Soviet government resented Ipatieff's "flight" and proclaimed him a traitor of his country. His own son, Vladimir, a gifted chemist and professor in Leningrad, had to renounce his father. His only daughter has no possibility to see her aged parents, nor have the grandchildren. The Ipatieffs lost a son, a brilliant young biologist, during the World War in action. Another son perished during a research study fighting malaria in the Belgian Congo.

Through it all, Ipatieff kept developing notable new chemistries regardless of the cruelties of life. For the Ipatieffs, having to continue working toward the end of their lives in conditions they would never have tolerated previously seems to sum up the inequities life threw at them (18g).

Vladimir and Barbara died 10 days apart, on November 29th and December 9th 1952. They were married for 60 years, and had known each other for 70 of his 85 years after having met at a summer resort in Russia as pre-teens (6).

References and Notes

1. Presented at the 256th National Meeting of the American Chemical Society, Boston, MA, Aug. 21, 2018, HIST 23.
2. C. P. Nicholas, "Dehydration, Dienes, High Octane, and High Pressures: Contributions from Vladimir Nikolaevich Ipatieff, a Father of Catalysis," *ACS Catalysis*, **2018**, *8*, 8531-8539. https://pubs.acs.org/doi/10.1021/acscatal.8b02310
3. M. Jacoby, "Vladimir Ipatieff is the Catalysis Superhero You've Never Heard of," *Chem. Eng. News*, **2019**, *97(May 11)*, 22-24.
4. L. Schmerling, "Vladimir Nikolaevich Ipatieff, 1867-1952," *Biogr. Mem. Natl. Acad. Sci. U.S.A.*, **1975**, *47*, 83-142.
5. P. Haensel, "V. N. Ipatieff in Russia," *Chem. Bull.*, **1940**, *27(4)*, 109-113. Published by the Chicago Section of the ACS, digitized by Northwestern University.
6. P. Hampson, "The Road to Success: A Sketch of Vladimir Ipatieff, Famed Oil Scientist," *Chicago Tribune*, Sept. 27, 1952, p 35.
7. J. L. Simonsen and D. H. R. Barton, *The Terpenes: the Sesquiterpenes, Diterpenes, and Their Derivatives*, Cambridge University Press, 2nd ed., Cambridge, UK, reprinted 1952.
8. A. Baeyer, "Ortsbestimmungen in der Terpenreihe," *Ber. Dtsch. Chem. Ges.*, **1894**, *27*, 3485-3498.
9. G. Wagner, "K stroyeníyu terpenov i im rodstvennykh soyedineníy [On the Structure of Terpenes and Related Compounds]," *J. Russ. Phys. Chem. Soc.*, **1896**, *28*, 56-108 (at p 95).
10. A. Baeyer and W. Ipatiew, "Ortsbestimmungen in der Terpenreihe: Über die Caronsäure," *Ber. Dtsch. Chem. Ges.*, **1896**, *29*, 2796-2802.
11. J. J. Bikerman, "Forced Marriage and Love Union: A Romantic Affair in the History of Russian Chemistry," *Ann. Sci.*, **1971**, *27*, 201-204.
12. G. B. Kauffman, "Terpenes to Platinum: The Chemical Career of Lev Aleksandrovich Chugaev," *J. Chem. Educ.*, **1963**, *40*, 656-665.
13. D. E. Lewis, *Early Russian Chemists and Their Legacy*, Springer, Heidelberg, Germany, 2012, "Into a New Century: Chemists Advancing the Legacies of Kazan, St. Petersburg, and Moscow," Ch. 5, section 5.3.2.1.
14. V. N. Ipatieff, *The Life of a Chemist: Memoirs of V. N. Ipatieff*, Stanford University Press, Stanford, CA, 1946. The book was translated by V. Haensel and R. Lusher, and edited by X. J. Eudin, H. D. Fisher and H. H. Fisher, from his memoirs written in Russian.
15. In Ipatieff's memoir of his time in Russia (Ref. 14) not a single reference to his father his made, but many times he writes of his mother and qualities she taught him.
16. H. Pines, *Genesis and Evolution of the Ipatieff Catalytic Laboratory at Northwestern University 1930-1970*, Department of Chemistry, Northwestern University, Evanston, IL, 1992. a) p 109. b) Ch. 1.
17. See the transformation in Figure 1 from images A-C to D & E. Also in Ref. 2 from Figure 2B and 2D to the well-known picture of Ipatieff as Lieutenant General to Figures 4, 5, 8, and 10, all of which are after Ipatieff's arrival in the US.
18. V. N. Ipatieff, *My Life in the United States: The Memoirs of a Chemist*, Northwestern University Press, Evanston, IL, 1959. Translated and edited from his memoirs largely written in Russian, but from a mixture of languages. a) p 111. b) p 9. c) p 16. d) p 29. e) p 6. f) p 106. g) p 82.
19. *Chem. Eng. News*, **1947**, *25(12)*, 829. https://pubs.acs.org/doi/10.1021/cen-v025n012.p829.
20. *Growth of the World's Urban and Rural Population, 1920-2000*. Department of Economic and Social Affairs, United Nations, New York, 1969.

    From Annex V: New York, London, Paris, Tokyo, Berlin, Chicago, Ruhrgebeit polycentric urban area, Buenos Aires, Philadelphia, Osaka were the top 10.
21. The campus and the three neoclassical buildings designated as a National Historical Chemical Landmark were

designed by Holabird and Root. https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/uoplaboratory.html (accessed Nov. 1, 2019).

22. Ipatieff was the 3rd highest paid ($21,500) employee at UOP in 1931-1935 with only Joseph G. Alther (CEO) and Egloff (CTO) paid more. This situation likely continued throughout Ipatieff's tenure with UOP, but I have not viewed payroll records post-'35.

23. Ipatieff neglects to mention Shura in his memoir, but shipping manifest and newspaper photos confirm this. Given Ipatieff's propensity for philanthropy, Shura could have simply been escaping a bad marriage.

24. C. Remsberg and H. Higdon, *Ideas for Rent: The UOP Story*, UOP, Des Plaines, 1994.

25. The Chicago border shown in gray is today's approximate border; the only substantive change to the border from 1930 when Ipatieff arrived in Chicago is the annexation of the land for O'Hare airport (ORD).

26. The *Chicago Examiner* published this title on Nov. 13, 1932. Similar stories were published in Lee Syndicate Papers from the AP wire. *Wisconsin State Journal*, Sunday, Nov. 13, 1932, pp 1 and 4 is one example. They used a headline of "Professor's Wife Aided Mate's Love Theft, Claim." Newspapers transliterated foreign names into English, so both the first and last names of the Seldowitsches have multiple spellings depending on source. Mrs. Ipatieff's name is usually spelled Barbara, but is other times spelled as Varvara.

27. V. N. Ipatieff and H. Pines, "Studies in the Terpene Series. I. Dehydration of Alcohols in the Terpene Series Under Pressure and in the Presence of Dilute Aqueous Salt Solutions," *J. Am. Chem. Soc.*, **1944**, *66*, 1120-1122.

28. V. N. Ipatieff, H. Pines and R. C. Oldberg, "Studies in the Terpene Series. V. The Action of Dilute Aqueous Salt Solutions on 3,3,5-trimethylcyclohexanol and 1,1,3-trimethyl-X-cyclohexene," *J. Am. Chem. Soc.*, **1946**, *68*, 1709-1710.

29. V. N. Ipatieff, G. J. Czajkowski and H. Pines, "Studies in the Terpene Series. XV. Cycloisomerization of α- and β-pinene, α-terpineol, and 1,8-terpin Hydrate," *J. Org. Chem.*, **1952**, *17*, 1431-1436.

30. V. N. Ipatieff, H. Pines, V. Dvorkovitz, R. C. Oldberg and M. Savoy, "Studies in the Terpene Series. VI. Cyclic Isomerization of Limonene," *J. Org. Chem.*, **1947**, *12*, 34-42.

31. V. N. Ipatieff, J. E. Germain, W. W. Thompson and H. Pines, "Studies in the Terpene Series. XII. Cyclic Isomerization of Limonene. Proof of the Structure of a New Bicycloterpene," *J. Org. Chem.*, **1951**, *16*, 272-285.

32. C. P. Nicholas, "Applications of Light Olefin Oligomerization to the Production of Fuels and Chemicals" *Appl. Catal. A* **2017**, *543*, 82-97.

33. H. Pines, A. Rudin, G. M. Bo and V. N. Ipatieff, "Studies in the Terpene Series. XIX. Hydroisomerization and Hydrogenolysis of Cyclohexene, Methylcyclohexene, and p-Menthene in the Presence of Hydrogenation Catalysts," *J. Am. Chem. Soc.*, **1954**, *76*, 2740-2743. Published posthumously.

34. V. N. Ipatyev, "Opyt Khimicheskogo Issledovaniia Struktury Stali," *Artilleriiskii zhurnal*, *1892*, No. part I, 937–954.

35. Original invitation held in the UOP Historical Archive. Another copy of the dinner program is part of the holdings at Northwestern University.

About the Author

Chris earned a B.A. at Kalamazoo College (Kalamazoo, MI) before coming to the Chicago area. He has a long history with Ipatieff, having earned his Ph.D. at Northwestern while studying with the 4th Ipatieff professor, Tobin Marks. Wolfgang Sachtler, the 3rd Ipatieff professor, was also part of his committee. In 2006, Chris joined the industrial portion of Ipatieff's US legacy, what is now Honeywell UOP. Chris has worked throughout the Research departments at UOP, primarily focused on inventing and catalytically testing new materials and processes. Particular foci have included heterogeneous catalytic processes, synthesis of inorganic materials, process engineering, molecular adsorption, and olefin metathesis. Chris is an inventor or co-inventor on more than 75 US and foreign patents and coauthor of 25+ peer-reviewed journal articles and a book chapter. A favorite project at UOP has been attempting to replace solid phosphoric acid, a material Ipatieff invented and which is still sold commercially, as the catalyst for olefin oligomerization.

EARLY HISTORY OF POLYANILINE—REVISITED: RUSSIAN CONTRIBUTIONS OF FRITZSCHE AND ZININ (1)

Seth C. Rasmussen, Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND; seth.rasmussen@ndsu.edu

Introduction

Organic polymers and plastics comprise one of the most ubiquitous chemical technologies of modern society. While the bulk of commercial plastics are made of various saturated organic polymers that exhibit insulating behavior, conjugated polymers (Figure 1) are a less common class of organic plastic materials that are native semiconducting materials. In addition, such conjugated materials are capable of enhanced electronic conductivity (in some cases even quasi-metallic) upon either oxidization (p-doping) or reduction (n-doping) (2-5). As a result, conjugated polymers are organic macromolecules that combine the properties of traditional inorganic semiconductors with many of the desirable properties of organic plastics, including low production costs and mechanical flexibility (4, 5). The study and development of these materials has led to the current field of organic electronics, with technological applications including sensors, electrochromic devices, field effect transistors, organic photovoltaics (solar cells), and organic light-emitting diodes (OLEDs) (2-5).

Although conjugated polymers are typically viewed as quite modern materials, the earliest examples of these polymers date back to the early 19th century (4-8). In fact, it has been recently argued that polyaniline not only represents the first reported conjugated polymer, but also the oldest known example of a fully synthetic organic macromolecule (7, 8). Species consistent with our modern understanding of polyaniline date to the 1834 work of German chemist F. Ferdinand Runge (1794-1867) (9), five years before the more commonly recognized synthesis of polystyrene (10). Of course, the long-chain, polymeric nature of *aniline black* (polyaniline) was not recognized until the early 1900s (5, 7), and the modern concept of the macromolecule was not introduced until the 1920s by the German chemist Hermann Staudinger (1881-1965) (11, 12).

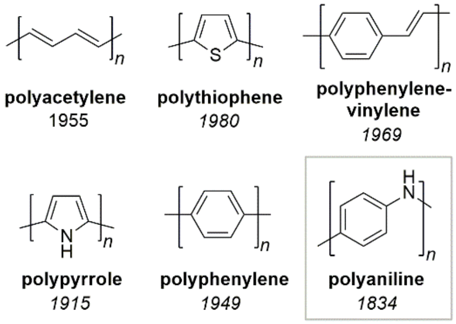


Figure 1. *Parent conjugated polymers and the years of their first reports in the literature.*

Although an in-depth early history of polyaniline up through the 1870s has been recently reported (7), that paper only touched on the aniline work of Nikolai Zinin in passing. In particular, neither the effect of greater accessibility of aniline via reduction of nitrobenzene nor Zinin's potential contributions to polyaniline itself were discussed. Thus, it seemed worthwhile to revisit the Russian contributions to early polyaniline in greater detail, particularly as the bulk of discussions on early polyaniline history tend to focus on either German or English contributions. In order to fully recognize Russian contributions during the formative years of aniline polymerizations, the following will present the work of Carl Julius Fritzsche (1808-1871) and Nikolai Nikolaevich Zinin (1812-1880) over the period of 1840-1845, along with a discussion on the impact of these efforts on later polyaniline studies.

Polymerization of Aniline

As the efforts of Fritzsche and Zinin discussed below predate all knowledge of the polymerization processes involved, as well as the molecular structures of the polymeric materials in question, it is worthwhile to briefly review our modern understanding of aniline polymerization. The following thus presents what is currently known about the mechanistic details of the polymerization methods under discussion, as well as a brief introduction of both redox- and acid-doping of polyaniline, in order to provide context to what will be presented in the subsequent sections.

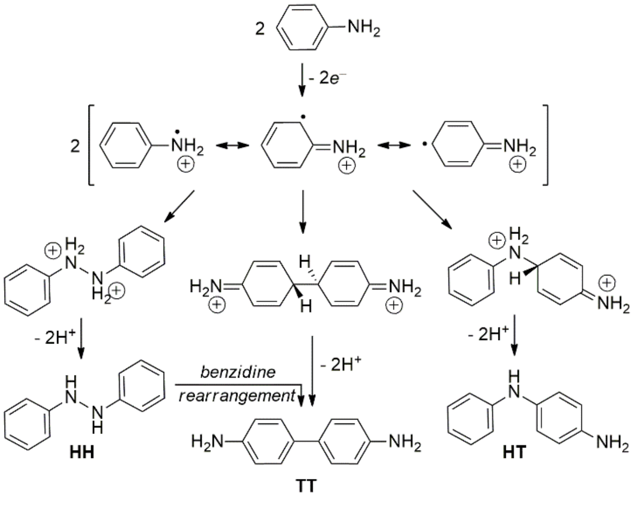


Figure 2. Initial dimerization of aniline.

Polyaniline is generated almost exclusively via oxidative polymerization (7, 13-18), which is a form of step-growth polymerization (19). In this process, the electron-rich aniline polymerizes anodically via either chemical or electrochemical oxidation of the π-system to form the corresponding radical cation, which can exist in multiple resonance forms (Figure 2). Spin density studies predict nearly equal distribution of the unpaired electron between the aniline nitrogen and the *para*-carbon of the benzene ring (18), which can result in three possible couplings: nitrogen-nitrogen (head-to-head, HH); nitrogen-arene (head-to-tail, HT); and arene-arene (tail-to-tail, TT) (13-18). This initial coupling is then followed by deprotonation to generate the neutral dimer.

Diarylhydrazine products formed via HH coupling are not stable, particularly under acidic conditions. Under these conditions, the HH dimer is converted to the TT dimer via the benzidine rearrangement (14). Alternately, two equivalents of the HH dimer can be converted to azobenzene (Ph-N=N-Ph) and two equivalents of aniline via disproportionation. As such, HH units do not contribute to the production of polyaniline (15). Of the remaining two possible regiocouplings, TT coupling is favored over HT coupling at the high radical cation concentrations typical of most polymerization conditions (i.e. large excess of oxidant and low pH) (16, 17).

Polymerization then continues through oxidation of the neutral dimers to form new radical cations (Figure 3). The oligomeric radical cations again undergo coupling, either with simple monomeric radical cations or radical cations of other oligoanilines, to generate still larger oligoaniline species after deprotonation. Thus, the overall step-growth process propagates via sequential oxidation, coupling, and deprotonation steps to ultimately give polymeric products (7, 13-18).

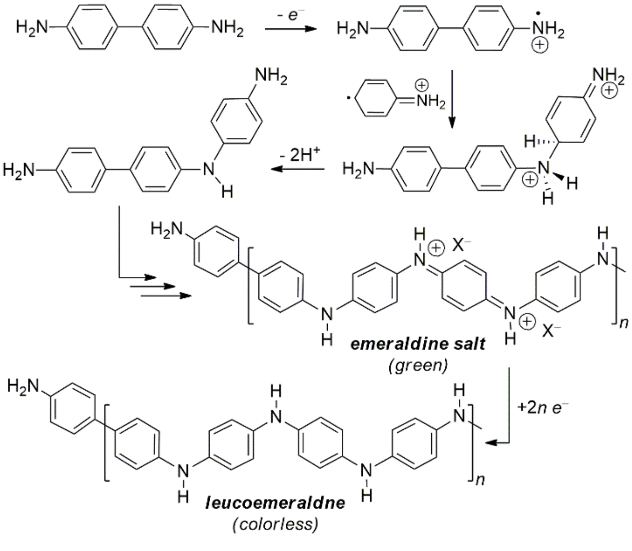


Figure 3. Continued polymerization mechanism from the initially produced dimer intermediates

As the polymer products undergo oxidation at lower potentials than either aniline or smaller oligomers, the materials generated via oxidative polymerization are initially produced in their oxidized state and require reduction in order to isolate the neutral form of the polymer. The most common oxidized form of polyaniline is the half-oxidized emeraldine (Figure 3), which can exist as both the violet-blue emeraldine base or the green emeraldine salt. As strongly acidic media are most commonly used for aniline polymerizations, however, the emeraldine salt is the typical product initially generated.

Fritzsche – From Germany to Russia

Carl Julius Fritzsche (Figure 4) was born on October 29, 1808 (20) in Neustadt, Saxony (7, 21-26) (now part of Germany), near the city of Stolpen (21, 22). His father was a physician and the district medical officer for the cities of Stolpen and Hohenstein. His mother was from the prominent Struve family (22). Although his given name was Carl, he appeared to go by his middle name Julius as neither Carl nor the initial C is found among any of his many publications, the majority of which he authored as simply J. Fritzsche (27).

Figure 4. *Carl Julius Fritzsche (1808-1871).*

In the city where Fritzsche spent his childhood, there was no Gymnasium, so he was educated through private lessons until the age of 14. Choosing to pursue pharmacy, he then moved to nearby Dresden to become apprentice to his uncle Friedrich Adolph August Struve (1781-1840) at the Salomons-Apotheke (22, 23). Five years later, he moved to Berlin to manage the laboratory of Johann Gottfried August Helming (1770–1830) (22). Although this was not strictly a scientific position, it enabled him to acquire a position as assistant to Eilhard Mitscherlich (1794-1863) at the University of Berlin in 1830 (7, 21-25).

It was in this position that Fritzsche is said to have developed his passion for science over the next two and a half years, largely due to his close relationship with Mitscherlich. It is also thought that Mitscherlich probably persuaded Fritzsche to enroll at Berlin in 1831 (22, 23), where he had already been attending lectures the previous year. In 1833, he acquired the Doctor of Philosophy (Dr. Phil.) degree with his "dissertatio de plantarum polline" (dissertation on plant pollen) (7, 21-25). As the subject of his doctorate was not chemistry, but botany, Mitscherlich is credited with all of Fritzsche's chemical training (7, 24). In his dissertation, Fritzsche clearly expressed his strong appreciation of Mitscherlich (22):

> In these times, I express the greatest affection for Mitscherlich. With the deepest gratitude I will remember him to the grave. With paternal precaution, he led my occupations and gave me the opportunity to complete my knowledge.

Fritzsche then emigrated to Russia in 1834 (7, 21-24), where he became the head of Struve's Institute of Artificial Mineral Waters (7, 28) established by his uncle Friedrich in St. Petersburg (21). Here, he continued his scientific pursuits, with his name appearing for the first time in the *Mèmoires des savants étrangers* of the St. Petersburg Academy of Sciences in 1836 (22). From that point on, all of his papers appeared initially in the publications of the Academy of Sciences, of which he became an adjunct member in 1838 (6, 21-23, 25). He was granted status as an extraordinary member in 1844 (6, 22, 23), and was appointed an academician (full member) in 1852 (7, 22, 23, 25) or 1853 (21). In addition to his decades of scientific activity in the Academy, he contributed his time to the Russian government through a number of service positions. This included serving as a member of the Imperial Commission for the Research and Utilization of the Caucasus Mineral Waters, as a chemist to the Medical Department, and as a consulting member of the Medical Council of the Minister of the Interior (22, 23). He also held various administrative posts within the Academy itself and served as a member of its Administrative Committee for three years (22).

Over the span of his career, he authored more than 60 papers, most covering various topics within organic chemistry (22, 23). His chemical work included research on various heterocyclic aromatic nitrogen compounds such as murexide and uric acid, and the hydrocarbons of coal tar, as well as the work that is the focus of the current discussion, his studies on indigo and its derivatives (7, 21-25).

All of the efforts discussed below were carried out in a small, modest laboratory next to his residence (7, 21-24). This was largely due to the fact that the laboratory of the St. Petersburg Academy was very primitive, and there were almost no funds for its support (29). However, upon completion of the new and spacious chemical laboratory of the Academy in 1866 (7, 22, 25) or 1867 (23, 29), he outfitted and occupied shared facilities there with Nikolai Zinin (22-25).

Although Fritzsche had always enjoyed excellent health, he suffered a stroke in 1869 (7, 22-25). Afterwards he did recover to some degree, but still suffered from paralysis on one side, and his speech and memory suffered (7, 22, 23, 25). To his friends, who had always known him as sprightly and cheerful, he suddenly changed. Seeing the hopelessness of his situation, Fritzsche even suggested that he preferred death to such a life (22, 23). Nevertheless, he did continue to work for some time (22-24), even if he rarely appeared for Academy sessions after that point (22). In the following year, he returned home to Germany in order to seek physical and spiritual relief (22, 23 , 25), finding the latter in the circle of those that gathered around him (22). His health continued to deteriorate, however, and he finally died on June 20, 1871 (7, 22-24, 30) in Dresden (26).

Aniline from Indigo

Indigo has been utilized as a dye and pigment throughout antiquity, with documented reports as far back as 27 BCE (31). The color of this dye originates from the organic species commonly known also as indigo. In addition to being the primary coloring agent of the indigo dye isolated from the indigo plant *Indigofera tinctorial*, it is also largely responsible for the color of the dye isolated from the plant woad, *Isatis tinctorial* (32, 33). Considering its long history, however, the indigo structure (Figure 5) was not determined until 1883 by Adolf Baeyer (1835-1917) (34).

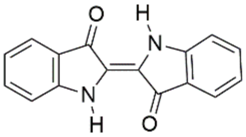


Figure 5. *The chemical structure of indigo.*

Fritzsche became interested in the chemistry of indigo sometime before 1839 (24), with his first paper on the reactions of indigo appearing in January of that year (35). However, it is his second indigo paper in 1840, that is of interest here (36). Unlike his first paper, which investigated decomposition products resulting from treatment with acid, his second paper focused on the base-induced decomposition of indigo. In the process, he found that treating indigo with a hot, highly concentrated KOH (or NaOH) solution gave a salt mass of reddish-brown color. If this salt mass is then heated in a retort, it is converted to an oily material with the simultaneous distillation of aqueous ammonia. Further heating of the brown, oily liquid resulted in the distillation of a color-less product to leave a brown, resinous body remaining in the retort. The final colorless product was found to be ca. 18-20% of the original indigo. He decided to call this new product *Anilin* (36) after *anil* (7, 8, 24), an older name for the indigo plant introduced by the Portuguese, which can ultimately be traced back to Sanskrit origins.

Fritzsche went on to characterize the product as an oxygen-free base that formed light and highly crystalline salts when treated with acids. In the process, he reported the corresponding salts generated from HCl and oxalic acid. Fritzsche reported that, in its purest state, Anilin strongly refracts light and exhibits a strongly aromatic, but unpleasant odor. He further determined its specific gravity to be 1.028 and its boiling point to be 228° C (37). Finally, combustion analysis led to the formula $C_{12}H_{14}N_2$, a doubling of the modern C_6H_7N formula (38).

Although Fritzsche believed Anilin to be a new species, it is now understood that modern aniline was independently discovered by multiple chemists (7, 8, 24, 39-46). The first of these was in 1826 (42), when Otto Unverdorben (1806-1873) reported the isolation of an oil that he named *Crystallin* (43) via the dry distillation of indigo. Then, in 1834, F. Ferdinand Runge isolated a volatile oil from the distillates of coal tar that he named *Kyanol* (44). Thus, Fritzsche's report in 1840 marked the third isolation of this species.

During the publication of Fritzsche's report of Anilin in the *Journal für praktische Chemie* (36b), the editor Otto Erdmann (1804-1869) recognized the similarity of Anilin with Unverdorben's Crystallin, and highlighted this in a postscript published directly following Fritzsche's paper (45). Erdmann began by bemoaning the fact that authors place more effort on the report of new compounds resulting from the decomposition of natural species than investigation of the chemical processes involved in their production. To drive this point home, he then followed this with a list of the unknowns not addressed by Fritzsche's publication, before going on to state (45):

> These and other questions that have to be imposed remain undecided. However, the last of these can almost certainly be answered. Anilin is most probably no other body than *Krystallin* described by Unverdorben already 14 years ago… Unverdorben's description of Krystallin is not complete. However, the agreement between the properties of Krystallin and of Anilin given by him is so great that Herr Fritsche, if there is a difference, had the obligation to prove it by specific experiments.

Erdmann then concluded his postscript with a side-by-side comparison of the known properties of the two species.

When Fritzsche's report was then republished in *Annalen der Chemie und Pharmacie* (36c), Justus von Liebig (1803-1873) added his own note to the end of the paper (46). This repeated Erdmann's paraphrased comments with Liebig's full agreement. Liebig, however, went even further than Erdmann, stating (46):

> Herr Erdmann…must not be surprised at the methods of Herr Fritzsche. Herr Fritzsche is one of those who mines by robbery; when he learns that some chemist is engaged in an investigation promising him valuable results, he undertakes not to help or render him any services, or to help carry the burden, but, like the corsairs, tries to unburden him in a quite particular way.

It is interesting to note here that neither Erdmann or Liebig mention Runge's Kyanol. It could be concluded that it was the fact that Anilin and Crystallin were both isolated from indigo that drew the ready comparison and the fact that Kyanol came from another source made its relationship less obvious. Still, confirmation that Crystallin, Kyanol, and Anilin were indeed all the same species had to wait until 1843, when August Wilhelm Hoffmann (1818-1892) presented conclusive evidence to support this conclusion (39).

Fritzsche's Oxidation Products of Aniline

Regardless of any criticisms relating to his "rediscovery" of aniline, Fritzsche did go on to study the oxidation products of his Anilin, something Unverdorben did not pursue in his previous isolation of Crystallin. Both Unverdorben (42) and Fritzsche (36) had observed the air oxidation of aniline to give a yellow color. Fritzsche, however, found that this yellow product was just an intermediate, with longer exposure times leading to a transition of the yellow color to brown, ultimately leading to the production of a resinous dark mass.

Extending this to the purposeful addition of oxidizing agents, Fritzsche found that the addition of nitric acid to aniline resulted in the formation of a blue or green material (36). This formation depended on the specific reaction conditions, but the resulting material did not appear to be indigo. However, its study was limited by the small quantities formed, and the fact that the solid continued to react with nitric acid resulting in decomposition.

Continuing his investigations, he found that dissolving aniline salts in chromic acid (H_2CrO_4, usually as a H_2SO_4 solution) resulted in the formation of a dark green precipitate, which ultimately became a dark blue-black (36). Unlike the case of nitric acid, the colored solid could be reproducibly produced under a variety of conditions, even in fairly dilute solutions. Combustion analysis revealed that the precipitate contained significant amounts of chromium, however, even for samples obtained from acid solutions.

Lastly, he treated aniline salts with potassium permanganate, resulting in the deposition of a brown precipitate containing manganese oxide. Fritzsche admitted that he had not been able to study these various color-forming reactions in much detail and planned to return to these in later publications (36).

While he did not follow up on most of these specific observations reported in 1840 (36), he did return to the treatment of aniline with chromic acid in 1843 (47). In this second report, he admitted that while he was able to reproducibly obtain the previously reported green product via the treatment of aniline with chromic acid, he was unable to obtain products of consistent composition. However, he did recognize that the product composition was affected by both the amount of chromic acid used, as well as the amount of other acids involved, even if he didn't understand exactly how these variables changed the nature of the products generated. Thus, he stated (47):

> Apart from the fact that the products are different in appearance, as one uses more or less chromic acid accordingly, or applies a greater or less excess of another acid, even apparently similar products give very different results in analysis, to which I still miss the key.

Fritzsche was much more successful, however, with the treatment of aniline with potassium chlorate (47). Thus, he found that the addition of an HCl solution of potassium chlorate to an aniline salt in alcohol resulted in the formation of a beautiful blue precipitate. If this product was then filtered and washed with alcohol, the blue color turned green, becoming dark green upon drying. Analysis of the product's composition revealed an empirical formula $C_{24}H_{20}N_4Cl_2O$, which is in near perfect agreement with the structure of the emeraldine salt given in Figure 3 ($X = Cl^-$) (47).

Lastly, Fritzsche reported that he had also produced analogous products via the successful application of H_2SO_4 solutions of either potassium bromate or potassium iodate (47). This 1843 report, however, seemed to be the last of Fritzsche's efforts concerning the oxidation products of aniline. Afterwards, he moved onto other subjects and focused his efforts elsewhere.

Zinin – Chemist by Dictate

Nikolai Nikolaevich Zinin (Figure 6) was born on August 25, 1812 (29, 48-50) in Shusha, a small town in the far southeast of the Russian Empire, located in the Caucasus mountains (29, 49-52). Shortly after his birth, both of his parents died (29, 50, 51), leaving him in the care of his step-sisters (50). These too, he lost a few years later in an epidemic (29, 50), after which Zinin was sent to live with his uncle in Saratov, on the Volga River (29, 50-53). It was in Saratov that Zinin received his early education, where it has been said that he excelled in Latin, mathematics, and physics (50, 51).

Figure 6. *Nikolai Nikolaevich Zinin (1812-1880).*

Although he initially planned to attend the St. Petersburg School of Engineering and Communication, the sudden death of his uncle left him without the necessary funds. Instead, he entered Kazan University in 1830 (29, 50-52), which was much less expensive than an institution in the northern capital. Zinin began his work at Kazan in the mathematical division under Lobachevskii, ultimately taking his *kandidat* degree in physics and mathematics in 1833 (29, 50-53), with a dissertation on the perturbation of the elliptical motions of planets (51-53). He was then appointed assistant in physics, before being made lecturer in analytical mechanics six months later. Teaching duties in hydrostatics and hydrodynamics were then added the following year (29, 50, 53).

About this time, however, the administration of the university had decided that the current professor of chemistry, Ivan Ivanovich Dunaev, needed to be replaced (51-54). Zinin had previously taken some courses in chemistry under Dunaev (51), and the administration determined that Zinin should be Dunaev's replacement (51-54). Thus, Zinin was relieved of his other teaching duties in 1835 and was ordered to teach only chemistry (50, 51).

Meanwhile Zinin was also preparing for his examinations for the *magistr* degree (i.e., master's degree), which he passed in April 1835 (51). For his subsequent *magistr* dissertation, the faculty then gave Zinin the topic "The Phenomena of Chemical Affinity and the Superiority of Berzelius's Theory about Constant Chemical Proportions over the Chemical Statics of Berthollet" (51, 53). His resulting dissertation, which he successfully defended in October 1836, was theoretical in nature and involved no laboratory work (51-53, 55). Zinin thus received the degree *magistr* of physical-mathematical sciences and was then quickly appointed as adjunct in 1837 (50-53).

Permission was then requested from the Ministry of Education in early 1837 to send Zinin abroad for two years for advanced training in chemistry (50, 51, 53). The request was granted and Zinin was sent to Europe in September 1837 (29, 51, 52). For the next three years, he visited chemical laboratories in Germany, Switzerland, France, and England, and also devoted attention to the current developments in medicine. In the process, he spent considerable time in Liebig's laboratory in Giessen (29, 50-55). Zinin's experience in Liebig's laboratory profoundly affected him and it was here that he began his career in chemical research (52), studying the reactions of benzoyl compounds (29, 55).

Zinin returned to Russia in late 1840, arriving in St. Petersburg in September (29, 50, 51, 53). There he sat for examinations for the doctoral degree at St. Petersburg University. By early November, Zinin had successfully completed the examinations and then quickly began to write his dissertation (51-53). He defended a dissertation based on the work he had carried out in Liebig's laboratory at the end of January 1841 (29, 50, 51, 53), for which he received his doctorate from St. Petersburg. Zinin then returned to Kazan where he was appointed to the chair of chemical technology (29, 49-55).

Zinin only remained at Kazan until 1847, when he was offered the chair in chemistry at the Medical-Surgical Academy in St. Petersburg (29, 50-55). He thus moved to St. Petersburg in 1848, during which time Zinin carried out his research in his private laboratory at home (29, 50), a room described as overflowing with apparatus, books, chemicals and equipment (29). He continued to work in his private laboratory until the Academy of Sciences built a new chemical laboratory in 1867 (50) and he was appointed to be Director of the Chemical Laboratory (29, 52).

Zinin played an active role in the formation of the Russian Physico-Chemical Society in 1868, and served as its President for the first ten years (52, 54). He retired from the Medical-Surgical Academy in 1874 and devoted himself to work in the St. Petersburg Academy of Sciences (29), of which he had been elected adjunct in chemistry in 1855 (50, 53). He was then elected extraordinary member in 1858 (50, 53) and academician in 1865 (50, 52, 53). Zinin continued active chemical work until the autumn of 1878, at which time he became ill (29, 50). He continued to hope that he would be able to return to his studies, but he gradually grew worse, and ultimately died on February 6, 1880 (29, 50).

Reduction of Nitrobenzene

Upon his return to Kazan in 1841, Zinin was faced with developing new research projects. The previous work he had carried out in Liebig's laboratory had utilized oil of bitter almonds (primarily benzaldehyde) as a key reagent, a material whose import into Russia was prohibited due to its toxicity (51, 52, 56). As a result, he instead began investigations of other related organic compounds, beginning with the action of hydrogen sulfide on nitroaromatics such as nitrobenzene and nitronaphthalene.

First reported in the spring of 1842 (57a), Zinin found that the addition of hydrogen sulfide (H_2S) to nitrobenzene in ammonia-saturated ethanol resulted in the formation of a mixture of elemental sulfur and yellow needles (57). After cooling at 0 °C, this mixture "almost completely solidified to a mass of fine, yellow needles." Letting this stand for a day, he then boiled the initial mixture and decanted the resulting solution from any solid sulfur. This isolated liquid fraction was then distilled to give an oil described as heavier than water and yellowish in color (57). Our modern understanding of this chemical process is outlined in Figure 7.

Zinin characterized the oil as an oxygen-free base that was insoluble in water, but miscible in either alcohol or ether, and distilled with a boiling point of ca. 200 °C (37). Combustion analysis led to the formula $C_{12}H_{14}N_2$, a doubling of the modern C_6H_7N (38), and he was also able to successfully form and characterize several salts of the base (sulphate, HCl, and mercuric chloride) (57). He ultimately named the oil *Benzidam,* based on its determined composition (57).

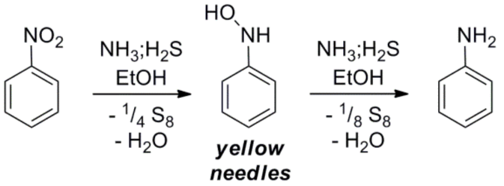


Figure 7. *Modern representation of Zinin's reduction of nitrobenzene.*

After reading Zinin's initial paper for the St. Petersburg Academy of Science (57a), Fritzsche added a short note on Zinin's paper when it was then published in the *Journal für praktische Chemie* (57b). In its entirety, Fritzsche's note stated (58):

> To the most interesting treatise of Mr. Zinin, I must add the remark that the base designated as new under the name of *Benzidam* is nothing but *Anilin*. In its properties, as well as in its composition and the composition of the salts, Benzidam agrees so perfectly with Aniline that there can be no doubt about its identity.

Of course, one can imagine that Fritzsche's own rebukes from Erdmann (45) and Liebig (46) might have been on his mind as he composed this statement. However, it is also interesting to note that Fritzsche speaks only of his own *Anilin* here and includes no mention of Unverdorben's *Crystallin* (42) or Runge's *Kyanol* (44). Nevertheless, all of these comparisons were confirmed the following year when Hoffmann presented strong evidence that Crystallin, Kyanol, Anilin, and Benzidam were indeed all the same compound (39). It should also be pointed out that while Fritzsche and Zinin ultimately shared space in the Academy of Sciences laboratory (22-25), in 1842 they were still separated by over 700 miles (Zinin in Kazan; Fritzsche in St. Petersburg) and Fritzsche's note may have been their first professional interaction.

Zinin's Oxidation of Aniline

Although Zinin did not specifically investigate the oxidation of aniline in the same way that Fritzsche did, he does make reference to reactivity in his papers which likely refer to oxidation processes. The first such statement occurs when he provides the basic properties of his isolated Benzidam, in particular its air stability. Thus, he states (57) that it is

> preserved after some time in contact with atmospheric air, but instantly turns red with strong nitric acid.

This is in contrast with the previous report of Fritzsche that nitric acid caused the conversion of aniline to a blue or green material (36).

The second statement comes when discussing the stability of the isolated aniline salts. In this case, he notes that the sulfate salt is not all that air stable, stating: "[The crystals] turn rose red in air, especially when wet" (57).

It should be pointed out that this is in stark contrast to the analogous HCl salt, which does not show this reactivity.

Thus, Zinin reports the formation of red products under two separate cases when aniline is under the influence of both air (i.e., oxygen) and an oxidizing acid. However, the identities of these red species are unknown and Zinin reported no attempts to analyze these products. What is clear is that these are not examples of polyaniline, as the macromolecule does not possess red forms under any known conditions (13).

A potential answer could come from later studies by first Heinrich Caro (1834-1910) in 1896 (59) and then Richard Willstätter (1872-1942) in the early 1900s (60). In efforts to determine the structure and identity of aniline black and other aniline oxidation products, they oxidized aniline under non-optimal conditions and then tried to identify products as potential intermediates in the production of aniline black. In the process, Caro successfully identified the yellow oxidized dimer phenylquinonediimide (Figure 8) (59), while Willstätter later isolated a blue compound which he concluded to be the half-oxidized tetramer (60). This tetramer could then be further oxidized to a red form (Figure 8).

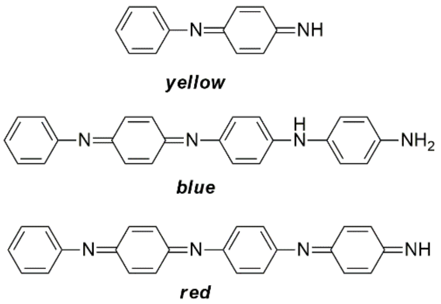


Figure 8. *Oligoanilines known between 1896-1907.*

The conditions under which Zinin observed his red species could be viewed as consistent with low levels of oxidant that could result in oligomeric, rather than polymeric, products. For this reason, Zinin's red product could well be the same as Willstätter's. Of course, this is only a proposed identity and it is not feasible to confirm this possibility with any certainty.

Impact of Fritzsche and Zinin on Later Polyaniline Work

At the most basic level, both Fritzsche and Zinin contributed to monomeric aniline, an obvious critical factor in the production of its macromolecule. Of the two methods for the production of aniline, Zinin's had by far the greatest impact, as this represented the first viable method for the mass production of aniline. As pointed out by others (40, 51, 53), Zinin's synthesis of aniline later became the key step in the synthesis of many coal tar dyes. This is true of polyaniline as well, which coincidentally represents the very first synthetic aniline dyes, as demonstrated by Runge in 1834 (9). Both Runge and Fritzsche made specific comments that their efforts were limited by the small quantities of the materials generated, with Runge specifically referring to the fact that significant amounts of aniline salts would be needed to make his dyes viable (9).

Interestingly, after Hoffmann had confirmed that Crystallin, Kyanol, Anilin, and Benzidam were all the same compound, he felt that only the original name Crystallin might be retained, although he favored the name *Phenamid* (39). Still, by 1845 Zinin was also using Fritzsche's name Anilin (61) and ultimately it was the name that endured as the modern aniline, the preferred IUPAC name for this aromatic amine. Thus, both men left lasting marks on the chemistry of aniline.

In terms of the aniline oxidation products, although Runge was the first to report materials now recognized as polyaniline (9), Fritzsche was still only the second to do so (36, 47). Furthermore, he was the first to produce these materials via potassium chlorate (47), which later became the basis for the production of the first commercial polyaniline dyes in the early 1860s (7). In addition, Fritzsche was the first ever to determine the chemical composition of a polyaniline sample (47) and did so with an empirical formula nearly identical to that expected by our modern knowledge of these materials (5, 7). As such, this was the first step in the ultimate determination of the structure and identity of these materials, even if it did take another 60 years for such determinations to really begin to take shape (4-8).

Acknowledgements

I would like to thank David Lewis for inviting me to participate in his HIST Award Symposium at the 256th ACS Meeting in Boston, thus leading to the current manuscript. In addition, thanks to Alan J. Rocke (Case Western Reserve University) and Ian Rae (University of Melbourne) for helpful feedback during the oral presentation of this work. Lastly, I would like to thank the Department of Chemistry and Biochemistry of North Dakota State University (NDSU) for continued support of my historical research, and the NDSU Interlibrary Loan Department, that always helps to track down various elusive and somewhat obscure sources.

References and Notes

1. Presented at the 256th National Meeting of the American Chemical Society, Boston, MA, Aug. 21, 2018, HIST 23 in the HIST Award Symposium Honoring David Lewis.
2. T. A. Skotheim and J. R. Reynolds, Eds., *Handbook of Conducting Polymers*, 3rd ed., CRC Press, Boca Raton, FL, 2007.
3. I. F. Perepichka and D. F. Perepichka, Eds., *Handbook of Thiophene-based Materials*, John Wiley & Sons, Hoboken, NJ, 2009.
4. S. C. Rasmussen, "Early History of Conductive Organic Polymers," in Z. Zhang, M. Rouabhia and S. Moulton, Eds., *Conductive Polymers: Electrical Interactions in Cell Biology and Medicine*, CRC Press, Boca Raton, FL, 2016, Ch. 1, pp 1-21.
5. S. C. Rasmussen, "Early history of Conjugated Polymers: From their Origins to the Handbook of Conducting Polymers," in J. R. Reynolds, B. Thompson and T. Skotheim, Eds., *Handbook of Conducting Polymers*, 4th Ed., CRC Press, Boca Raton, FL, 2019, Ch. 1.
6. S. C. Rasmussen, "Electrically Conducting Plastics: Revising the History of Conjugated Organic Polymers," in E. T. Strom and S. C. Rasmussen, Eds., *100+ Years of Plastics. Leo Baekeland and Beyond*, ACS Symposium Series 1080, American Chemical Society, Washington, DC, 2011, pp 147-163.
7. S. C. Rasmussen, "The Early History of Polyaniline: Discovery and Origins," *Substantia*, **2017**, *1*(2), 99-109.
8. S. C. Rasmussen, "Revisiting the Early History of Synthetic Polymers: Critiques and New Insights," *Ambix*, **2018**, *65*, 356-372.
9. F. F. Runge, "Ueber einige Produkte der Steinkohlendestillation," *Ann. Phys. Chem.*, **1834**, *31*, 513-524.
10. E. Simon, "Ueber den flüssigen Storax (Styrax liquidas)," *Ann. Pharm.*, **1839**, *31*, 265-277.
11. D. Feldman, "Polymer History," *Designed Monomers Polym.*, **2008**, *11*, 1-15.
12. Y. Furukawa, *Inventing Polymer Science: Staudinger, Carothers, and the Emergence of Macromolecular Chemistry*, University of Pennsylvania Press, Philadelphia, 1998, pp 48-92.
13. E. M. Geniès, A. Boyle, M. Lapkowski and C. Tsintavis, "Polyaniline: A Historical Survey," *Synth. Met.*, **1990**, *36*,139-182.
14. C. L. Heth, D. E. Tallman and S. C. Rasmussen, "Electrochemical Study of 3-(*N*-alkylamino)thiophenes: Experimental and Theoretical Insights into a Unique Mechanism of Oxidative Polymerization," *J. Phys. Chem. B*, **2010**, *114*, 5275-5282.
15. D. Wei, C. Kyarnstrom, T. Lindfors, L. Kronberg, R. Sjoholm and A. Ivaska, "Electropolymerization Mechanism of *N*-methylaniline," *Synth. Met.*, **2006**, *156*, 541-548.
16. R. L. Hand and R. F. Nelson, "Anodic Oxidation Pathways of *N*-alkylanilines," *J. Am. Chem. Soc.*, **1974**, *96*, 850-860.
17. J. Bacon and R. N. Adams, "Anodic Oxidations of Aromatic Amines. III. Substituted Anilines in Aqueous Media," *J. Am. Chem. Soc.*, **1968**, *90*, 6596-6599.
18. G. D'Aprano, E. Proynov, M. Leboeuf, M. Leclerc and D. R. Salahub, "Spin Densities and Polymerizabilities of Aniline Derivatives Deduced from Density Functional Calculations," *J. Am. Chem. Soc.*, **1996**, *118*, 9736-9742.
19. The distinction between the two primary polymerization mechanisms, step-growth and chain-growth polymerization, was introduced by Paul J. Flory (1910-1985) in 1953: P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, p 38.
20. October 17, 1808, by the Julian Calendar.
21. J. C. Poggendorff, *Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften*, Vol. 1. J. A. Barth, Leipzig, 1863, pp 808-809.

22. A. Butlerow, "Carl Julius Fritzsche," *Ber. Dtsch. Chem. Ges.*, **1872**, *5*, 132-136.
23. A. V. Harcourt, "Anniversary Meeting, March 30th, 1872," *J. Chem. Soc.*, **1872**, *25*, 341-364.
24. F. E. Sheibley, "Carl Julius Fritzsche and the Discovery of Anthranilic Acid, 1841," *J. Chem. Educ.,* **1943**, *20*, 115-117.
25. D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer Briefs in Molecular Science: History of Chemistry, Springer, Heidelberg, 2012, p 45.
26. B. W. Feddersen and A. J. von Oettingen, Eds, *J. C. Poggendorff's Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften*, Vol. 3, J. A. Barth, Leipzig, 1898, p 481.
27. Although some publications give the alternate spelling of Fritsche.
28. Fritzsche's uncle Friedrich A. A. Struve, a doctor of medicine and pharmacist from Neustadt, was a pioneer in the commercialization of artificial mineral water. Together with Rudolf Bloch, he established the first institution for artificial mineral water curatives in Dresden in 1818, with additional institutions later added in Leipzig, Berlin, Brighton (England), Königsberg, Warsaw, Moscow, St. Petersburg, and Kiev. All of these later institutes were overseen by students of Struve. See (a) *Allgemeine Deutsche Biographie*, Vol. 36, Duncker & Humblot, Leipzig, 1893, pp 676–677; (b) W. Kirkby, *The Evolution of Artificial Mineral Waters*, Jewsbury & Brown, Manchester, UK, 1902, pp 33, 92-93.
29. H. M. Leicester, "N. N. Zinin, an Early Russian Chemist," *J. Chem. Educ.*, **1940**, *17*, 303-306.
30. June 8, 1871, by the Julian Calendar.
31. M. V. Orna, "Historic Mineral Pigments: Colorful Benchmarks of Ancient Civilizations," in Seth C. Rasmussen, Ed., *Chemical Technology in Antiquity*, ACS Symposium Series 1211, American Chemical Society, Washington, DC, 2015, Ch. 2, pp 17-69.
32. P. E. McGovern and R. H. Michel, "Royal Purple Dye: The Chemical Reconstruction of the Ancient Mediterranean Industry," *Acc. Chem. Res.*, **1990**, *23*, 152-158.
33. Z. C. Koren, "Modern Chemistry of the Ancient Chemical Processing of Organic Dyes and Pigments," in *Chemical Technology in Antiquity*, Seth C. Rasmussen, Ed., *Chemical Technology in Antiquity*, ACS Symposium Series 1211, American Chemical Society, Washington, DC, 2015, Ch. 7, pp 197-217.
34. A. Baeyer, "Ueber die Verbindungen der Indigogruppe," *Ber. Dtsch. Chem. Ges.*, **1883**, *16*, 2188-2204.
35. J. Fritzsche, "Vorläufige Notiz über ein neues Zersetzungsproduct des Indigo durch Salpetersäure," (a) *Bull. Sci. Acad. Imp. Sci. St. Petersb.*, **1839**, *5*, 159-160; (b) *J. Prakt. Chem.*, **1839**, *16*, 507-508.
36. J. Fritzsche, (a) "Ueber das Anilin, ein neues Zersetzungsproduct des Indigo," *Bull. Sci. Acad. Imp. Sci. St. Petersb.*, **1840**, *7*, 161-165; (b) "Ueber das Anilin, ein neues Zersetzungsprodukt des Indigo," *J. Prakt. Chem.*, **1840**, *20*, 453-457; (c) "Ueber das Anilin, ein neues Zersetzungsprodukt des Indigo," *Ann. Chem. Pharm.,* **1840**, *36*, 84-88.
37. As determined by modern means, the density of aniline is 1.0297 g/mL, with a boiling point of 184.13 °C.
38. Such doubling of formulas was typical of the time period, usually the result of utilizing an atomic weight of 6 for carbon.
39. A. W. Hofmann, "Chemische Untersuchung der organischen Basen im Steinkohlen-Theeröl," *Ann. Chem. Pharm.*, **1843**, *47*, 37-87.
40. H. Dussauce, "Aniline—Its History, Properties, and Preparation," *Sci. Am.*, **1867**, *17*, 321-322.
41. C. M. Jackson, "Synthetical Experiments and Alkaloid Analogues: Liebig, Hofmann, and the Origins of Organic Synthesis," *Hist. Stud. Nat. Sci.,* **2014**, *44*, 319-363.
42. O. Unverdorben, "Ueber das Verhalten der organischen Körper in höheren Temperaturen," *Ann. Phys. Chem.*, **1826**, *8*, 397-410.
43. Although most authors give the name as *Krystallin*, Unverdorben clearly spelled it *Crystallin* in his original 1826 paper. The use of the more common alternate spelling dates as far back as the 1840 postscript by Erdmann (see Ref. 45).
44. F. F. Runge, "Ueber einige Produkte der Steinkohlendestillation," *Ann. Phys. Chem.*, **1834**, *31*, 65-78.
45. [O.] Erdmann, "Nachschrift," *J. Prakt. Chem.*, **1840**, *20*, 457-459.
46. J. Liebig, "Bemerkung zu vorstehender Notiz," *Ann. Chem. Pharm.*, **1840**, *36*, 88-90.
47. J. Fritzsche, "Vorläufige Notiz über einige neue Körper aus der lndigoreihe," (a) *Bull. Classe phys.-math. Acad. Sci. St.-Pétersbourg*, **1843**, *1*, 103-108; (b) *J. Prakt. Chem.* **1843**, *28*, 198-204.
48. August 13, 1812, by the Julian Calendar.
49. J. C. Poggendorff, *Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften*, Vol. 2, J. A. Barth, Leipzig, 1863, p 1415.
50. A. M. Butlerow and A. P. Borodin, "Nikolaus Nikolajewitsch Zinin," *Ber. Dtsch. Chem. Ges.*, **1881**, *14*, 2887-2908.
51. N. M. Brooks, "Nikolai Zinin and Synthetic Dyes: The Road not Taken," *Bull. Hist. Chem.*, **2002**, *27*, 26-36.
52. Ref. 25, pp 42-44.
53. N. M. Brooks, "Nikolai Zinin At Kazan University," *Ambix*, **1995**, *42*, 129-142.

54. S. N. Vinogradov, “Chemistry at Kazan University in the Nineteenth Century: A Case History of Intellectual Lineage,” *Isis*, **1965**, *56*, 168-173.
55. 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.
56. The toxicity of oil of bitter almonds is due to a small amount of cyanide content (ca. 0.5% by weight).
57. (a) N. Sinin, “Beschreibung einiger neuer organischer Basen, dargestellt durch die Einwirkung des Schwefelwasserstoffs auf Verbindungen der Kohlenwasserstoffe mit Untersalpetersäure,” *Bull. Sci. Acad. Imp. Sci. St. Petersb.*, **1842**, *10*, 273-285; (b) N. Zinin, “Beschreibung einiger neuer organischer Basen, dargestellt durch die Einwirkung des Schwefelwasserstoffs auf Verbindungen der Kohlenwasserstoffe mit Untersalpetersäure,” *J. Prakt. Chem.*, **1842**, *27*, 140-153; (c) N. Zinin, “Organische Salzbasen, aus Nitronaphtalose und Nitrobenzid mittelst Schwefelwasserstoff entstehend,” *Ann. Chem. Pharm.*, **1842**, *44*, 283-287.
58. J. Fritzsche, “Bemerkung zu vorstehender Abhandlung des Hrn. Zinin,” *J. Prakt. Chem.*, **1842**, *27*, 153.
59. H. Caro, “Zur Kenntniss der Oxydation des Anilins,” *Verh. Ges. Dtsch. Naturforsch. Ärzte*, **1896**, *68*(part II, 1st half), 119-120.
60. R. Willstätter, and C. W. Moore, “Über Anilinschwarz. I.,” *Ber. Dtsch. Chem. Ges.*, **1907**, *40*, 2665-2689.
61. N. Zinin, “Ueber das Azobenzid und die Nitrobenzinsäure,” *J. Prakt. Chem.*, **1845**, *36*, 93-107.

About the Author

Seth C. Rasmussen is Professor of Chemistry at North Dakota State University (NDSU) in Fargo. He received his B.S in chemistry from Washington State University in 1990, before continuing his graduate studies at Clemson University under Prof. John D. Petersen. After completing his Ph.D. in 1994, he moved to the University of Oregon to study conjugated organic polymers as a postdoctoral associate under Prof. James E. Hutchison. He then accepted a teaching position at the University of Oregon in 1997, before moving to join the faculty at NDSU in 1999. Attaining the rank of full professor in 2012, Prof. Rasmussen also spent the spring of 2018 as a Fulbright Senior Scholar and visiting professor at the Centre for Organic Electronics of the University of Newcastle, Australia. Active in the fields of materials chemistry and the history of chemistry, his research interests include the design and synthesis of conjugated materials, photovoltaics (solar cells), organic light emitting diodes, the history of materials, chemical technology in antiquity, and the application of history to chemical education. Prof. Rasmussen served as the Program Chair for the History of Chemistry (HIST) division of the American Chemical Society from 2008 to 2017 and currently serves as the HIST Chair-Elect. In addition, he serves as the series editor for the book series *Springer Briefs in Molecular Science: History of Chemistry* and *Perspectives on the History of Chemistry*, as an editor of the journal *Cogent Chemistry*, and on the advisory board for the journal *Substantia: An International Journal of the History of Chemistry*.

Erratum

In the article “On the Origins of a Tool for Chemists, The Dean-Stark Apparatus,” (this Journal, **2013**, *38(1)*, 67-72), one of the inventors of the apparatus was named incorrectly. The Dean of the apparatus was Ernest Woodward Dean (1888-1959), not Edward Woodward Dean as printed in the article.

CHEMIST AT WAR: WORLD WAR II ROLES OF JONAS KAMLET, CONSULTING CHEMIST

Dean F. Martin and Marwa Elkharsity, Institute for Environmental Studies, Department of Chemistry, University of South Florida Tampa, FL, USA; dfmartin@usf.edu

Introduction

The role of chemists in our daily lives probably deserves a greater consideration and reflection than it commonly receives. Typically we recognize that chemists are involved in industry, academe, and government service. But it seems appropriate to reflect on the activities of chemists during times of political crises, such as wartime. Here we consider the World War II roles of Jonas Kamlet with the aid of the extensive information available in his personal and professional papers.

Previous publications (1, 2) described the creation and development of the Kamlet Laboratories, a small but singularly active consulting firm. It was founded by Jonas Kamlet (1914-1960) and his wife Edna (1915-2011). The University of South Florida was able to obtain the entire collection of the files of the Kamlet Laboratory (3), owing to the generosity of the late Edna Yadven Kamlet Rogers, who provided funds for transport of the files to USF and a sum to support the archiving of the papers in the USF Tampa campus library (1).

When the United States entered World War II late in 1941, Kamlet Laboratories in New York City was in the first year of development. The first couple of years were run at a net deficit (2), so it was fortunate that Jonas Kamlet had been granted a deferment.

The advent of World War II brought major changes into the lives of so many in the United States, including professional chemists. They responded in a variety of ways. Many chemists were associated with the now-famous Manhattan Project that led to the development of the atomic bomb (4).

At the Pennsylvania State College, for example, Dr. Frank Whitmore, college dean and an organic chemist, managed to obtain deferments for chemistry graduate students. His view was stated firmly in a letter to the college president, Ralph D. Hetzel (5):

> Personally, I shall fight to the last ditch to keep every chemist, chemical engineer, and physicist either actual or in training, where he can do the most good for the national effort. He must be used in technical work and nowhere else.

By the end of World War II, Dr. Whitmore, as chairman of The United States War Manpower Commission on Chemists and Chemical Engineers, had written more than 7,000 letters to draft boards requesting draft deferments for technical workers (5).

Though Kamlet was evidently an able-bodied person, married, but with no children, he was not drafted by the Selective Service Local Board 15 in New York City. He provided good reasons, that all of his work pertained directly to the war effort or to the maintenance of public health (6). He was on the National Roster of Scientific Personnel from its very inception. He wrote “I am also the head of the New York chemical research laboratory of the Miles Laboratories,” and he added (6)

> I am under contract to the Miles Laboratories, Inc., in whose behalf we have developed and are in the process of developing, a number of processes and products directly pertaining to public health, and in some instances, to the War Effort. Among these are the following: aids in medical diagnosis, synthesis of vitamins, derivation of vitamin-rich food concentrates by the microbiological utilization of industrial wastes, syntheses of anti-malarials, manufacture of tablets for the sterilization of contaminated water, manufacture and assembly of the ingredients of Army ration kits.

Aids in Medical Diagnosis

As noted previously (1, 7, 8), there was a major need for an analysis of glucose for monitoring its concentration in patients afflicted with diabetes then and now. Kamlet devised a method (8), but he needed a means of stirring the reactants placed in the blood or serum sample. A collaboration with a Miles Laboratories expert on effervescence, Maurice Treneer (9), led to a product called Clinitest, a pill which both delivered reagents and stirred them into the sample. Clinitest could be used to measure glucose colorimetrically. Moreover the task could be done in a doctor's office, and the results obtained in a short time (7, 9). The product was considered valuable for over forty years, before the development of the Clinistix system by Alfred and Helen Free at Miles (7, 9).

A second important diagnostic aid was the invention of a tablet that added to urine would detect acetone or acetoacetic acid. A color produced could be used to detect the constituents qualitatively and, using Beer's Law, quantitatively. The kit had a high degree of accuracy and could be used in a physician's office without specialized training or laboratory equipment (8). It could also have been used to screen *draftees* who may have been borderline diabetics. We found no proof that draftees were screened by a Kamlet method, but there was no superior method available. Unfortunately for the potential financial benefit of Miles and Kamlet Laboratories, Acetone Clinitest was not developed by Miles Laboratories, and a related product was successfully developed by Denver firm unknown to us (10).

Synthesis of Vitamins

Miles Laboratories' history includes a notable tendency to identify an human need, then to work to meet that need. In the early 1940s, it was malnutrition related to vitamin deficiencies. Accordingly, Miles personnel created vitamin supplements, and Walter Compton, M.D., actively encouraged this activity (9). Kamlet, possibly owing to his close association with Miles Laboratories, was interested in the synthesis of vitamins, and three examples of his interest and efforts are provided here.

One is his development of a synthesis for riboflavin, a substance that had been identified as identical with Vitamin B2. The synthesis eliminated steps from the contemporary synthesis, and it did not require the use of the pentose sugar D-ribose, which was not only difficult to obtain but also expensive (11).

Second, Kamlet mentioned the considerable amount of work (12) that had been done with the incorporation of Vitamin D and its precursors in soap for the purpose of compensating for the loss of irradiated ergosterol from the skin on washing. Ergosterol, (a precursor to Vitamin D), if absorbed in the diet can be transmitted to the skin where it is irradiated by ultraviolet light of the sun and is reabsorbed by the body as an anti-rachitic vitamin. Unfortunately, washing the skin results in a relatively great loss of ergosterol. But Kamlet devised a sound basis for incorporating Vitamin D into soap. This seemed useful because since the start of World War II, the Jergens-Woodbury Soap Company stopped producing soap containing Vitamin D because of the difficulty in obtaining ample supplies of this vitamin. However, Kamlet felt that the so-called yeast fat fraction (a source of the yeast *Torula utilis*) was ideally suited for vitaminized soap. He was looking forward to finding a ready market for some or all of the yeast fat fraction, even without recovery of ergosterol (12).

Third, Kamlet was interested in producing vitamin-rich food concentrates by microbiological utilization of paper mill wastes. It was later reported that in 1942 Kamlet helped develop a process for recovering from such wastes what had been a costly substance used to produce vitamin B2 riboflavin (13).

This interest became a joint project between Miles Laboratories (of Elkhart, Indiana) and International Paper Company. Kamlet was concerned (12, 13) with a patent application on deriving value from sulfite waste liquor. Sulfite solutions are used to remove lignin from wood pulp, leaving behind separated cellulose and a problem of disposing of the remaining sulfite liquor, which smells and would remove oxygen if disposed of in an aqueous environment. But sulfite liquor also contains wood sugars. Kamlet believed that the yeast *Torula utilis* could be brought up to the potency needed for use as a base of multi-vitamin tablets. His modification was to add crude riboflavin (Vitamin B2) to the fermenting medium because unlike most yeasts, *Torula* was able to assimilate riboflavin from a riboflavin-enhanced medium, perhaps as much as 120 µg of riboflavin per gram of dry yeast. He also noted a precedent, namely that Anheuser-Busch personnel obtained *Torula* concentrates amounting to 7000 µg/gram of yeast. He was confident of his ability to do equally well (12).

He reported two fermentations with the addition of 50 g of synthetic riboflavin per liter of sulfite liquor. The vitamin concentrate was derived as usual (12). The resulting concentrate gave a very strong qualitative color reaction for riboflavin and seemed to be much richer in this vitamin than concentrates derived from unfortified sulfite liquor. He forwarded about ten grams of the resulting vitamin concentrate to Miles Laboratories and requested analysis for riboflavin and thiamin, which their personnel were well equipped to do (9, 13).

Tablets for the Sterilization of Contaminated Water

Kamlet thought Halazone tablets for water sterilization would satisfy a need of the U.S. Army. He had "previously done quite a bit of work on these tablets" and the files were said to be among the files of a Miles secretary (9). In addition to Halazone (*p*-dichlorosulfonamidobenzoic acid), the tablets contained sodium bicarbonate, sodium chloride and sodium acid phosphate. The staff at Miles Laboratories had given insignificant attention to the possibilities of Halazone, a compound already known to have disinfectant properties, until the advent of the K-Ration and related projects (13). (K-Rations were individual nutritional packages issued to some mobile combatants, and some rations included Halazone tablets.) Kamlet noted that there were numerous samples of Halazone tablets in the closet of Dr. Conklin's office. He knew of the tablets because he would frequently would provide samples of compounds of interest, either as powders or as tablets.

The information concerning the location in an office closet may seem odd at first glance, and some background information is helpful. First of all, Kamlet had been retained by Miles Laboratories (9), so he would have visited several times, and he knew the organization of the facilities. Secondly, owing to manpower shortages during World War II, laboratory management went to assist in the war effort. Conklin, a popular local physician, had been asked to assume part-time administrative responsibilities at Miles Laboratories (9), so he may not have been familiar with everything in his Miles office.

Kamlet concluded his letter by noting that two firms were making Halazone tablets: Abbott laboratories and a smaller, unnamed firm (13). A Dr. Milligan evidently had some misgivings about the soundness of the physiological principles involved, so Kamlet reviewed a patent (2,322,689) to provide background about current practice by the U.S. Navy (14).

Potable water is the goal of treating water. One requirement of such water is that it be hypotonic, diffusible into body tissues rather than drawing water from them. Kamlet reviewed the properties of a 1 *M* solution of sodium citrate (based on an Indian publication that he had ordered), which would give a calculated 1.21 moles of ions. Then he showed the results of calculations that seawater treated with sodium citrate could be made isotonic, but the potable water should be "slightly acid (pH 5.8)" to avoid a flat taste.

An employee of the Sunshine Mining Company, (Alexander Goetz) invented a process for producing potable water from non-potable saline water (15). He considered the taste aspect: A slight acidity would enhance the taste and would counteract a tendency toward alkalosis when much of the composition was ingested.

Kamlet proposed adding a small amount of solid organic acid (e.g., citric) by using the amount of silver citrate that would give a liter of potable water (14). Citric acid alone tended to react with the other component (bicarbonate) on prolonged standing and the tablets would crumble. Also, he noted concentration of citrate ion would be exceedingly low, considering that the values of successive citric acid dissociation constants K_1:K_2:K_3 would have ratios of $1:10^{-5}:10^{-10}$. Use of silver citrate effectively enhanced the concentration of citrate ion, but the treated water needed to be filtered to remove the silver chloride. The Goetz procedure was what the U.S. Navy currently used, but Kamlet noted that it did not diminish sodium ion concentrations. And Kamlet wanted to pursue the matter further (14).

Manufacture and Assembly of the Ingredients of Army Ration Kits

In April 1943, Kamlet brought to the attention of Miles management some opportunities he identified as a result of the discontinuation of K Rations (16, 17). The War Production Board (WPB) had announced that as of the end of March [1943], the manufacture of Ration K was to be discontinued. This would free up some Miles personnel and tablet machines for other work. The U.S.

armed forces would need a different supply of flavorants. If vanilla flavoring were produced in tablet form, it would reduce shipping weight and space by 90% compared to extract solutions. In addition, there would be a gain of accuracy in the concentration of the active component, an accuracy not easily attained by measuring a volume. Lack of such accuracy was a problem of contemporary medicine.

He further noted that such a product was already produced by a company in New York City. The product consisted of vanillin, coumarin, and an effervescent base with one five-grain pill equivalent to an "old fashioned teaspoon measure." As noted elsewhere, Miles, manufacturer of Alka-Seltzer, a well-known remedy for upset stomach (and hangover), had considerable experience with effervescent materials (9).

Kamlet wrote on April 1, 1943 (16):

> The Van Amerigen-Haebler Company, 315 Fourth avenue [NYC] have developed such a tablet and are selling it to the Army … We could make such a tablet with no difficulty at all. I am getting samples of this tablet from Van Amerigen and Haebler and will forward them to you as soon as they arrive.

On April 23, 1943, he had obtained the samples and had prepared his own tablets with formulation that differed in a significant respect: it was measured by weight, rather by volume. It, too, contained an effervescent component, a feature Miles Laboratories would have been very comfortable with (9). He was sending pills that he had prepared from the samples, and his letter concluded with the observation that there was a large market that could be met by using the equipment at Miles (17).

He also noted that a great savings could be passed on to the consumer and that the patriotic aspect involved in saving large amounts of glycerine and alcohol would appeal to the civilian market (17).

Syntheses of Sulfonamides

The discovery of sulfonamides in the early 1930s introduced the first and only effective antibiotic prior to penicillin (18). One compound became highly popular, and the unwise application led to the "sulfa craze" at a time when no testing was required. "Elixir Sulfanilamide" caused deaths of over 100 persons because the material was provided as a solution of ethylene glycol (a toxic liquid used as anti-freeze in car radiators), rather than ethanol, and no toxicity tests were made. The disaster resulted in the passage of the U.S. Federal Food, Drug, and Cosmetic Act in 1938 (19).

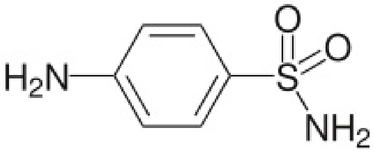


Figure 1. *Structure of sulfanilamide*

Jonas Kamlet was 24 years old when he was awarded his first patent (20) that described a novel synthesis of sulfanilamide (Figure 1). This was surely a miracle drug for its time including some remarkable cures obtained with its use in the treatment of gonorrhea. He reported obtaining the desired product "in an exceptionally pure state and in quantitative yield by submitting benzamide-*p*-sulphonamide to a Hoffman reaction" (20). Sulfanilamide was widely used in field first aid kits during the war, so Kamlet had done work potentially useful in World War II even before its outset. (There is no evidence, though, that his patent was used to produce wartime sulfanilamide.)

And Afterwards—Post August 1945

Jonas Kamlet expanded his consultancies (1), and managed to cover most of the United States and to become involved with a number of foreign countries. Unfortunately he died in the prime of his life and career. He was returning from Chicago after a consulting trip as a passenger on a United DC-8 jet that collided with a Trans World Airlines piston-engine Super Constellation over Staten Island on Friday December 16, 1960 (21). All 128 passengers on the two airplanes and six persons on the ground were killed. His widow, Edna Yadven Kamlet, continued on activities of the firm for an additional twenty years before her retirement (1).

The contributions of chemists during World War II were major ones, but those of Jonas Kamlet during this time provide a useful example of the contribution an individual chemist can make even in stressful, demanding times.

Acknowledgments

We gratefully acknowledge the assistance of Special Collections personnel, including Mr. Andy Huse, Mr. Bob Cracolici, Ms. Melanie Griffin, Mr. Matt Knight, and Ms. Pat Tuttle. Mrs. Barbara Martin kindly read the copy at various stages. We thank two anonymous reviewers for their careful reading of the original manuscript and for their helpful suggestions.

References and Notes

1.. D. F. Martin and B. B. Martin, "Jonas Kamlet (1914-1960) Chemist/Entrepreneur," *Florida Scientist*, **2007**, *70*, 40-44.

2. D. F. Martin and K. Bidani, "Deficit and Surplus Data for the Kamlet Laboratories, 1941-1955," *Bull. Hist. Chem.*, **2012,** *37*, 96-101.

3. A. Huse, Guide to the Jonas and Edna Kamlet/Kamlet Laboratories Records, 1913-1989, Special Collections, Tampa Library, University of South Florida. http://digital.lib.usf.edu/content/SF/S0/03/18/67/00001/U29-00049-K27.pdf (accessed Nov. 7, 2019). The letters written by Dr. Kamlet and described in the present publication are available in the Kamlet papers, housed in the USF Special Collections of the USF Tampa Campus Library.

4. M. B. Stoff, J. F. Fanton, and R. H. Williams, Eds., *The Manhattan Project: A documentary Introduction to the Atomic Age*, Temple University Press, Philadelphia, 1991.

5. K. A. Yarmey, *Labors and Legacies: The Chemists of Penn State, 1855-1947,* The Pennsylvania State University, University Park. 2006, p 158, letter dated May 18, 1942. Whitmore wrote in the same letter:

> I maintain that any individual who willingly leaves chemistry, chemical engineering, or physics to enter the armed forces for non-technical work is merely a complicated kind of traitor even though he may be posing as a patriot.

6. Kamlet to Selective Service Local Board No 15, New York City, May 15, 1944.

7. D. F. Martin and B. A. Reiger, "Kamlet Laboratories and Clinitest: Idea to Product," *Technology and Innovation,* **2013**, *15*, 81-86.

8. J. Kamlet, "Diagnostic Composition and Method," US Patent 2,283,262, issued May 19, 1942; assigned to Miles Laboratories, Elkhart, Ind.

9. W. C. Cray, *Miles 1884-1984: A Centennial History,* Prentice Hall, Englewood Cliffs, NJ, 1984.

10. Kamlet to John Gawley, Miles Laboratory, Oct. 18, 1943. The letter was written in response to a query made by Gawley. The development of a similar product by a rival firm was one of over 23 instances when Kamlet had been "scooped," i.e., ideas that for one reason or another did not ripen to proper fruition. Kamlet noted at the end of his letter:

> The above information is for your own edification. It really should not concern us very much, since every Research organization has a whole morgue of ideas and even completed projects on which they were "scooped." It's all in the Game. It's the Future that concerns us, not the past. Some examples are listed in Table 1.

11. J. Kamlet, "Synthesis of Riboflavin and Intermediates Therefor," US Patent 2,406,774, issued Sept. 3, 1946; assigned to Miles Laboratories.

12. Kamlet to Raymond L. Conklin, Apr. 1, 1943, File XXII, Joint Project with Ontario Paper Co. Re: Utilization of Yeast Fat Fraction.

13. Kamlet to Conklin, Miles Laboratories, Mar. 17, 1944, File K-XIII, Joint Project with the International Paper Company. The procedure involved "dissolving torula in dil. NaOH, precipitating protein with HCl at pH 4.5, filtering off the protein, evaporating the filtrate under reduced pressure and drying overnight at 70°C."

14. J. Kamlet to Conklin and Morris P. Milligan, Miles Laboratories, July 12, 1943, File XLVII, Rendering Seawater Potable. Citric acid can exist as a monohydrate which is slightly deliquescent in moist air, and this property could make it difficult to get an exact amount of pure citric acid. Using crystalline silver citrate would obviate the hydrate, deliquescent problem.

15. A. Goetz, "Chemical Process for Production of Potable Water from Nonpotable Saline Water," US Patent 2,322,689, issued June 22, 1943; assigned to Sunshine Mining Company of Yakima, Washington.

16. Kamlet to Conklin, Miles Laboratories, Apr. 1, 1943, "Vanilla Flavoring Tablets."

17. Kamlet to Conklin, Miles Laboratories, Apr. 23, 1943, "Vanilla Flavoring Tablets."

18. K. Gould, "Antibiotics: from Prehistory to the Present Day," *J. Antimicrobial Chemotherapy*, **2016**, *71(3)*, 572–575.

19. C. Ballentine, "Sulfanilamide Disaster," *FDA Consumer Magazine*, June 1981, available at https://www.fda.gov/about-fda/histories-product-regulation/sulfanilamide-disaster (accessed Nov. 7, 2019). J. Epstein, "Drugs That Shaped the FDA: From Elixir Sulfanilamide to Thalidomide," *Bull. Hist. Chem.*, **2018**, *43(2)*, 102-110.

20. J. Kamlet, "Manufacture of Sulphanilamide," US Patent 2,111,913, issued Mar. 22, 1938.

21. "Biographical Sketches of Victims Aboard Two Airliners That Crashed Here," *New York Times*, Dec. 17, 1960, p 12.

About the Authors

Dean F. Martin, Distinguished University Professor Emeritus at the University of South Florida, continues to be an active researcher. Marwa Elkharsity was a preprofessional chemistry major at the University of South Florida and is currently a student at the Arthur A. Dugoni School of Dentistry at the University of the Pacific.

BOOK REVIEWS

The Posthumous Nobel Prize in Chemistry. Volume 2. Ladies in Waiting for the Nobel Prize, E. Thomas Strom and Vera V. Mainz, Eds., American Chemical Society, Washington, DC, ACS Symposium Series 1311, Distributed in Print by Oxford University Press, 2018, xiii + 328 pp, ISBN 9780841233911 (ebook ISBN 9780841233904) $150 (Print).

The concept for this book emerged prior to publication of the *Posthumous Nobel Prize in Chemistry. Volume 1*, based upon the ACS symposium in March 2016, when it was noted with justifiable chagrin that all thirteen scientists profiled in Volume 1 were males. A second symposium, "Ladies in Waiting for the Nobel Prize in Chemistry. Overlooked Accomplishments of Women Chemists" took place in August 2017. The most obvious example is Lise Meitner, who co-discovered nuclear fission with Otto Hahn in 1939, yet did not share the 1944 Nobel Prize in Chemistry with Hahn. Rosalind Franklin was cheated not by the Nobel Committee, but by her own tragic premature death at the age of 40. Probably the most famous of all thirteen female scientists presented is Rachel Carson.

The Preface, by the co-editors, notes that all women featured in the 2017 symposium are discussed therein, except for Martha Chase, Joan Folkes, Thérèse Tréfouël, and Dorothy Wrinch. Added are chapters about Marjory Stephenson, Margherita Hack, and Isabella Karle. Table 1 in the Preface neatly summarizes Nobel prizes awarded in chemistry and physics awarded to women before 1965 including number of times nominated in these fields. The 1965 date was dictated by the requirement that the nomination material in the Nobel Prize archive can only be accessed fifty years after nominations were submitted. Istvan Hargittai has published a book, *The Road to Stockholm: Nobel Prizes, Science, and Scientists* (Oxford University Press, 2002), with great detail about the history and regulations pertaining to the Nobel prizes. Alfred Nobel's will was quite brief, and the *Statues of the Nobel Foundation* are more detailed and have been amended throughout the century-plus years that followed. (See A.W. Levinovitz and N. Ringertz, Eds, *The Nobel Prize. The First 100 Years*, Imperial College Press and World Scientific Publishing Co. Pte Ltd, 2001.) A leitmotif in the present book is the so-called "rule of three:" no more than three persons (distinct from named organizations) can share a Nobel Prize. Although this practice was rigorously adhered to from the start in 1901, Levinovitz and Ringertz document (p 17) that it was finally formalized in the *Statutes* in 1968. Through 1965 only twelve women were nominated for the Nobel Prize in Chemistry with three winners (Marie Curie (1911), Irène Joliot-Curie (1935), and Dorothy Crowfoot Hodgkin (1964)), and two women were awarded Nobel Prizes in Physics: Marie Curie (1903) and Maria Goeppert-Mayer (1963). The Preface updates the Nobel Prize in Chemistry to include Ada Yonath (2009). Following publication, Frances Arnold was awarded a Nobel Prize in Chemistry in 2018 (featured in a fascinating profile in *The New York Times* "Science Times" May 28, 2019). And in 2018, Donna Strickland was awarded a Nobel Prize in Physics. Briefly mentioned in the Preface is the award-winning screen actor Hedy Lamarr. Recent books and films have documented her scientific genius, having been posthumously inducted into the National Inventor's Hall of Fame for her design, during World War II, of a new communication system for guiding torpedoes and preventing interception of radio frequencies, today considered a forerunner of modern wireless communication.

Chapter 1, "Women Scientists: An Uphill Battle for Recognition," by Magdolna Hargittai, describes obstacles that have faced brilliant female scientists over centuries, especially female astronomers. She mentions, as well, Marie Paulze Lavoisier, Antoine's gifted wife. To this, the present reviewer would add Elizabeth Fulhame, who published *An Essay on Combustion* (London, 1794). Hargittai, author of *Women Scientists: Reflections, Challenges, and Breaking Boundaries* (Oxford University Press, 2015), focuses on six distinguished scientists (Isabella Karle, Lise Meitner, Marietta Blau, Ida Noddack, Rosalind Franklin, and Charlotte Auerbach); each, with the exception of Auerbach, is treated in depth in subsequent chapters. Hargittai is an independent, accomplished scientist as well as a collaborator with her scientist husband, a mother of two accomplished children and has first-hand knowledge of the gender and "life-balance" issues that add challenges (and joys) to a career. World War II plays a significant role in the careers of four of the scientists in this chapter. Both Meitner and Blau were Jews whose careers were drastically affected by Nazi persecution. A citizen of Austria, Meitner worked occasionally with Otto Hahn at the Kaiser Wilhelm Institute in Berlin over a thirty-year period having achieved the rank of Professor in 1925. They were co-equal discoverers of nuclear fission but when Germany annexed Austria (the Anschluss) in March 1938, she became a German citizen and fled to Stockholm. No longer working with Hahn in Berlin, important scientific correspondence continued that further supported her sharing the Nobel Prize which was awarded solely to Hahn in 1944. Marietta Blau, a Jewish Austrian physicist, developed the photographic method for detecting nuclear processes in 1925. This had the advantage compared to the Wilson cloud chamber of detecting short-lived particles. Blau and her former student Hertha Wambacher developed an improved emulsion that made a major contribution to the study of newly discovered cosmic rays—in particular "fixing" the "disintegration stars" that recorded collisions between cosmic rays and heavy nuclei. Working at the Radium Institute in Vienna since 1923, she left Vienna days before the Anschluss, moving to Norway, Mexico, then the United States before returning to Vienna in 1954. Blau and Wambacher were nominated by Erwin Schrödinger in 1950, but the 1950 Nobel Prize went to Cecil Powell for related work, for his discovery of the π-meson using the photographic technique. Ida Noddack (née Tacke), a German chemist, co-discovered with her husband Walter, the element rhenium. In 1934 she reinterpreted Enrico Fermi's results from bombarding uranium with neutrons and postulated nuclear fission. The Noddacks also claimed discovery of the missing element 43—"masurium" subsequently disproven. Charlotte Auerbach, a German-Jewish geneticist, was forced to leave Germany in 1933, making her way to Edinburgh, where she earned her Ph.D. at the age of 36. Although never nominated for a Nobel Prize, she is considered to be the founder of the field of chemical mutagenesis. Much has been written about Rosalind Franklin and further discussion is reserved until later in this review. Particularly interesting is Hargittai's discussion of Isabella Karle. Magdolna and Istvan Hargittai have been close friends of Isabella and Jerome Karle for decades. The Karles, both American-born, met as students at the University of Michigan. Jerome Karle and Herbert Hauptman developed the mathematical technique to solve the so-called "phase problem" that allowed solution of X-ray crystallographic data previously considered unsolvable. However, it was Isabella Karle who worked out the methods to experimentally solve structures and prove to skeptical scientists that the phase problem had been solved. Jerome Karle and Hauptman shared the 1985 Nobel Prize in Chemistry. Jerome Karle was deeply disappointed and Hauptman very surprised that Isabella Karle did not share the Prize. Hargittai quotes the distinguished British crystallographer Alan Mackay: "Isabella Karle should have been included because it was her work that made the whole thing believable."

Chapter 2, "Politics, Persecution, and the Prize: Lise Meitner and the Discovery of Nuclear Fission," by Ruth Lewin Sime, focuses on the woman most unjustifiably denied a Nobel Prize. Meitner (1878-1968) was nominated 19 times for the Nobel Prize in Chemistry and 29 times for the Nobel Prize in Physics. Otto Hahn and Meitner were friends and colleagues whose collaborative research started in 1907. They discovered the element protactinium in 1918.Their research interests diverged in the 1920s but they began to collaborate in 1934 on uranium chemistry and physics. Soon Fritz Strassmann, an analytical chemist, joined them in Berlin. In 1934 Ida Noddack had advanced the heretical idea that hitting a uranium atom with a neutron could cause fission. By 1937 the Berlin team attempted to explain their results by postulating creation of transuranium elements as Enrico Fermi had earlier. The Anschluss forced Meitner to escape Germany, smuggled across the Dutch border, and she joined the Nobel Institute for Physics in Stockholm, a very negative experience, and the author examines the Manne Siegbahn-Meitner relationship. But more critical is the fact that, although geographically separated from Hahn and Strassmann, correspondence and collaboration continued, including a secret meeting between Hahn and Meitner in Copenhagen in November 1938. The discovery in Berlin that upon capture of a neutron uranium-238 does not produce radium as originally thought but rather barium stimulated Meitner and her cousin Otto Robert Frisch, also a physicist, to develop a theory of fission. Sime points out that it took decades and access to historical records to fully uncover the co-equal partnership between Hahn and Meitner. This chapter certainly makes the strong case supporting Meitner as appropriately a Nobel Laureate.

Chapter 3, "Marjory Stephenson: Founder of Microbial Biochemistry", by M. F. Rayner-Canham and G. W. Rayner-Canham, provides an illustration of a mother's faith, intellectual gifts, and inspired mentorship overcoming disadvantages of opportunities and expectations for a woman born in 1885 England. The Rayner-Canhams have published extensively about women in chemistry. The insistence of Stephenson's mother that her daughter obtain a university education (Newnham College, a women's college at the University of Cambridge) led to her exposure to the inspiring Newnham Lecturer of Chemistry, Ida Freund. Barred from obtaining a formal degree, Stephenson passed her final examination and took a teaching position at the Gloucester School of Domestic Science. In 1910 she took a position at King's College for Women in London, but in 1911 accepted an invitation to work with Robert Plimmer, University College London to teach advanced courses in the chemistry of nutrition and conduct research which gained her a Beit Memorial Fellowship in 1913. After the outbreak of war in 1914, Stephenson used her domestic science skills to serve as a cook in France for soldiers returning from the front. Her skills led to leadership positions in hospitals in Europe. She returned to England at war's end by which time she was 33. Such a four-year hiatus would have side-tracked the careers of most, but Stephenson was able to reactivate her Beit Fellowship and had the great good fortune of joining the Cambridge research group of Sir Frederick Gowland Hopkins (1929 Nobel Prize in Medicine and Physiology). "Hoppie's" research group was renowned for its incredibly supportive environment and Stephenson thrived and independently chose to explore and then pioneer the field of bacterial metabolism. The Rayner-Canhams address early success of women in biochemistry, a new field, not yet fully enshrined, yet needing considerable human resources. But they aver that "…having a mentor is always an important factor for women scientists." Amen to that! The Rayner-Canhams describe her research, around 1930, on hydrogenase and methane fermentation in a river polluted by a sugar-beet factory. This led to studies of adaptive enzymes in bacteria growing in the presence of an external influence. Her 1930 monograph on *Bacterial Metabolism* became the classic in the field. In 1944 Stephenson cofounded the Society for General Microbiology and became its President in 1948. In 1945, she along with Kathleen Lonsdale became the first two women elected as Fellows of the Royal Society. Stephenson died of breast cancer in December 1948. As the founder of bacterial biochemistry, the Rayner-Canhams feel strongly that she was fully worthy of a Nobel Prize.

Chapter 4, "Marietta Blau: A Near but Justifiable Miss?" was written in a delightful sui generis manner by Virginia Trimble, who even composed a narrative of the youth and appearance of Blau (1894-1970). The author asks rhetorically: "…why comment on her [Blau's] appearance? Because Marietta Blau was a Jewish woman at a place and time (1920-1930s Vienna) where both could be considered disadvantages." Incidentally, in 2018 asteroid 9271Trimble was named to honor the author, who commented: "With roughly 7 billion people in the world and 700,000 known asteroids one person in 10,000 could have one of those entities named after them, so it's not that big a deal." Trimble comments that Blau was "… never paid for her years at the Radium Institute, either before 1938 or after 1960." (Indeed, Lise Meitner came to Berlin in 1907 as an "unpaid 'guest'" (Chapter 2).) Blau's quite complex story has been very helpfully organized into a table as well as a section, "A Sort of Timeline," along with an Appendix. Blau and her doctoral student and subsequent colleague Hertha Wambacher at the Radium Institute in Vienna developed the nuclear emulsion plate, a thick film layer including silver chloride, having very uniform grain size, which was effective in photographing extremely fast phenomena including collisions of gamma rays with nuclei in the plate leading to "disintegration stars." The method was superior to the Wilson Cloud chamber since it could record and preserve super-fast events. The breakthrough paper presented images obtained on a plate exposed at an altitude of 2300 m. With Anschluss, Blau was ultimately helped to resettle at the Mexican Instituto Politécnico Nacional, for a teaching position without serious research opportunity. She arrived in New York in 1944, had various industrial associations, moved to Columbia University in 1948, became a U.S. citizen and moved to Brookhaven National Laboratory. Although the significance of Blau's development of the nuclear emulsion plate was recognized by awards and five Nobel Prize nominations, the 1950 Nobel Prize in Physics was awarded to Cecil F. Powell. In 1947, the discovery of the pion (π-meson), using photographic emulsions, was announced in a publication authored by Cesare M. G. Lattes, Giuseppe P. S. Occhialini, and Powell. There was no mention of the development of this technique by Blau and Wambacher. Trimble concludes (perhaps ruefully) that the 1950 Prize was "a near but justifiable miss."

Chapter 5, "Ida Noddack: Foreteller of Nuclear Fission," by James L. Marshall, is an extensively researched presentation of the discovery of nuclear fission, presaged by the suggestion in 1934 by Ida Noddack that the observations by Fermi and associates from hitting uranium with neutrons was not formation of transuranium plutonium but rather fission. This "heretical" suggestion, widely discounted, was proven in 1938 by Hahn, Meitner, and their associates Strassmann and Frisch. In addition to very considerable documentation of correspondence, this chapter is enhanced by seventeen photographs, including ten from the author. As many readers will know, James L. Marshall and his wife Virginia (Jenny) Louise Marshall, who passed away in 2014, were collaborators on their "Rediscovery of the Elements" project, which contributed numerous photographs and essays toward enhancing our knowledge of the history of the periodic table and the chemical elements. A very brief outline of the Noddack story is presented in chapter one of this monograph and the extensive citations in Marshall's chapter cannot simply be summarized. As previously described, Walter and Ida Noddack were among other distinguished chemists who erroneously identified element 43 ("eka-manganese"). Another missing element was right below 43—"dvi-manganese", element 75. Marshall informs readers that "eka" and "dvi" signify "1" and "2" in Sanskrit. The Noddacks published their discovery of elements 43 ("masurium") and 75 (rhenium) in 1925. The experimental results for "masurium" could not be replicated by other researchers. However, rhenium was a successful discovery. As Marshall shows graphically, it is more closely related to molybdenum than manganese chemically, an example of the diagonal relationships often observed in the periodic table. In co-discovering nuclear fission, Hahn dismissed Ida Noddack's 1934 theory by saying "one mistake is enough"—a thinly-vailed allusion to "masurium." Among many interesting details, Marshall refers to a comment by Emilio Segrè, who claimed to observe Walther Noddack in a Nazi uniform. Noddack's affiliation with the Nazi party is discussed in this chapter.

"The Remarkable Life and Work of Katharine Burr Blodgett (1898-1979)," by Margaret E. Schott, Chapter 6, describes the lifework of a pioneer of surface science and what would become decades later nanoscience. In 1893 George Reddington Blodgett became head of the patent department of General Electric, which had recently relocated to Schenectady. That year he married Katharine Buchanan Burr. Schott writes: "Sadly, he died at age 35, leaving behind his wife, a son George, and an unborn child, Katherine." Katharine was raised in privileged circumstances, was precocious, and entered Bryn Mawr College at age fifteen. Opened in 1885, its vision was to provide its students "all the advantages of a college education offered to young men." Over Christmas break during her senior year she returned to Schenectady and was given a tour by Dr. Irving Langmuir. Completing her A.B. in physics in 1917, she pursued masters degree research on the surface of activated carbon for gas masks as part of the war effort and completed her degree in 1918. Blodgett then worked with Langmuir at GE, improving tungsten filaments for light lamps, until 1924 when she would commence her doctoral studies at Cambridge with Ernest Rutherford, recommended to him by Langmuir. Rutherford was known for treating junior colleagues respectfully and advocating for women in science. Clearly, this is one of many instances in this monograph demonstrating that very positive mentoring aids in the development of outstanding women scientists. Blodgett's research involved study of the movement of electrons through mercury vapor, an area of interest to GE as well. She completed her doctorate in 1926 and returned to GE. Years earlier Langmuir began to employ apparatus designed by Agnes Pockels (1862-1935) that deposits a soap monolayer on water. Blodgett began work with Langmuir's apparatus and demonstrated the transfer of a soap (e.g. sodium stearate) molecular monolayer onto the surface of a glass slide substrate. She demonstrated the ability to build films from successive layers using the Langmuir-Blodgett technique and designed a film thickness gauge capable of measuring millionths of an inch using step-wise layers of calibrated thickness. Schott's descriptions, figures and photos very nicely clarify these processes. During World War II, Langmuir and Blodgett worked on the design of particles used for smoke screens. Among numerous honors, Blodgett received the ACS Francis P. Garvan Medal in 1951. She retired from GE in 1962. Blodgett was never recommended for a Nobel Prize. Among the reasons the author considers is that Langmuir received the Nobel Prize in Chemistry in 1932, therefore explicitly recognizing surface science. Additionally, the full impact of Blodgett's research would only be recognized decades later, some of it beyond her lifetime.

"Erika Cremer and the Origins of Gas-Solid Adsorption Chromatography, 1944-1947," Chapter 7, by Jeffrey Allan Johnson, is a tale of destruction and lost opportunities for a brilliant physical chemist on the German side of World War II. Unlike the existential threats to the lives of Marietta Blau and Lise Meitner, the war "only" severely impacted the research efforts of Erika Cremer (1900-1996) and, the author argues, cost her a share of the 1952 Nobel Prize in Chemistry awarded to Archer J. P. Martin and Richard L. M. Synge for the development of gas liquid partition chromatography (GLPC). Cremer was born to a family of academicians, and the need for men in World War I opened German universities to women. Cremer attended the University of Berlin to study physical chemistry and her first lecturer was Walther Nernst (Nobel Prize 1920). She remained in Berlin and completed doctoral studies in 1927 with the expert in thermodynamics and kinetics Max Bodenstein and published her thesis as sole author. As outstanding as her thesis was, it gained her only limited opportunities and she spent a decade moving from research lab to research lab, including periods in Fritz Haber's Kaiser Wilhelm Institute, George de Hevesy (Nobel in Chemistry, 1943), Michael Polanyi, Nikolai N. Semenov (Nobel in Chemistry, 1956), and Kasimir Fajans among others. With Polanyi she applied quantum theory to the kinetics and thermodynamics of interconversion of the two spin nuclear states of molecular hydrogen. Johnson describes Cremer as "…demonstrating a flair both for using complex theory as well as technical apparatus in experimentation." In addition to having to work extended periods without pay, Cremer had to hide when the Director of the national physics laboratory PTR, Johannes Stark, a Nazi who tolerated no women in his institute, entered the area. Once again, as men were needed for the war effort, opportunities opened for Cremer and in 1940 she was given teaching privileges (in 1942 instructor's rank) at the new physical chemistry institute in Innsbruck. Although not an absolute requirement, Cremer was pushed by colleagues and "registered" with the Nazi party in 1941. (Johnson notes that in 1947 she was cleared of being a formal member of the Nazi party.) At Innsbruck she tackled the important problem of separation of ethylene from acetylene. Interested in the thermodynamics of adsorption, her research evolved into a separation technique. She submitted her key manuscript to the final war issue of *Naturwissenschaften*, the equivalent of *Nature*, in fall 1944. It was accepted but never published due to the war. In December 1944, allied bombing heavily destroyed the institute and what could be salvaged was rebuilt about eight miles from Innsbruck. In 1947, Cremer and her student had a functioning gas chromatograph. In 1951 Cremer was promoted to Associate Professor, in 1959 to a chaired professorship. She retired in 1970. The author argues that the delays and the lack of publicity were factors in thwarting Cremer's share of the 1952 Nobel Prize.

Chapter 8, "Dame Kathleen Lonsdale: Scientist, Pacifist, Prison Reformer," by Maureen M. Julian and Mary Virginia Orna describes the impactful and eventful career of the first distinguished female crystallographer Kathleen Lonsdale (née Yardley, 1903-1971). Lonsdale's career is also of significance to the sociology of science. One of the co-authors, Professor Julian, has written extensively about her post-doctoral mentor—Lonsdale. X-ray crystallography has benefitted from a series of distinguished women over the course of nearly a century (G. Ferry, *Nature*, **2014**, *505*, 609-611). The authors describe Yardley's brilliant performance as a physics undergraduate, which inspired Nobel Laureate William Henry Bragg to invite her to pursue graduate research with him at the University of London. J. D. Bernal was also working with Bragg. In future years Dorothy Crowfoot Hodgkin worked with Bernal. She won the 1964 Nobel Prize in Chemistry for determining the structures of penicillin and vitamin B12. Ferry comments: "Bragg protégés such as Lonsdale and Bernal and their students fostered egalitarian lab cultures." Olga Kennard, née Weisz, worked with Bernal. She founded the Cambridge Crystallographic Data Centre. Yardley married Thomas Lonsdale in 1927 and it is clear he was very supportive of her career. During the late 1920s they were attracted to Quakerism and in 1936 embraced it. During World War II she resisted the requirement to register for civil defense duties and was jailed in Holloway Prison for thirty days. The experience inspired Lonsdale to be an activist for prison reform. Following the atomic bomb attacks on Japan, Lonsdale was a charter member of the Atomic Scientists Association. Her activism continued throughout her life until her death in April 1971. The authors list nine significant scientific achievements. Lonsdale is perhaps best known for establishing that the benzene ring is planar. The authors provide detail into the history and significance of her work in this area. Benzene is a liquid at room temperature and this required difficult lower-temperature studies. In 1928 E. Gordon Cox determined only that benzene had a center of symmetry. In 1929 Lonsdale performed the very challenging accurate study of crystalline hexamethylbenzene and determined unambiguously that the ring is planar. Beginning in 1935 and fully concluded in 1946 following the war years, Christopher Kelk Ingold using deuterated benzene isomers, infrared and Raman to determine that benzene itself is a planar hexagon. But Lonsdale's studies of diamagnetic susceptibilities on aromatics, as well as amides, esters, among other crystalline compounds demonstrated the delocalization of π-bonding in these species. This furnished experimental verification of theoretical models of π- and σ-bonding. As noted earlier, in 1945 Marjory Stephenson and Kathleen Lonsdale became the first two women elected as Fellows of the Royal Society. The authors conclude: "Linus Pauling received the Nobel Prize in both Chemistry and Peace. Surely, Dame Kathleen Lonsdale deserved no less."

Chapter 9, "Rachel Carson: The Right Person, at the Right Time, with the Right Message," by Amanda Hofacker Coffman, is a rather unique chapter in that Rachel Carson (1907-1964) would never have been a serious contender for the Nobel Prize in Chemistry. She notes that Carson published few purely scientific papers. However, Carson's impacts on the public perception of ecology and human health and its subsequent impact are worldwide and extremely consequential. The present reviewer wonders why not a Nobel Prize in Literature or, for that matter, a Nobel Peace Prize? While most of the Nobel Prizes in Literature have been awarded for fiction or poetry, Sir Winston Churchill's 1953 Nobel in Literature, for example, was awarded for historical and biographical description and brilliant oratory. Linus Pauling received the 1962 Nobel Peace Prize for his campaign against nuclear weapons testing. As Professor Coffman notes, Carson's 1941 *Under the Sea-Wind* and its 1951 sequel *The Sea Around Us* did much to stimulate public interest in the oceans and its wildlife. *The Sea Around Us* was the number one bestseller on *The New York Times* non-fiction list for six months. This was followed by another best-seller, *The Edge of the Sea*, in 1955. Toward the end of the fifties, Carson agreed to write an investigative article for *The New Yorker* on the impact of DDT and other pesticides. This project evolved into her masterwork, *Silent Spring*, published by Houghton Mifflin in 1962. For context, Dr. Paul Hermann Müller was awarded the Nobel Prize for Physiology or Medicine in 1948 for discovery of the high efficacy of DDT against arthropods, including mosquitos. DDT has most certainly saved millions of lives, including World War II soldiers and citizens of tropical climates, from malaria. However, *Silent Spring* disclosed the nefarious nature of DDT and other pesticides on ecology and on human health. It popularized the concept of bioconcentration explaining the impact upon apex predators such as eagles whose eggs had shells thinned to the point of non-viability. Coffman presents the social and political atmosphere of the 1950s and 1960s and documents reactions positive and negative. Predictably, Carson's conclusions were attacked by industry interests as well as some political conservatives. In 1964, Carson died of breast cancer at the age of 56, still too early to witness the full impact of her book. In 1980, President Jimmy Carter awarded Carson posthumously the Presidential Medal of Freedom. The year 2012 marked the fiftieth anniversary of *Silent Spring*. The American Chemical Society designated the book a National Historic Chemical Landmark. And all-too-predictably, many of the same sources attacked her work as pseudo-science. Sadly, such revisionist history is ascendant today.

Chapter 10, "Marguerite Perey (1909-1975): Discoverer of Francium," by Sarah S. Preston, explicitly raises the question: is discovery of a new element, as difficult and important as that is, sufficient to merit a Nobel Prize in Chemistry or Physics? Tragedy struck Marguerite Perey's family when her father died in 1914 and a stock market crash caused loss of the family's flour mill. Instead of pursuing a medical career she enrolled at École d'Enseignement Technique Féminine, a vocational school for training female chemical technicians. But fortune smiled upon her in 1929 when Marie Curie, Professor at the Radium Institute in Paris, requested the top person in the graduating class as her assistant. Perey became personal laboratory assistant to the frail scientist who would die of radiation poisoning in 1934. With Madame Curie, Perey began her life-long study of actinium (Ac, atomic number 89), discovered by Andre-Louis Debierne in 1899 from pitchblende residue remaining from Curie's isolation of radium and polonium. Very difficult to purify, Perey's samples were employed for Pieter Zeeman's spectroscopic characterization of the metal. The discovery of atomic number by Henry G. J. Moseley in 1913 exposed seven remaining "holes" to be filled in the periodic table and the race was on! Preston's chapter describes several false alarms in the hunt for missing element 87. When Marie Curie died, Debierne became Director of the Radium Institute but Perey worked closely with Irène Joliot-Curie. Her subtle, laborious work on radiation by-products is detailed by Preston. In late 1938 Perey became convinced that she was observing radiation from a new element. In early 1939, Jean Perrin was asked to make the announcement of her discovery, but he remained unconvinced. Others also questioned the discovery, and it was only in 1946 that it was accepted and the name Francium, favored by Irène Joliot-Curie and Frédèric Joliot, was adopted by her. Honors followed: she was nominated in 1949 to become Chair of Nuclear Chemistry at the University of Strasbourg. In 1955 the University and the CNRS formed the Centre de

Recherches Nucléaires and Perey was appointed Director of the Département de Chimie Nucléaire. Perey was the first woman elected to the French Academy of Sciences (1962), an honor that eluded Marie Curie (two Nobel Prizes) and her daughter Irène (one Nobel Prize). Even so, Perey's election as corresponding member fell short of an "academician seat"—a full member. She received, as of 1968 (reported in 2018), five Nobel Prize nominations but, as in the case of others who discovered the other six "missing elements," no Nobel Prize. Marguerite Perey died of cancer in early 1975 sharing the fate of her first mentor Marie Curie. (Irène Joliot-Curie died of leukemia in 1956 at the age of 58.)

In Chapter 11, "Rosalind Franklin: Her Pathway to DNA," Bertron H. Davis and E. Thomas Strom employ the love of the young Rosalind Franklin (1920-1958) for mountain climbing as their organizing metaphor. The public came to know Franklin through James D. Watson's 1968 bestseller *The Double Helix*. Davis and Strom aver that "A memorable book should have memorable heroes." In this case, Watson and Crick the heroes, Linus Pauling the wily competitor, and Rosalind Franklin as the villain. While somewhat overstated here, despite a mild apology at the end, Watson's portrait of Franklin is certainly a negative one. But a 1987 BBC film, hard to find today, *The Race for the Double Helix*, depicts a vivacious, flesh-and-blood, Rosalind Franklin. The authors have Franklin climbing three "mountains": 1) structure of coal, 2) crystallographic study of the structure of DNA, 3) structure of the tobacco mosaic virus (TMV). In 1941 Franklin obtained her degree in physical chemistry from Newnham College at Cambridge. Awarded a research scholarship with Ronald G. W. Norrish (Nobel Prize in Chemistry, 1967), she felt disrespected and took a position at the British Coal Utilization Research Association (CURA) and remained until 1947, completing her Ph.D. in physical chemistry. From there Franklin moved to Paris, where she enjoyed a supportive supervisor, Jacques Mering, and during this period thrived and learned X-ray crystallographic techniques. In late 1950 she moved to King's College expecting to work with John Randall's department on proteins but was told in December 1950 that her assignment was structural study of DNA. Here was the origin of the Franklin-Maurice Wilkins misunderstanding described in part by Watson. Davis and Strom provide other views as presented in books by Anne Sayre and others. What is abundantly clear is that Wilkins' sharing Franklin's excellent crystallographic photo of the B-form of DNA without her knowledge clearly violated the norms of professional scientific ethics. Although Watson painted a picture of Franklin's approach as being systematic, accurate but unimaginative, subsequent authors clearly established that she understood DNA was a helix with the deoxyribose polymer chain outside and the bases inside. The third mountain was her crystallographic work on TMV with her student Aaron Klug. Franklin and Klug, corresponding professionally with Watson and Crick, proved that the helical RNA in TMV is not in the center of the virus protein core but intimately associated within the proteins. Tragically, Franklin died in 1958 of ovarian cancer. The authors note that the first nomination for solving the structure of DNA (Watson, Crick, and Wilkins) was submitted in 1960. In 1962, there were five nominations for Watson and Crick and the trio won the 1962 Nobel Prize in Physiology or Medicine. Davis and Strom consider various Nobel Prize scenarios for the DNA discovery had Franklin lived six more years or beyond. They also offer one other intriguing scenario, sharing the Nobel Prize with her former student and passionate advocate Aaron Klug who was the 1982 Nobel laureate.

Chapter 12, "Isabella Karle: Crystallographer Par Excellence," by Lou Massa expands some of the scientific and personal details in Magdolna Hargittai's introductory chapter. As noted earlier, Isabella Karle (née Lugoski, 1921-2017) and Jerome Karle began their research in the field of gas-phase electron diffraction, under Lawrence Brockway, at the University of Michigan. Both worked on the Manhattan Project, where Isabella demonstrated experimental skills in inorganic chemistry totally distinct from her Michigan experience. The Karles then moved on to the Naval Research Laboratory where they spent the remainder of their careers. As Massa notes, around 1950, the electron and X-ray societies were small enough to hold joint meetings and this is where Jerome Karle and Herbert A. Hauptman, who had recently joined Jerome Karle's NRL group, learned of the phase problem of X-ray crystallography, thought to be mathematically unsolvable. The author, Massa, does a masterful job in outlining the difficulties and the solution to the phase problem—at least to a level somewhat accessible to the present reviewer. Still, there was widespread disbelief in the crystallography community. Isabella Karle, with assembled apparatus and lacking computer power, developed the direct methods for turning X-ray data into structures, supporting the theoretical solution to the phase problem and opening the modern era of X-ray crystallography. Massa also does a service to readers interested in the sociology of science. Jerome Karle and Herbert Hauptman were undergraduate friends at City College of New York. Not long after their shared award of the 1985 Nobel Prize in Chemistry there was estrangement between them. This also involved a third crystallographer, David Sayre, who developed an independent solution to the phase problem. Massa knew all the principals personally—especially a thirty-plus-year friendship between the Karle family and his own. At a 1985 meeting at the Fox Chase Cancer Center in Philadelphia, he was introduced by Miriam Rossi, a crystallographer at Vassar College to the Karles. Rossi, who was Massa's undergraduate student at Hunter College of CUNY, had been a postdoctoral researcher with the host, Jenny Glusker, herself, earlier a student and collaborator of Dorothy Hodgkin. Such is the beauty of science which is cosmopolitan and international and yet intimate in specialized groups. Massa strongly states that excluding Isabella Karle from sharing the Nobel Prize "…was an intellectual injustice for the simple reason that Isabella was responsible for the experimental proof that the mathematics of direct methods did indeed correctly predict crystal structure." The author observes: "What I admire most about Isabella is the greatness of her work, which carried on apace after the Nobel Prize. The work itself was the prize for her, not any external recognition for doing it."

"Margherita Hack: Friend of the Stars," by Marco Fontani and Mary Virginia Orna (Chapter 13), introduces readers to a woman whose scientific accomplishments and public outreach, radical leftist views, and popular interest gave her an almost outsize presence in the Italian public. Born in Florence 1922, she came of age during the emergence of fascist Italy. In the words of the co-authors: "Like any Florentine, 'La Hack'—even if of middle-class bourgeois extraction—was impressively different and proud of her freedom; averse to all forms of regimentation, be they cultural, social or academic." In short, a Force of Nature. The authors describe Hack's young days and the impact of the war in delaying her education, finally receiving her undergraduate degree in astrophysics from the University of Florence in 1945. In addition to studies, in 1941 and 1942 she won important national events in the long and high jumps. She married her childhood sweetheart, Aldo De Rosa, a classics scholar, in 1944. Thrown into career flux following the war, in 1950 Margherita Hack accepted a permanent staff position at the Arcetri Observatory (Florence), followed by a move to the Observatory of Brera, near Milan, and successive moves to Utrecht and Berkeley. In 1964 she settled at the University of Trieste where she remained until retirement in 1992. Hack remained very active and highly visible in communicating good science, including popular and technical monographs, and debunking pseudoscience. In 2002, she embarked on her political career. As late as 2013 she was still involved even as her views became "even more radical." Margherita Hack's principal contributions involved employing the ultraviolet spectrum to study stars. In the mid-1950s she began to examine the supergiant Epsilon Aurigae, 6500 light years away and 200,000 times brighter than the sun. In 1955 Hack proposed a model for this extraordinarily complex system. Ultraviolet light is typically divided into three ranges: UVA (315-400 nm), not absorbed by the atmosphere, UVB (280-315 nm), mostly absorbed by the atmosphere, and UVC (100-280 nm) which is virtually entirely absorbed by the atmosphere. Her model was largely supported in 1978 by the satellite International Ultraviolet Explorer (IUE) which had two spectrographs aboard for recording in the 115-200 nm and 185-320 nm ranges respectively. This reviewer wishes a bit more was said about the limitations of investigating the UV spectra of stars from the Earth. In Hack's honor, an asteroid discovered in 1995, was named 8558Hack. Hack died in 2013 following years of illness. Aldo De Rosa, her husband of 69 years, died in 2014. They had agreed to have no children.

The final chapter, "Professor Emerita Darleane Christian Hoffman: Determination Wins," by Caroline F. V. Mason, presents one of the pioneer researchers of transuranium elements, the natural occurrence of plutonium, and the environmental impact of radionuclides. As an undergraduate, Darleane Christian (b 1926) worked on the 68-MeV synchrotron at Iowa State University. She received her Ph.D. in 1951 and married Dr. Marvin Hoffman and accompanied him to his new position at Los Alamos National Laboratory (LANL) where work was active in analyzing the residue of a 10.4 megaton H-bomb test ("Mike") in the Pacific. She was not offered a position immediately: "For three frustrating months I sat and waited while others were discovering einsteinium and fermium in the test debris." Today, with increasing frequency, it is the husband who is the "accompanying spouse." Dr. Rod Spence, head of the nuclear test group, met Darleane Hoffman at a reception and immediately hired her. Analyzing debris from the bomb test, she discovered plutonium-244, half-life 80 million years, and she imagined that it might be naturally-occurring at ultra-trace levels. From a mine in California, she found 20 million atoms (!) of this isotope in 85 kg of ore. In 1971 Hoffman discovered the symmetric nuclear splitting of some isotopes of fermium—results initially treated with skepticism. Following a one-year stay in Oslo, she commenced study of the environmental distribution of radioisotopes in nuclear waste. In 1979 Hoffman became Division Leader of the Isotope Nuclear Chemistry Division—the first woman to head a division at LANL. Her research focused on "one-atom-at-a-time" studies of short-lived rutherfordium, dubnium, seaborgium, and bohrium. In 1984 Hoffman moved to a tenured professorship at the University of California, Lawrence Berkeley Laboratory, as Glenn Seaborg was retiring. She became the first director of the Glenn T. Seaborg Institute for Transuranium Science. In 2017, her team created livermorium (Lv, 116) and oganesson (Og, 118). Among many honors are three major awards from the ACS Nuclear Chemistry (1983), Garvin-Olin Medal (1990) and the Priestley Medal (2000), the Society's highest award. In 1997 President Clinton honored Hoffman with the 1997 National Medal of Science. Clearly, Professor Emerita Hoffman has enjoyed an amazing career as scientist, administrator and, as the author specifically highlights, family member.

There are many threads woven throughout this book. These include the barriers faced by women scientists, enormous strength in adversity, the vital importance of good mentoring and a conducive environment, the number of brilliant women who worked without pay at various points in their careers, and the impact of World War II. The women presented herein include those who this reviewer feels were deserving of Nobel prizes and those who were "merely" extraordinary and deserving of more exposure to scientists and non-scientists alike.

Arthur Greenberg, Professor of Chemistry, University of New Hampshire; Art.Greenberg@unh.edu

---

African American Women Chemists in the Modern Era, Jeannette E. Brown, Oxford University Press, New York, 2018, viii + 290 pp, ISBN 978-0-19-061517-8, $35.

This book can be considered to be a sequel of sorts to a previous Jeannette Brown volume. Her first book, *African American Women Chemists*, was enthusiastically reviewed seven years ago in the *Bulletin* by Sibrina N. Collins (**Vol. 37**, No. 2, pp 106-107 (2012)). That particular book dealt with women chemists from civil war times to the civil rights era. Brown, an ACS Fellow, has been very active in programming symposia at ACS meetings with an emphasis on matters of diversity. Her graduate degree comes from the University of Minnesota, where she was a student of C. Frederick Koelsch, of Koelsch's radical fame. Brown has had a successful career in the pharmaceutical industry.

This new book tells the stories of twenty African American women chemists with accomplishments in industry, academia, and government service. In general, these biographical sketches come from Brown's oral history interviews carried out through the Chemical Heritage Foundation, now known as the Science History Institute. Almost all of these oral histories have been turned into third person narratives. However, two of the histories, those from Sondra Barber Akins and Sibrina N. Collins, are in the first person.

The book consists of an introduction, chapters about the principals described, a concluding section focused on the future, a listing of selected publications from the twenty chemists, and a bibliography of useful sources on women scientists. After the introductory Chapter 1, Chapter 2 deals with "Chemists Who Work in Industry," with subjects Dorothy Jean Wingfield Phillips, Charlynlavaughn Bradley, Sharon Janel Barnes, and Sherrie Pietranico-Cole. Chapter 3 treats "Chemists Who Work in Academia," with chemists Etta C. Gravely, Sondra Barber Akins, Saundra Yancy McGuire, Sharon L. Neal, and Mande Holford. "Chemists Who Are Leaders in Academia or Organizations" is the heading for Chapter 4, with examples Amanda Bryant-Friedrich, Gilda A. Barabino, Leyte Winfield, and La Trease E. Garrison. The classification for Chapter 5 is "Chemists Who Work for the National Labs or Other Federal Agencies," who are Patricia Carter Ives Sluby, Dianne Gates Anderson, Allison Ann Aldridge, LaTonya Mitchell-Holmes, and Novella Bridges. Chapter 6 is the first person narrative of just Sibrina N. Collins and is titled "Life After Tenure

Denial in Academia." The final chapter is called "Next Steps."

The chapters based on the oral histories of the 20 chemists were all excellent. Because of Brown's interviewing skill, the personalities of these women come through with clarity. One common thread is that almost all of these women had parents who were strongly focused on their children's education. A college degree was not an afterthought for them, but a goal right from the beginning. The women had to fight through three kinds of barriers: poverty for many, sexism, and prejudice against African Americans. Some of the subjects were born during the Jim Crow era, and those born at a later time still had to deal with residual racism. For example, Saundra McGuire knew that she couldn't drink from certain fountains or go to certain stores. Her parents explained to her that this came from the ignorance of the people instituting those policies, and had nothing to do with anyone being inferior. As a result, Saundra grew up with healthy self-esteem, "never thinking she was better than anybody else, always knowing that she was just as good."

A number of these ladies received their undergraduate training at historically black colleges and universities (current abbreviation HBCUs). Although nowadays previously forbidden colleges are open to them, many felt that the faculty at an HBCU were much more nurturing of their students than the faculty at previously all white institutions. From her experience in a formerly all white graduate program, Novella Bridges feels that African American students have become something of a commodity. The professors wanted minority students in their group, because it would help their programs get grant proposal money.

The chapter titles quoted previously demonstrate the broad coverage of this book, as careers in industry, academia, and government are covered. What, then, are we to make of the title of Chapter 6, "Life After Tenure Denial in Academia"? Dr. Sibrina Collins mentions this fact briefly in the first paragraph of her first person narrative and refers to it just once more in a short paragraph later in this six and a quarter page chapter. Collins went to high school in Detroit, graduated with a chemistry degree from Wayne State University, and earned her Ph.D. from Ohio State under mentor Bruce Bursten, a former ACS president. She did a post doc at LSU, worked for AAAS, and taught at Claflin University, an HBCU in South Carolina. She later joined the faculty at the College of Wooster, where she ultimately was denied tenure. She then worked at Detroit's Wright Museum of African American History. Presently she is at Lawrence Technological University in Michigan, where she is the first executive director of the university's Marburger STEM Center. My point is that Dr. Collins is so much more than a person who was denied tenure. She is an accomplished chemist of wide accomplishments. The chapter title is misleading and, I feel, unfortunate.

Clearly this is a minor complaint about what I believe is an excellent book. Any student wondering about careers in chemistry would find useful information in these diverse chapters, while chemists farther along their career paths will enjoy learning how these strong women navigated their way to success. A few years ago I noticed Brown's first book on display in the non-fiction section of my local branch of the Dallas Public Library. That was an unusual event, as my local library branch seems to shun science-based books. Yesterday I made an inquiry at the library about Brown's new book. I was delighted to learn that the library had just ordered two copies. I recommend that you readers consider buying this reasonably-priced book. *African American Women Chemists in the Modern Era* gives the reader much to learn and much to admire.

E. Thomas Strom, Adjunct Professor of Chemistry, Department of Chemistry and Biochemistry, University of Texas at Arlington, estrom@uta.edu.

A Lab of One's Own: Science and Suffrage in the First World War, Patricia Fara, Oxford University Press, 2018, 352 pp, ISBN-10 0198794991, ISBN-13 978-0198794998, $24.95.

I was greatly attracted by the title of this book; setting up a lab of my own was my goal from the time I left graduate school until I was able to do so. I expected that the book would include in-depth descriptions of women scientists who did just that.

However, most of the book concerns the history of the women's suffrage movement during this period. What is suffrage? It is defined as *the right to vote in political elections*. However, discrimination against women or disenfranchisement reached across many fields both before and during World War I, as factory workers, munitions experts, medicine, sports (cricket!), as well as in areas of science—botany, geology, physics, chemistry—were discriminated against in factories, labs, and schools. The book reaches across many areas of employment but does not concentrate specifically on laboratories, chemistry or otherwise.

Chapter 10 was the most interesting to me, as it was concerned with women ***chemists***, detailing the lives of Ida Smedley (1877-1944, a biochemist) and Martha Whiteley (1866-1956, a chemist and mathematician), and discussing the Chemical Society founded in England in 1841. One of the aims of the Chemical Society was to hold meetings for "the communication and discussion of discoveries and observations, an account of which shall be published by the Society." In 1847, its importance was recognized by a Royal Charter, which added to its role in the advancement of science and the development of chemical applications in industry. Membership was open to all those interested in chemistry, but fellowship was long restricted to men.

In 1880 (20 years after its founding), the Society considered a suggestion allowing amendment of its constitution to allow the admittance of women, but it was shelved several times. In 1904 (another 20 years), Marie Curie was recommended for membership but as a married woman. She was banned as a normal fellow; however, she could be admitted as a foreign fellow.

In the first years of the 20th century, Smedley and Whiteley sent in a petition with 17 of their female colleagues pointing out that during the past 30 years, there had been an estimated 150 women who were authors or co-authors of papers in Chemical Society publications. Ironically, the major opponent of this motion was Smedley's research supervisor, Henry Armstrong, who maintained that the duty of female chemists was to produce baby chemists. FINALLY, in 1919 (after almost another 20 years), 21 females were elected to the Chemical Society.

As a matter of interest, the signatories to the 1904 petition are Lucy Boole, Katherine Alice Burke, Clare de Brereton Evans, Elizabeth Eleanor Field, Emily Fortey, Ida Freund, Mildred Gostling, Hilda Hartle, Edith Humphrey, Dorothy Marshall, Margaret Seward, Ida Smedley, Alice Emily Smith, Millicent Taylor, M. Beatrice Thomas, Grace Toynbee, Martha Whiteley, Sibyl Widdows, and Katherine Isabella Williams. Only Ida Smedley and Martha Whiteley are discussed in this book; Grace Toynbee is mentioned once. Another signer of the petition, Edith Humphrey, was an inorganic chemist, thought to be the first British woman to gain a doctorate in chemistry (at the University of Zurich). On the occasion of the 150th anniversary of the Royal Society of Chemistry, the successor of the Chemical Society, a sample of the original crystals synthesized by Humphrey for her Ph.D. were sent to them by the Swiss Committee of Chemistry, together with a modern circular dichroism spectrum of a solution of one crystal. This box of crystals remains on display in the exhibition room of the Royal Society of Chemistry.

For me as a chemist, chapter 10 was the highlight of the book. While I am deeply interested in the history of suffrage movements, the title led me to expect more coverage of chemists. A book dealing with the status of women scientists at the time of World War I and beyond is bound to be mixture of sociology and science. I feel that the science got covered up by the sociology. Other readers with more tolerance for sociology may feel differently, so they might want to give this book a try.

Connie Hendrickson, Arkon Consultants, Irving, TX, hendrickson@arkonconsultants.com

From Transuranic to Superheavy Elements: A Story of Dispute and Creation, Helge Kragh, Springer Nature, Switzerland, 2018, viii + 106 pp, ISBN 978-3-319-75812-1, $69.99

Plenum enuntiatum: I, the reviewer, am an actor in the "dispute" but will confine my comments as much as possible to the published perspective.

Author Helge Kragh is a prolific and well-known Danish scholar in the history of science with advanced degrees in both philosophy and science and an academic career at Aarhus University and the Niels Bohr Institute. A timely contribution for the International Year of the Periodic Table, this Springer Brief on transuranics and superheavy elements is reasonably complete in its coverage of the international intrigue, competition, duels and eventual cooperation in extending the reach of the Periodic Table by twenty-five percent. In keeping with the philosophy behind the Springer Briefs, this is accomplished in just 80 pages of text including an unobtrusive few figures and tables. The presentation proceeds on a logical timeline with a concise recast of the discovery of radioactivity over a century ago and continuing through the official public disclosure of *oganesson*, element 118 just below *radon* on the Table.

Much of the description of the six-decade trek from transuranics *neptunium* through *oganesson* is presented in a crisp, clear manner. Initial production of *einsteinium* and *fermium* (99 and 100) as the result of an early H-bomb test (now known as a thermonuclear fission-fusion-fission bomb) is the most unusual of the production routes. Syntheses of the elements are not nearly as interesting as the disputes that arose as a consequence of human competitive spirit. Particular emphasis of the story is placed on the more remarkable element discoveries starting with *nobelium* whose discovery by a Swedish-led team was found later to be unsupported and reassigned to the Soviet Union, but with no name change.

The highpoint of the history is the extensive discussion of competing claims between Soviet and American researchers and the battle for names understandably tied to priority for those discoveries. For two decades, element 104 was known both as *rutherfordium* and *kurchatovium*, Igor Kurchatov being the "father of the Soviet atomic bomb project." A subsidiary conflict for element 105 between *hahnium* and *dubnium* was also in play. Attempts by international societies to resolve the conflicts were ineffective, arguably because the quarrel was during the peak of the Cold War. Most formal among the conciliation attempts was the formation of the "TWG," the Transfermium Working Group in 1991, a nine-member panel appointed by the International Union of Pure and Applied Physics (IUPAP) and the International Union of Pure and Applied Chemistry (IUPAC). Criticism of that group's constitution, charge, integrity, conclusions and methodology are accurately covered. The 1992 decision on priorities of discovery assignments, the entitlement to name a discovery, and the acceptability of names was brutally condemned by the nuclear science community although that point is not made clearly enough in Kragh's history. The TWG did do a great service by constructing a formal set of criteria for the discovery of new elements. Imposing these criteria allowed the transuranium element numbers through atomic number 109 to be acknowledged as "discovered" and, with the exception of 106, named. Kragh also notes the neologism "transfermium wars" (coined by this reviewer in 1994) as an expression of the battle over assigned but disputed discovery priorities for the transuraniums, but that was not exactly the case. Transfermium Wars was a phrase introduced to express the outrage felt by all competing discovery institutes and researchers with IUPAC, IUPAP and the TWG over their intrusive diktats on priority and name assignments. Furthermore, the situation was not helped by IUPAC's insistence that unproven element names should be based on a greco-latin three-letter system advocated by J. Chatt in 1979, *ununennium* (Uue) being an example of the only approved name (and symbol) for element 119. This silly system was scorned by the entire nuclear physics and chemistry communities and Kragh does a good job of recognizing its rejection (something IUPAC still does not accept).

And then we get to "*seaborgium*", named in 1994 by the Berkeley heavy element group in honor of then 82-year old Glenn Seaborg, nuclear chemistry behemoth, figuratively and literally. (Seaborg was six feet three inches tall.) Kragh tells us about the attempts of IUPAC to asphyxiate naming of a new element after a living person, a denial of discoverers' rights never before implemented as Kragh clearly describes, although, as Kragh notes, *einsteinium* was named *ante mortem* by the discovery group. This exclusion catalyzed the "war," there being no such obstructive rule in existence (1). Furthermore, IUPAC proclaimed itself the sole body empowered to name a new element in transparent defiance of well-established tradition. Part of the untold history is that this arrogant move by IUPAC was nearly their undoing as an effective international science cooperative.

A beneficial outcome of all this disruption was formation of a new oversight group, the "JWP," Joint

Working Party on the discovery of new elements. "Joint" because it was convened in collaboration between IUPAP and IUPAC. The JWP was chaired by this reviewer for its four incarnations between 1999 and 2016. Kragh did err on the composition and chairmanship of the JWPs in his presentation. Furthermore, there is little recognition of the JWP's deep reliance on the existing (1991) criteria as guidance in concluding their recommendations.

There is a hint of bias (pro-physics) in the author's testimony, but this does not detract in any significant way from the history although it is somewhat irksome to this chemistry chauvinist. In noting that chemistry Nobel laureate Edwin McMillan was not a chemist (he co-discovered the first transuranic, *neptunium*, with Philip Abelson using entirely chemical techniques), Kragh continues to buttress that perceived slight by citing other laureate "physicists" also so miscategorized: Rutherford (yet with an undergraduate degree in chemistry), Marie Curie (a chemist), Francis Aston (who did organic chemistry research), Peter Debye (chair of the Cornell University Chemistry Department), and Gerhard Ertl (surface physical chemist and winner of the Wolf Prize in Chemistry). Kragh refers to "physicist" Lew Keller of the Oak Ridge Transuranium Institute whose training was actually in biochemistry. This reminds me of the continued reference over the past two decades to solar neutrino Nobel Laureate in Physics Ray Davis Jr., as a physicist when he was, in fact, a physical chemist.

There are some curious errors in the work. For instance, "ms" is correctly used in half life values for "milliseconds," but paradoxically, "meV" is incorrectly employed multiple times for "mega (or million) electron volts" rather than the conventional "MeV." A formula on p 64 relating fission half life to Z^2/A is wrong.

The final chapter on philosophical issues is lucid and thought-provoking, discussing the meaning of "discovery," of "element," and of the controversial territorial conflict between chemistry and physics over superheavy elements. The latter should irritate the chemistry readership and hearten some physicists. The discussion, though, is an excellent way to exit the story (for now).

Among unfortunate omissions is speculation on the probable existence of superheavy elements in nature as a result of neutron star collisions and black hole collisions, a surprising oversight considering the author's background in astronomy and cosmology. The index is inadequate and the many acronyms will prove irksome to the nonexpert reader. Al Ghiorso's partially successful early attempt to synthesize element 110 is not mentioned and there is a missed opportunity to explore Amnon Marinov's unconvincing yet intriguing claims for superheavy element discoveries through $Z = 122$ in more detail.

This reviewer was disappointed in the author's reliance on secondary sources rather than original references with many citations extracted from other historical reviews. Finally, an alternative publication (270 pages, Bloomsbury Sigma Press) by Kit Chapman, *Superheavy* has also just been released and covers the same territory but with a greater emphasis on personal stories, conversations, site visits and character insight.

The History of Science and Technology series has 17 titles so far. A companion Springer Briefs series on the History of Chemistry is edited by HIST chair-elect Seth Rasmussen and has 21 titles to date. The Series are an elegant concept and this reviewer looks forward to further publications.

Paul J. Karol, Department of Chemistry, Carnegie Mellon University, pk03@andrew.cmu.edu

Reference

1. This is the equivalent of the following seasonally appropriate fable: Knute Rockne, Notre Dame football coach and chemist, invented and deployed the forward pass. Imagine what the sport would be like today if the opposing coach had then successfully challenged the forward pass insisting it was not allowed despite there being no rule against it!

Instructions for Authors

Can be found at http://acshist.scs.illinois.edu/info/bull-info.php.

The Back Story

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

Koji Nakanishi (May 11, 1925-March 28, 2019), Magician Supreme

When I look back at the most recent Golden Era of Organic Chemistry, I am struck by the overabundance of characters, the mavericks who populated the most elevated ranks of our community. These include, of course, the rock star R. B. Woodward. The contentious H. C. Brown. The anecdote-blessed Vladimir Prelog. The ego-driven, always-marketing Carl Djerassi. The belligerent Michael Dewar. The unconstrained Barry Sharpless. The Mahatma Albert Eschenmoser. The classicist Rolf Huisgen. The towering John D. Roberts. And the magician Koji Nakanishi.

Why do I call Nakanishi a magician? First, his chemistry was magical. Nakanishi and his groups—one at Columbia University, the other at the Suntory Institute for Bioorganic Research—specialized in organic chemistry of highly unstable, short-lived biologically-relevant systems present at vanishingly low concentrations. As summarized by his long-time collaborator Nina Berova (Columbia), Koji "developed microscale isolation and identification protocols for structural and mode of action studies of over 200 molecules, many being endogenous factors or members of new classes of natural products." He invented a exciton-coupled circular dichroism method to determine relative and absolute configuration of polyhydroxyated compounds, especially oligosaccharides. He was attracted to unusual pigment biological properties controlled by chemical processes. For example, he explained the chemistry of a pigment from the tunicate, a marine filter-feeder invertebrate, that sequesters vanadium and phenolic peptide pigments. He studied the structure and function of proteins responsible for visual transduction, responses to light, and proton and chloride pumping. He discovered that porphyrins enhanced night vision in bovine rhodopsin, a pigment found in the rods of the retina. Koji also helped reveal the relationship between ginkgolides and memory. He studied mitomycin C-DNA adducts, juvenile hormones and crustacean molt-inhibiting hormones, antisickling and desickling agents, brevetoxins, radioligands for ecdysone receptors, shark repellants, antimutagens from plants, and so on. Does all of this not sound magical?

Nakanishi practicing a new trick with his wife and two children, 1960.

Koji was a much sought after as a seminar speaker. But he also, literally, was a magician. What was extraordinary, indeed unique about Koji's lectures was the magic show he'd perform afterwards. It took no effort for a seminar organizer to get Koji to agree to a performance. And did the audiences ever howl with joyful appreciation. It was like bringing pizza and beer to a fraternity house! As Koji related in his autobiography (1)

> Before a magic performance for a big audience, I become very nervous until it starts; I seldom become nervous before a lecture. Yasuko [Koji's wife] does not like for me to perform; she says she feels like she is married to a migrating circus entertainer, and says that I perform because I like the limelight. This is not so. Performing magic with tiny, seemingly innocent objects, under a variety of conditions, is a challenge. When I manage to distract an audience of more than 200 by simply moving one hand a mere 20 centimeters, this gives me a feeling of accomplishment. Probably I like to please people, and therefore seeing the audience enjoying themselves satisfies me. The greatest satisfaction comes from mystifying people with tricks based on very simple principles that could be explained in seconds, especially when the trick is one that I have devised. When I have a new trick, either newly bought or a variation of my own, I perform it first for Yasuko. Because over the years she has acquired a fine feeling for how I misdirect people, she is a good litmus test.

Friendships are also magical. I miss my friend. But fortunately, Koji's magic remains.

I thank Nina Berova for helpful discussions.

1. K. Nakanishi, *A Wandering Natural Products Chemist*, In *Profiles, Pathways and Dreams* (J. I. Seeman, Ed.) American Chemical Society, Washington, DC, 1995.

BULLETIN FOR THE HISTORY OF CHEMISTRY

William B. Jensen, Founding Editor
Paul R. Jones, Editor (1995-2010)

EDITOR
Dr. Carmen J. Giunta
Department of Chemistry
Le Moyne College
Syracuse, NY 13214-1301
giunta@lemoyne.edu

ASSOCIATE EDITOR
Dr. Vera V. Mainz
2709 Holcomb Drive
Urbana, IL 61802
mainz@illinois.edu

BOOK REVIEW EDITOR
Dr. E. Thomas Strom
1134 Medalist Dr
Dallas, TX 75232-3021
ethomasstrom@gmail.com

HIST OFFICERS, 2019

Dr. Daniel Rabinovich, Chair
Department of Chemistry
UNC Charlotte
9201 University City Blvd.
Charlotte, NC 28223-0001
drabinov@uncc.edu

Dr. Seth C. Rasmussen, Chair Elect
Dept. Chemistry and Biochemistry
North Dakota State University
NDSU Dept. 2735, P.O Box 6050
Fargo, ND 58108-6050
seth.rasmussen@ndsu.edu

Dr. Vera V. Mainz, Sec/Treas
2709 Holcomb Drive
Urbana, IL 61802
mainz@illinois.edu

Dr. Nicolay V. Tsarevsky, Program Chair
Department of Chemistry
Southern Methodist University
3215 Daniel Ave.
Dallas, TX 75275
nvt@smu.edu

Dr. Mary Virginia Orna, Councilor
Department of Chemistry
College of New Rochelle
New Rochelle, NY 10805
mvorna@cnr.edu

Dr. Roger A. Egolf, Councilor
Pennsylvania State University - Lehigh Valley Campus
2809 Saucon Valley Road
Center Valley, PA 18034
rae4@psu.edu

Dr. Arthur Greenberg, Alternate Councilor
Department of Chemistry
University of New Hampshire
Parsons Hall
Durham, New Hampshire 03824
art.greenberg@unh.edu

Dr. David E. Lewis, Alternate Councilor
Department of Chemistry
UW-Eau Claire
PO Box 4004
Eau Claire, WI 54702-4004
lewisd@uwec.edu

Dr. John B. Sharkey, Archivist
1559 Grouse Lane
Mountainside, NJ 07092
johnbsharkey@me.com

Dr. Gary Patterson, Historian
3725 Wauna Vista Drive
Vancouver, WA 98661
gp9a@andrew.cmu.edu

The BULLETIN FOR THE HISTORY OF CHEMISTRY (ISSN 1053-4385) is published biannually by the History of Chemistry Division of the American Chemical Society. All matters relating to manuscripts, book reviews, and letters should be sent to Dr. Carmen J. Giunta, Editor. Subscription changes, changes of address, and claims for missing issues, as well as new memberships, are handled by the Sec./Treas.

BULLETIN FOR THE HISTORY OF CHEMISTRY
Dr. Carmen J. Giunta, Editor
Le Moyne College
Department of Chemistry
1419 Salt Springs Rd.
Syracuse, NY 13214-1301

Non-Profit Org
U.S. Postage
PAID
Permit No. 2471
Syracuse, NY

BULLETIN FOR THE HISTORY OF CHEMISTRY
Subscription and Membership Application

____ ACS Member at $20/year (includes HIST Division membership)
____ Associates: $25/year
____ Associates outside North America: $30/year
____ Annual Library Subscription: $40/domestic; $44/foreign

Begin subscription with the year 20 __

Name ____
Address ____
Signature ____

Return to Dr. Vera V. Mainz, HIST Secretary/Treasurer, 2709 Holcomb Drive. Urbana, IL 61802.
Checks should be made payable to the Division of the History of Chemistry, American Chemical Society.