Atomic Volumes from a Forgotten Physical Chemist

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The Cover … Atomic Volumes from a Forgotten Physical Chemist. See p. 74.

INTRODUCTION TO AN ENGLISH TRANSLATION (ABRIDGED) OF KIZHNER'S PIONEERING PAPERS ON DEOXYGENATION

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Translators' Preface (1)

Just over a century ago, in 1911, the two papers that are the subject of this abridged translation (2) appeared in the *Zhurnal Russkago Fiziko-Khimicheskago Obshchestva.* The first describes the reactions of the hydrazones (generically called alkylidenehydrazines in the papers) from saturated ketones with potassium hydroxide to give the corresponding saturated hydrocarbon. The second describes the reaction of the hydrazones of aldehydes and unsaturated ketones with potassium hydroxide to give hydrocarbons. These two papers established the basic requirements for the reduction of carbonyl compounds through base-promoted decomposition of the hydrazones. Eighteen months later, Ludwig Wolff published his version of the same reaction, by heating semicarbazones with sodium ethoxide to give the corresponding hydrocarbons (3).

Nikolai Matveevich Kizhner (1867-1935) led one of the most eventful lives of any organic chemist of Russia during the late Imperial and early Soviet periods of Russian history. A student of Markovnikov at Moscow, he was recruited to Tomsk, in Siberia, as the inaugural Professor of Organic Chemistry at the Imperial Tomsk Technological Institute (now Tomsk Polytechnic University) immediately following his graduation into the Dr. Chem. degree. The most comprehensive biographies of Kizhner (4) are almost all in Russian; materials in English include a brief biographical sketch (4d), a somewhat longer biography (4e), and a paper analyzing Kizhner's career in Tomsk (4f).

Kizhner worked at Tomsk for the first fourteen years of the twentieth century, building a first-rate laboratory, and discovering the two reactions that carry his name. After just three years at Tomsk, he fell victim to "gangrene of the limbs," which eventually necessitated the amputation of both legs below the knee. He discovered both of the reactions for which he is known after he had lost both lower legs and was confined to a wheelchair. His progressive political activities proved to be dangerous in a conservative city like Tomsk; he was exiled from the city and the steppes region of Siberia early in 1906, by orders of the Governor-General of western Siberia. His reinstatement over a year later on the orders of the Minister of Education did not meet with universal approval, and in 1912 he resigned his position, albeit under duress.

His return to Moscow, where he spent the rest of his life, began in 1914 with an appointment to the Shanyavskii People's University. This was quickly followed by the October Revolution and the establishment of the Soviet state in 1917, with the accompanying seismic shift in research priorities from basic to applied research topics. For Kizhner, this meant his transfer in 1919 to become the Director of the Aniline Trust Institute (a relatively thankless and monotonous task), where he built the Soviet dye industry, eventually becoming an Honorary Member of the Soviet Academy of Sciences. Like many Russian organic chemists at the time, his creativity and productivity was curtailed during the Soviet era, as a result of his efforts becoming focused on industrial problems instead of basic scientific questions to meet the mandates of the new Soviet economic system.

Nevertheless, he continued to carry out original research, in addition to studying the problems in applied chemistry demanded by the Soviet economic plan.

The historical importance of these papers, neither of which has ever appeared in English, lies in their report of an unprecedented reaction, for which Ludwig Wolff initially received the accolades, even though his publication (3) appeared some eighteen months later. Because a small minority of native speakers of western European languages can read Russian, these papers have not been as accessible to readers as those in French or German. The two papers also provide excellent examples of the practice of organic synthesis in early twentieth-century Russia by a superb (and prolific) practitioner of the art.

Kizhner was a meticulous experimenter, so his work provides a window into the practice of organic synthesis in the era before chromatography and modern spectroscopy. These two papers are especially instructive in how structural information was gleaned from measurements of physical constants. Combustion analysis for carbon and hydrogen, and the Dumas method for determining nitrogen (5), were the cornerstones of characterization of new compounds. In the absence of chromatography, mixtures were separated by fractional crystallization for solids, and by both fractional distillation and by steam distillation for liquids. All boiling points were reported using calibrated thermometers, and with the pressure specified, thus allowing them to be corrected to normal boiling points. The refractive index and density of compounds were important parameters of molecular structure and composition by virtue of their combination into the molecular refractivity (A, but R was used by Kizhner) of the compound. This fascinating constant was much used by Kizhner in his work. It is a measure of the total polarizability of a mole of the substance. The definition currently used is

$$R = \frac{\left(n^2 - 1\right)}{\left(n^2 + 2\right)} \frac{M}{\rho} ;$$

it has the advantage that it is almost independent of the density, temperature and aggregation state of the compound, and that it can be predicted on the basis of simple addition of the of contributions from bonds, atoms or groups (CH, CH_2, CH_3, CO, etc.) within the molecule. The value may also be approximated by

$$A = \frac{M}{\rho} \frac{n^2 - 1}{3}$$

(6). The usefulness of this constant lay in the fact that the value of the molar refractivity could be calculated, and that measured values that diverged significantly from the calculated values were suspect, and could be used as evidence that a proposed structure was wrong.

The Translations

Russian presents an interesting challenge to the translator in several ways. There is, of course, the difference in alphabet: Russian uses the Cyrillic alphabet. This difference is somewhat exacerbated because the papers translated here were written before the Russian Revolution of 1917. In 1918, four letters of the alphabet that occur in the original documents (Table 1) were eliminated from Russian orthography during the period when the spelling of Russian was simplified and consolidated; these letters were eliminated due to their compete homophony with those that were retained.

Table 1. Letters eliminated from the pre-Revolutionary Russian alphabet in 1918

Letters eliminated in 1918	Modern Russian equivalents
I i	И и
Ѳ ѳ	Ф ф
Ѣ ѣ	Е е
V v	И и

In addition, other spelling simplifications were instituted at the same time for much the same reason: complete hompohony with existing letter combinations. Thus, words ending in "аго" before 1918 now carry the ending "-ого" instead (the pronunciation of both is identical); likewise, the consonantal combination, "зс" was replaced by the combination "сс," as illustrated in the words изслѣдованіе and исследование (investigation)—again, the pronunciation of both spellings is actually identical.

The next major complication for the translator is that the verb "to be" is almost never used in the present tense, which means that many sentences have no explicit main verb. Moreover, there are neither direct nor indirect articles in Russian, which means that it is the job of the translator to supply them as appropriate. The next, and

perhaps most significant, challenge to the translator is the fact that since all words except prepositions are either declined or conjugated, word order is of relatively less importance in the sentence. In some ways, this makes translating Russian rather like translating Latin: the endings of the words specify their function in the sentence, so the exact order of words in the sentence has less impact. But, at the same time, word order *does* matter: it is often found that the most important idea in the sentence comes either at the beginning of the sentence, or at the end; how this emphasis is handled in the English translation is frequently one of the most difficult jobs for the translator.

As with any translation, a literal (or close to literal) translation of the original would result in very stilted English prose. In part, this comes from the propensity of Russian authors to write exceptionally long sentences. In fact, it is not unusual to find that a whole paragraph may consist of a single sentence—Kizhner's writing certainly fits this pattern. This situation is clearly untenable in English, so we have permitted ourselves the small luxury of breaking overly-long Russian sentences into smaller English ones. There are also a number of paragraphs in these papers that are composed of single, short sentences, where the ideas are so closely connected that translating them as separate paragraphs in English is effectively ungrammatical. These sentences we have consolidated into single paragraphs, as would be required by good English prose. In making these stylistic changes, we have sought to preserve the author's meaning, while making the English readable. We hope that we have accomplished this goal in the translations that follow.

Fortunately, Kizhner's Russian is fairly straightforward and free of idioms, making the two papers relatively easy to read and translate into good idiomatic English. As an added bonus for the translator, at least, the archaic names for some compounds add an interesting patina to the first translations of the original documents (for example, potassium ferricyanide is the "bloody red salt," and potassium permanganate is "chameleon"). In this translation, archaic and European usages have been changed to modern American usage (e.g. 21°,48 is rendered as 21.48°), but Kizhner's characterization of the hydrazones as alkylidenehydrazines has been retained. The name, "camphane" has also been retained in place of the more modern "bornane."

The references and notes have been re-numbered sequentially, and gathered at the end of the translations in conformity with *Bulletin* practice; they have been cast in their modern forms, but the original version of each citation has been preserved as well. The reproduction of the original drawings directly from the original papers by scanning or other methods gave poor results, and therefore the original drawings have been re-drawn using modern drawing programs, while preserving an appearance as close to the original as possible.

As with any translation, there are places where a literal translation of the original into English leads to ambiguity. In those places, we have chosen to preserve, as best we could, Kizhner's intended meaning, rather than adhering slavishly to a verbatim translation. This translation is the work of a native speaker of Russian, Mr. Suntsov, who is a recent graduate with a B.S. in biology and chemistry, while he was an undergraduate student at UW-Eau Claire. He prepared a relatively modern translation of Kizhner's original papers, and Dr. Lewis, who is a native English speaker, edited the translation to restore some of the chemical subtleties that would not be common knowledge to an undergraduate student in biology. Any deficiencies in this translation should be attributed to Dr. Lewis.

References and Notes

1.   Transliteration from the Cyrillic alphabet presents a recurring problem for western writers, translators and publishers referring to Russian authors and articles. The exact transliteration used will depend on the writer, and on the language into which the article or name is translated/transliterated. In this paper, we have adhered to our previous practice of transliterating the Cyrillic using the BGN/PCGN romanization system for Russian as the most intuitive for English speakers. In this system, the name of the subject chemist becomes Kizhner.

2.   We have availed ourselves of the opportunity to place the complete text of both papers in Supplemental material accompanying the translations. This has allowed us to minimize the amount of repetitive characterization data in the experiments, while retaining the narrative of the experiments. For the Supplemental material, go to the journal's website, www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

3.   L. Wolff, "Methode zum Ersatz des Sauerstoffatoms der Ketone und Aldehyde durch Wasserstoff," *Justus Liebigs Ann. Chem.*, **1912**, *394*, 86-108.

4.   There are relatively few biographies of Kizhner available, and almost all are in Russian. Most are focused on his scientific accomplishments and contain relatively little personal information: (a) S. S. Nametkin, *N. M. Kizhner. Issledovaniya v Oblasti Organicheskoi Khimii [N. M. Kizhner. Investigations in the Field of Organic Chemistry]*, Akad. Nauk SSSR, Moscow, 1937. (b) T. V. Boratova and E. A. Zaitseva, "Nikolai Matveevich Kizhner," *Khimiya*, **1996**, *39*, 2. For a biographical sketch

containing more personal details during his Tomsk period, see: (c) V. D. Yushkovskii, "IV. Iz istorii Tomskogo Politekhnicheskogo Universiteta. Protivostoyanie Tomsk v sud'be professora Kizhnera [From the history of Tomsk Polytechnic University. Confrontation in the fate of Professor Kizhner at Tomsk]," *Izv. Tomskogo Pol-ka. Uni-ta.,* **2002**, *305*, 208-221. (d) D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer, Heidelberg, 2012, pp 105-106. (e) D. E. Lewis, "Disability, Despotism, Deoxygenation—From Exile to Academy Member: Nikolai Matveevich Kizhner (1867-1935)," *Angew. Chem. Int. Ed.*, **2013**, *52*, 11704-11712. (f) V. Suntsov and D. E. Lewis, "A Century of Base-promoted Decomposition of Hydrazones: the Early Career of Nikolai Metveevich Kizhner (1867-1935)," *Bull. Hist. Chem.*, **2014**, *39*, 43-52.

5. A more modern variant involved replacing the oxygen gas with a mixture of copper oxide and calcium carbonate and lowering the oxidation temperature to 550°C to slow down the combustion process and thus avoid loss of volatile materials and nitrogen: F. Shea and C. E. Watts, "Dumas Method for Organic Nitrogen," *Ind. Eng. Chem. Anal. Ed.*, **1939**, *11*, 333-334.

6. M. Born and E. Wolf, *Principles of Optics*, 4th ed., Pergamon Press, Oxford, 1970, pp 88-90.

About the Authors

Vladislav Suntsov was born in Russia and moved to the United States in 2007. He graduated from the University of Wisconsin-Eau Claire in May 2013, with a major in biology and a minor in chemistry. He carried out research in organic synthesis and the history of chemistry with Dr. David E. Lewis during his senior year. He is currently a medical student at Arizona College of Osteopathic Medicine. He is beginning his clinical studies at the Chicago campus.

David E. Lewis is Professor of Chemistry at the University of Wisconsin-Eau Claire and a former Chair of HIST. A frequent contributor to the *Bulletin*, he is most recently author of *Advanced Organic Chemistry* (Oxford University Press, 2016) and a forthcoming Russian translation of his collected papers in the history of chemistry (Kazan University Press).

PRIMARY DOCUMENTS

25. THE CATALYTIC DECOMPOSITION OF ALKYLIDENEHYDRAZINES AS A METHOD FOR THE PREPARATION OF HYDROCARBONS (ABRIDGED)

N. Kizhner
Zhurnal Russkago Fiziko-Khimicheskago Obshchestva, **1911**, *43*, 582-595.
Translated by Vladislav Suntsov and David E. Lewis

Supplemental Material

Introduction

The oxidation of primary hydrazines of the aliphatic and cyclic series, our studies have shown, yields the same products as oxidation of primary aromatic hydrazines. Just as in the last case, the identity of the oxidation products depends on the conditions under which the oxidation takes place.

During oxidation in an alkaline medium, the hydrazine group is substituted by hydrogen; the reaction proceeds so smoothly that it can be used as a method for producing hydrocarbons. During oxidation in an

acidic medium, the hydrazine group is replaced by the acid radical. This reaction is common to primary hydrazines of all classes: chlorobenzene is obtained from the oxidation of phenylhydrazine with copper sulfate in hydrochloric acid solution (Gattermann); under the same conditions, menthylhydrazine yields menthyl chloride and menthene, as the products of the decomposition of the first compound (Kizhner).

The sequence of the mechanism by which acidic oxidation of hydrazines occurs is clear: the reaction forms a diazonium salt intermediate, which dissociates in the conditions of the earlier reaction, forming a halo derivative of the hydrocarbon:

$$C_6H_5NHNH_2 \rightarrow C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$$

$$C_{10}H_{19}NHNH_2 \rightarrow [C_{10}H_9N_2Cl] \rightarrow$$
$$C_{10}H_{19}Cl \rightarrow C_{10}H_{18} + HCl$$
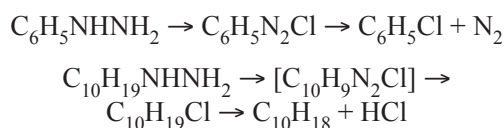
The work of E. Fischer confirms the correctness of this view of the process of oxidation of primary hydrazines: careful oxidation of phenylhydrazine sulfate with silver oxide results in formation of benzenediazonium sulfate. E. Fischer has obtained a salt, $C_2H_5N=NSO_3K$, of the explosive diazoethanesulfuric acid by the oxidation of potassium ethylhydrazine sulfate, with silver oxide. With regard to the mechanism of the oxidation of hydrazines in alkaline medium, one is limited just to guesses.

Working on this question 11 years ago (1), I settled on this explanation of the process: I can only explain the transformation of the hydrazine to saturated hydrocarbons during oxidation in alkaline medium by formation of an intermediate product of this type: $[C_nH_{m-1}].N=NH$. I see the probability of the formation of such a substance being easier in the oxidation of primary hydrazines of the type, R–NHNH$_2$, in comparison to secondary hydrazines

$$\begin{array}{c} R \\ \\ R \end{array}\!\!\Big\rangle N\!-\!NH_2,$$
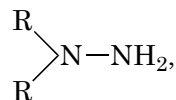
which points to greater mobility of the hydrogen on the NH group compared to that of hydrogens on the amide group. In this case, the first product of the oxidation of the primary hydrazines could be a substance of this type of structure: R–N(OH)–NH$_2$. Loss of water will lead to a product, R–N=NH, which decomposes with the formation of saturated hydrocarbons and nitrogen according to the following equation (2)

$$[C_nH_{m-1}]N:NH \rightarrow C_nH_m + N_2$$
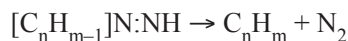
The data I obtained recently while studying alkyli-

denehydrazines (C_nH_{m-2}):N–NH$_2$ convince me that the views presented on the mechanism of the oxidation of primary hydrazines in alkaline medium are correct.

When heated in the presence of a small amount of solid potassium hydroxide, alkylidenehydrazines decompose according to following equation:

$$[C_nH_{m-2}]:NNH_2 \rightarrow C_nH_m + N_2$$

Thus the catalytic decomposition of alkylidenehydrazines leads to the formation of the very products that are obtained in the oxidation of primary hydrazines with an alkaline solution of potassium ferricyanide.

If we assume that in the last reaction, the alkylidenehydrazine is formed as the first intermediate, one would have to assume that the alkylidenehydrazine would decompose in an aqueous alkaline solution at low temperature (below 100°) according to this equation:

$$[C_nH_{m-2}]:N–NH_2 \rightarrow N_2 + C_nH_m.$$

However, experience has shown that alkylidenehydrazines can be steam distilled from a concentrated solution of caustic alkali without showing any noticeable trace of degradation. It follows that they cannot be the intermediates in conversion of hydrazines into hydrocarbons. The most likely explanation is the one previously mentioned: the formation of an unstable "diazo" form:

$$[C_nH_{m-1}]N=NH$$

The mechanism of the conversion of alkylidenehydrazines to hydrocarbons can be explained if prior isomerization of the alkylidenehydrazone into an unstable "diazo" form by the action of the caustic alkali is allowed:

$$[C_nH_{m-2}]:N–NH_2 + KOH \rightarrow$$
$$[C_nH_{m-1}].N—NH_2 \rightarrow$$
$$|$$
$$OK$$
$$[C_nH_{m-1}].N=NH + KOH \rightarrow C_nH_m + N_2$$
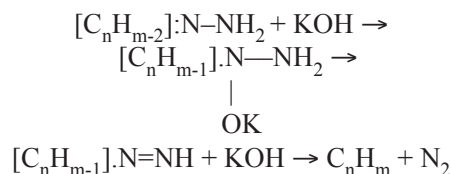
Experimental Part

The decomposition of alkylidenehydrazines was usually conducted as follows:

A Wurtz flask is connected to a dropping funnel and a water-cooled condenser; 1 to 2 grams of dry potassium hydroxide are placed in the flask prior to that. After adding a small amount of the alkylidenehydrazine, the mixture is heated on a grid (3) until nitrogen is evolved, after which the reaction continues by itself, and the hydrocarbon is distilled

into the receiver flask. Of all the alkylidenehydrazines studied, the decomposition of cyclohexylidenehydrazine hydrate is the most energetic; if enough of this substrate is used at one time, the reaction may end with an explosion.

Decompositions of the following alkylidenhydrazines are described in this article:

1. 1,3-methylcyclohexylidenehydrazine *[Now known as 3-methylcyclohexanone hydrazone —translators]*

2. Thujylidenehydrazine *[thujone hydrazone]*

3. Camphylidinehydrazine *[camphor hydrazone]*

4. Fenchylidinehydrazine *[fenchyl hydrazone]*

5. Cyclohexylidenehydrazine hydrate *[cyclohexanone hydrazone hydrate]*

The decomposition of cyclohexylidenehydrazine hydrate is interesting in that, besides producing the normal decomposition product, cyclohexane, it yields cyclohexanol (in almost equal proportions), which is responsible for cleavage of the nitrogen in the form of hydrazine hydrate.
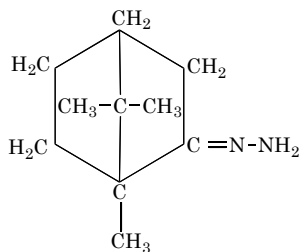
1. Catalysis of 1,3-methylcyclohexylidenehydrazine. $CH_3C_6H_9{:}NNH_2$.

... [For the complete experimental details, see the Supplemental material.]

2. Catalysis of thujylideneehydrazine $C_{10}H_{16}{:}N{-}NH_2$.

... [For the complete experimental details, see the Supplemental material.]

3. Camphylidinehydrazine and its conversion to camphane:

Camphylidinehydrazine was obtained by continuous boiling of an alcoholic solution of camphor and hydrazine hydrate. Because the conversion of camphor to camphylidinehydrazine is accompanied by a change in the sign of optical rotation, the reaction could be followed with a polarimeter; the rotation was measured after each 11 to 12 hour period of continuous boiling. The reaction

was conducted using 200 g of camphor, 200 g of a 50% solution of hydrazine hydrate, and 750 cc of alcohol; the resulting solution was boiled on a hot water bath for a total of 170 hours. Before boiling the optical rotation of the solution was: $\alpha = +7.23°$.

Here is a table of the rotations measured at indicated time intervals:

1) +2.60°; 2) +1.17°; 3) +0.26°; 4) –0.52°; 5) –1.28°; 6) –1.93°; 7) –2.35°; 8) –2.83°; 9) –3.14°; 10) –3.36°; 11) –3.72°; 12) –3.94°; 13) –4.28°.

After distillation of the alcohol on the water bath, the camphylidinehydrazine is separated from the water, and extracted with ether. The ether is thoroughly dried with fused potassium carbonate. After distilling the ether, the product is distilled under reduced pressure.

Camphylidenehydrazine boils at 143° at 33 mm; upon cooling it crystallizes into a white crystal mass, which melts at 53-55°.

Determination of N.

Weighed:	0.1709 g: 25.9 cc N (18.5°, 750 mm)
$C_{10}H_{18}N_2$ calculated % N –	16.86
Found % N –	17.14

Rotation in absolute ether solution:

Concentration: 9.9000 g in 100 cc of solution
$\alpha = -4.77°$; $[\alpha]_D = -40.81°$

Rotation in 90% alcohol:

Concentration: 5.309 g in 100 cc of solution
$\alpha = -1.65°$; $[\alpha]_D = -32.74°$

Camphilidinehydrazine and water form a liquid hydrate, which is soluble in water. Apparently, this leads to reduction in optical rotation when it is in alcohol-water solution.

The hydrochloride $C_{10}H_{16}{:}NNH_2 + HCl$ forms a white precipitate when dry hydrogen chloride is passed through a solution of camphylidinehydrazine in absolute ether. The precipitate is washed with absolute ether and vacuum dried at 180°.

Determination of N

Weighed 0.2012 g; 24.1 cc N (19°, 757 mm)

$C_{18}H_{18}N + HCl$ Calculated % N – 13.65

Found % N – 13.82

The hydrochloride is easily dissolved in water. The solution may be stored for long periods of time without degrading at room temperature.

Rotation in aqueous solution:

Concentration: 0.8521 g in 10 cc of solution;
$\alpha = -2.67°$; $[\alpha]_D = -31.33°$.

When a solution of camphylidehehydrazine is boiled with excess hydrochloric acid, total hydrolysis to camphor and the salt of hydrazine takes place. The camphor obtained has the following rotation:

Solvent: absolute alcohol

Concentration: 0.7998 g in 10 cc of solution;
$\alpha = +3.34°$; $[\alpha]_D = +41.76°$.

Camphanazine $C_{10}H_{16}{:}N\text{-}N{:}C_{10}H_{16}$

Camphanazine was synthesized by A. Angeli and V. Castellana (4) during the reduction of pernitrosocamphor

$$C_8H_{14} \Big\langle \begin{matrix} C{:}N_2O_2 \\ | \\ CH_2 \end{matrix}$$
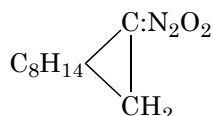
I prepared this compound by hydrolyzing camphylidinehydrazine.

In excess hydrochloric acid, as previously noted, camphylidinehydrazine is completely decomposed into camphor and hydrazine hydrochloride, as follows:

$C_{10}H_{16} : NNH_2 + 2\ HCl + 2\ H_2O \rightarrow C_{10}H_{16}O + N_2H_4 2HCl.$
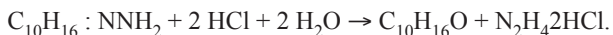
However, if during the hydrolysis of one molecule of camphylidinehydrazine only one molecule of hydrochloric acid is used, in other words, the hydrolysis of camphylidinehydrazine hydrochloride $C_{10}H_{16} : N\text{–}NH_2$. HCl occurs, a significant amount of camphanazine is formed, in addition to the camphor.

Shown schematically, the process of forming camphanazine under these conditions can be expressed by the equation:

$$C_{10}H_{16} : NNH_2.HCl + C_{10}H_{16}O \rightarrow$$
$$C_{10}H_{16} : N\text{–}N : C_{10}H_{16} + H_2O + HCl.$$
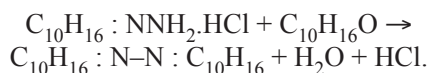
This equation, however, does not explain the actual mechanism of camphanazine formation. This is evident from the fact that camphanazine results from the hydrolysis of camphylidinehydrazine hydrochloride in an aqueous solution, where camphor should be removed from the reaction due to its insolubility in water. In addition, direct experiments have shown that camphor does not react with camphylidinehydrazine even after prolonged boiling in alcohol solution.

A solution of camphylidinehydrazine (80 grams) with an equivalent (1 mol) of hydrochloric acid was boiled on a water bath for a few hours; a copious precipitate, which was a mixture of camphor and camphanazine, deposited. The camphor was removed from the mixture by means of steam; the remainder (22 g) is almost pure camphanazine. The yield is 27%, based on camphylidinehydrazine. If the hydrolysis of the hydrochloride is performed in ethanol solution, instead, the yield does not change.

To a solution of 30 g. of camphylidenehydrazine in 200 cc of alcohol were added 15 cc of fuming hydrochloric acid (1 mol). After boiling the solution under reflux on a water bath for three hours, the alcohol and camphor were removed by steam distillation. The residue yielded 7 g of camphanazine (23%).

From ethanol, camphanazine crystallizes as large octahedral crystals or as hexagonal plates. Melting point 185-186° (Angeli's: 185°).

Determination of nitrogen:

Weighed:	0.1865 g: 15.4 cc N (23°, 780 mm)
$C_{10}H_{32}N_2$ calculated % N –	9.33
Found % N –	9.51

On heating with fuming hydrochloric acid on a water bath, camphanazine is decomposed quantitatively according to the equation:

$$C_{10}H_{16} : N\text{–}N : C_{10}H_{16} + 2\ H_2O + 2\ HCl \rightarrow$$
$$2C_{10}H_{16}O + N_2H_4 . 2HCl.$$
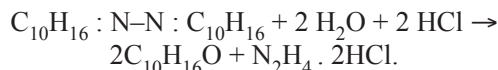
From 13 g of the azine were obtained 12 g of camphor and 4 g of hydrazine hydrochloride salt. By theory, 13.2 camphor and 4.5 g hydrazine hydrochloride should be obtained.

Camphanazine rotates the plane of polarization plane to the left, but the magnitude of the rotation varies greatly depending on the nature of the solvent.

1. Solvent: benzene;

concentration: 0.5708 g in 10 cc of solution,
$\alpha = -5.27°$. $[\alpha]_D = -92.33°$.

2. Solvent: ether (abs.);

concentration: 0.4064 g in 10 cc of solution,
$\alpha = -3.66°$. $[\alpha]_D = -90.66°$.

3. Solvent: CH_3OH;

concentration: 0.3542 g in 10 cc of solution,
$\alpha = -1.32°$. $[\alpha]_D = -37.27°$.

4. Solvent C_2H_5OH;

concentration: 0.5769 g in 10 cc of solution,
$\alpha = -1.11°$. $[\alpha]_D = -19.25°$.

5. Solvent $CH_3CH_2CH_2OH$;

concentration: 0.5501 g in 10 cc of solution,
$\alpha = -0.78°$. $[\alpha]_D = -14.18°$.

Rotation in benzene and absolute alcohol mixtures:

90% C_6H_6 + 10% C_2H_5OH; $[\alpha]_D = -47.80°$.

57.4% C_6H_6 + 42.6% C_2H_5OH; $[\alpha]_D = -30.15°$.

16.3% C_6H_6 + 83.7% C_2H_5OH; $[\alpha]_D = -25.39°$.

Camphane from Camphylidinehydrazine

... [For the complete experimental details, see the Supplemental material.]

4. Conversion of Fenchone to Fenchane.

In collaboration with A. Proskuryakov

... [For the complete experimental details, see the Supplemental material.]

The structure of the resulting hydrocarbon is deduced from the structure of fenchone, and if Semmler's formula for the latter is adopted, a description of the transformations can be expressed as follows:

Fenchone   Fenchylidenehydrazine   Fenchane
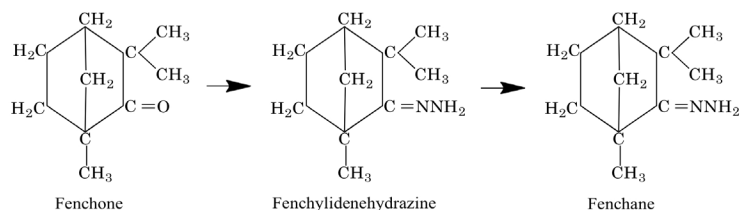
... [For the remainder of this section of the experimental, see the Supplemental material.]

5. Catalysis of Cyclohexylidinehydrazine

... [For this section of the experimental, see the Supplemental material.] Tomsk, March 7, 1911

Supplemental Material

An unabridged translation of this paper can be found in the Supplemental Material for the *Bulletin for the History of Chemistry* at the journal's website,

www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

References and Notes

1. N. Kizhner, "O prevrashcheniyahk bromaminov pod vliyaniem okisi serebra i gidroksilamina [On the transformation of bromoamines with silver oxide and hydroxylamine]," *Zh. Russ. Fiz.-Khim. O-va.*, **1905**, *31*, 1033-1062. Cited in the original as Ж. Р. Х. О. 31, 1043 (1899).

2. [In some reactions, Kizhner used reaction arrows and sometimes equals signs to separate products from reactants. He sometimes also used equals signs within formulas to indicate a double bond. We use a reaction arrow consistently for the former purpose. —translators]

3. [This appears to be a specific type of heating apparatus, but we are unable to identify it. —translators]

4. A. Angeli and V. Castellana, "Ueber einige Derivate des Kamfers." *Chem. Zentralbl.*, **1905**, *II*, 623-624. Abstracted article: "Sopra alcuni derivati della canfora," *Atti R. Accad. del Lincei Roma* [*5*], **1905**, *14*, I, 669-677. Cited in the original as Cbl *1905*, II, 623.

PRIMARY DOCUMENTS

27. ON THE CATALYTIC DECOMPOSITION OF ALKYLIDENEHYDRAZINES. (SECOND PART) (ABRIDGED)

N. Kizhner

Zhurnal Russkago Fiziko-Khimicheskago Obshchestva, **1911**, *43*, 951-962.
Translated by Vladislav Suntsov and David E. Lewis

Supplemental Material

In the previous article, a method for obtaining hydrocarbons based on the catalytic decomposition of alkylidenehydrazines of the type $R:N–NH_2$ in the presence of potassium hydroxide, was described.

In this direction, so far only alkylidenehydrazines originating from ketones (cyclic and bicyclic series) have been studied. In terms of the generalization of the method, it was interesting to explore the decomposition of alkylidenehydrazines of the aldehyde type, as well as to extend it to hydrazine derivatives with the character of an unsaturated ketone.

In this paper, the extension of our method to two series of unsaturated cyclic ketones, dihydrocarvone and carvenone, and the two unsaturated fatty aldehydes, citronellal and citral, is described.

$\Delta^{8(9)}$-Menthene from Dihydrocarvone

Dihydrocarvone was obtained by Wallach (1) by direct reduction of dextrorotatory carvone (from Schimmel: $[\alpha]_D = +61.58°$) with zinc dust and caustic potash in aqueous alcohol solution; the properties of dihydro-

carvone (from the bisulfite compound): boiling point 222.5° at 752 mm.; $[\alpha]_D = -18.36°$.

The compound of dihydrocarvone with hydrazine, $C_{10}H_{16}:NNH_2$, was obtained as follows: a solution of 17 g. of dihydrocarvone and 25 g. 50% hydrazine hydrate in alcohol was boiled under reflux for 5 hours, after which the alcohol and part of the hydrazine hydrate were distilled from an oil bath (bath temperature 140°). The base was dried by warming with fused potash on a water bath.

The decomposition of the base when heated with potassium hydroxide is very easy. The hydrogen [*hydrocarbon?* —translators] was distilled with steam, washed with 50% acetic acid, then with water, and dried with calcium chloride. Yield: 8 g. of hydrocarbon. Purified

dihydrocarvone

$\Delta^{8(9)}$-menthene

by boiling over sodium, the hydrocarbon boils at 170° at 750 mm. The smell of the hydrocarbon is very weak, only slightly reminiscent of menthene.

... [For the characterization data, see the Supplemental material.]

Since it is derived from dihydrocarvone, the hydrocarbon should have the structure of $\Delta^{8(9)}$-menthene [see scheme above].

The $\Delta^{8(9)}$-menthene obtained by Perkin (2) from n-menthanol(8) [i.e. 8-hydroxy-p-menthane —translators] boils at 170-170.5° at 746 mm.

Isomerization of the Hydrocarbon

6 cc of the hydrocarbon were converted into the bromide $C_{10}H_{19}Br$ by first shaking with 20 cc of fuming hydrobromic acid, cooling in ice water, and subsequently at room temperature. Yield: 8 g of the bromide (in place of 7.75 g). On distillation with aniline, the bromide was converted to a hydrocarbon. After washing to remove aniline, and boiling over sodium, the hydrocarbon had the following properties: boiling temperature: 170.5-172.5° at 752 mm; $d\frac{20}{0} = 0.8182$; $n_D = 1.4560$; mol. ref. (3) R^2

= 45.85. Calc. for $C_{10}H_{18}$ $R^2 = 45.63$. Optically inactive.

The increase in the weight of the fraction boiling higher than the starting hydrocarbon is due to the partial isomerization of $\Delta^{8(9)}$-menthene to $\Delta^{4(8)}$-menthene:

$\Delta^{8(9)}$-menthene $\Delta^{4(8)}$-menthene
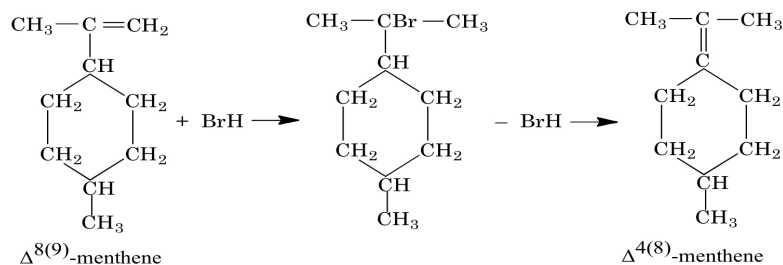
$\Delta^{4(8)}$-Menthene, obtained by Wallach (4) by the slow distillation of 4-methylcyclohexene-isobutyric acid boils at 172-174°; $d_{21} = 0.831$; $n_D = 1.4647$; when boiled with dilute sulfuric acid, $\Delta^{4(8)}$-menthene is isomerized to Δ^8-menthene (5). With this purpose, the hydrocarbon described above was heated under reflux for 8 hours with 20% sulfuric acid. After that, the hydrocarbon boiled at

170-171.5° at 766 mm.; $d\frac{20}{0} = 0.8156$; $n_D = 1.4540$.

... [For the characterization data, see the Supplemental material.]

1. Inactive Δ^3-menthene from carvenone.

Carvenone was prepared as follows: 1 vol. dihydrocarvone was dissolved in 1½ vol. of fuming hydrobromic acid under cooling in ice-water; when diluted with water

carvenone Δ^3-menthene
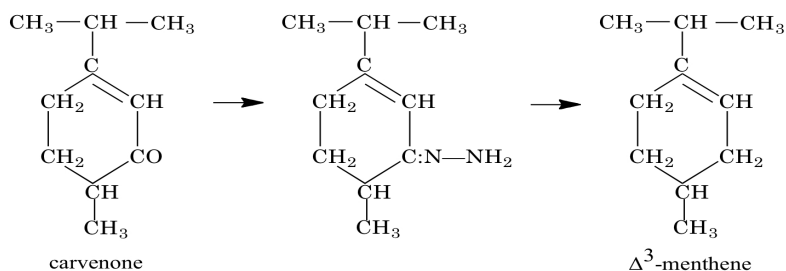
a dense bromide precipitated, from which carvenone with the following properties was obtained by decomposition with alcoholic alkali by heating on a water bath: b.p.

233.5-234.5° at 750 mm.; $d\frac{20}{0} = 0.9263$; $n_D = 1.4828$;

optically inactive; semicarbazone melts at 201°.

The compound of carvenone with hydrazine $C_{10}H_{16}$:NNH_2 was obtained by refluxing an alcoholic solution of 8 g. of carvenone and 8 g. of 50% hydrazine hydrate. After distilling off ethanol in an oil bath at 140°, the base was dried with fused potash by heating on a water bath, and then decomposed by distillation in the presence of fused potassium hydroxide. The distillate was redistilled with steam, washed with 50% acetic acid and water and dried over calcium chloride. The yield was 4 g. of hydrocarbon. After boiling over sodium, the hydrocarbon boiled at 168.7° at 750 mm.

... [For the complete experimental details of this part of this section, see the Supplemental material.]

The conversion of carvenone to Δ^3-menthene may be expressed as follows [see scheme above].

2. The conversion of citronellal to the hydrocarbon

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \Big\rangle C : CH . CH_2 . CH_2 . CH(CH_3) . CH_2 . CH_3.$$
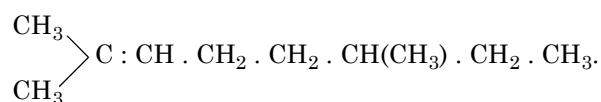
... [For the complete experimental details of this section, see the Supplemental material.]

The structure of the hydrocarbon, as shown by a study of the products of its oxidation with potassium permanganate, corresponds to the terpinolene form of citronellal:
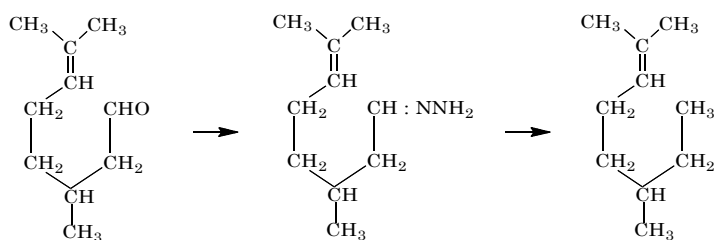
For the oxidation of 18 g. of the hydrocarbon, a total of 39 grams $KMnO_4$ (3 atoms O(6)) were required. The first stage of oxidation, the formation of the corresponding glycol (13 g. $KMnO_4$), was carried out under cooling with ice water. After the potassium permanganate had been decolorized, a further 13 g. of $KMnO_4$ was added, and the mixture was heated in a water bath at 50°. After complete reduction of the permanganate, the volatiles were distilled off. The oily layer was separated from the remaining aqueous solution, and, after pre-saturation of the solution with potash, acetone was isolated by distillation. It was characterized by its iodoform reaction, and its conversion to the *p*-bromophenylhydrazone (by the action of *n*-bromophenylhydrazine in 50% acetic acid); shiny flakes, m.p. 93° from ligroin. No acetaldehyde was found.

The oily distillate containing unmodified hydrocarbon was treated with semicarbazide to give a crystalline precipitate of the semicarbazone, which was pressed on a porous plate and decomposed with 10% sulfuric acid. The oily product was isolated by steam distillation, saturated with potash, and dried with fused potash. The substance boils at 218° at 755 mm, and corresponds to a keto-alcohol, $C_{10}H_{20}O_2$.

Analysis.

Weight	0.1704 g.:	CO_2 –	H_2O –
		0.4289 g.;	0.1773 g.

$C_{10}H_{20}O_2$.	Calculated	% C –	69.70
	"	H –	11.71
	Found	% C –	68.65
	"	H –	11.58

$$d\frac{20}{0} = 0.9069;\ n_D = 1.4363.$$

Mol. ref. $R^2 = 49.62$. Calc. for $C_{10}H_{19}$:O $R^2 = 49.84$.

The keto-alcohol is recovered after heating with ammoniacal silver oxide solution; it does not give a color with fuchsinsulfurous acid [*Schiff's reagent; fuchsin and sodium bisulfite* —translators]. The semicarbazone is sparingly soluble in methyl alcohol, from which it crystallizes in rhombohedral plates; from hot benzene solution it crystallizes as needles, m.p. 125-126°.

... [For the complete experimental details of the rest of this section, see the Supplemental material.]

The active amylacetic acid $\begin{matrix} CH_3 \\ \\ C_5H_9 \end{matrix}\Big\rangle CHCOOH$ boils at 212-214° (7); the corrected boiling point is 221° at 760 mm; $d_{20} = 0.9149$; $[\alpha]_D = +8.44°$ at 20° (8). With these results, the study of oxidation products the structure of the hydrocarbon $C_{10}H_{20}$ is well established:

(intermediate product)
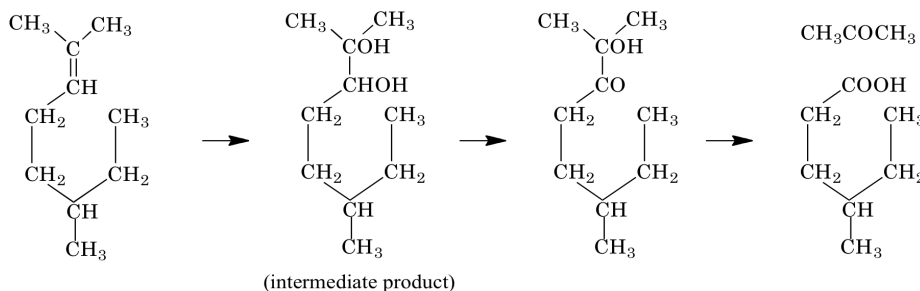
The Action of Hydrogen Bromide on $C_{10}H_{20}$

12 cc of the hydrocarbon were converted into the bromide $C_{10}H_{21}Br$ by shaking with 35 cc of fuming hydrobromic acid, first at 0°, then at room temperature. The bromide was washed with water and soda and dried with calcium chloride. Yield: 12 g. Specific gravity of

the bromide $d\frac{20}{0} = 1.0772$; $n_D = 1.4578$. Mol. ref. R^2 = 55.83. Calc. for $C_{10}H_{21}Br$ $R^2 = 56.01$. On distillation of the bromide with aniline, one obtains a hydrocarbon, $C_{10}H_{20}$, with physical properties very close to the original

hydrocarbon: b.p. 163.5-164.5°, $d\frac{20}{0} = 0.7515$, $n_D = 1.4293$; mol. ref. $R^2 = 48.12$; calc. for $C_{10}H_{20}$ $R^2 = 47.74$.

Rotation: $[\alpha]_D = +4.39°$.

Reduction of the Hydrocarbon $C_{10}H_{20}$

3 cc of the hydrocarbon were heated in a sealed tube with 15 cc of hydriodic acid, sp. gr. 1.96, for 15 hours at 200°. The hydrocarbon boils at 159-159.5° at 742 mm.

... [For the characterization data, see the Supplemental material.]

If the reduction of the hydrocarbon $C_{10}H_{20}$ with hydriodic acid is not accompanied by isomerization, then the saturated hydrocarbon $C_{10}H_{22}$ may be represented as 2,6-dimethyloctane
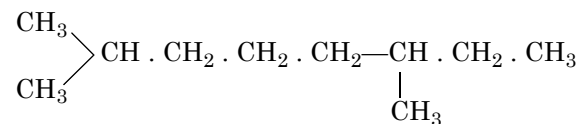
V. Markovnikov and A. Reformatskii (9) obtained a hydrocarbon $C_{10}H_{22}$ with b.p. 158-159° at 745 mm and $d\frac{20}{0} = 0.7554$ on reduction of roseol (l-citronellol) with hydriodic acid. The boiling point of the M. and R. hydrocarbon coincides with the boiling point of our hydrocarbon; as for the difference in specific gravity, in the M. and R. paper, there is a note (10):

> The specific gravity found inspires some doubt, as it is significantly higher than the specific gravity of all known decanes. Unfortunately, it could not be tested due to lack of material.

According to the method of their preparation, both hydrocarbons should be identical.

Recently, A. Skita and G. Ritter (11) isolated a decane with the following properties from the reduction of citral by the method of Sabatier: b.p. 148-152° (?);

$d\frac{18}{4} = 0.7348$; $n = 1.4138$.

The Hydrocarbon $C_{10}H_{18}$ from Citral

(Preliminary report)

The compound of citral with hydrazine $C_{10}H_{16}$:NNH_2 was prepared by refluxing an alcohol solution of 23 g. of citral (from Schimmel, b.p. 126° at 25 mm) and 23 g. of 50% hydrazine hydrate. After the alcohol was distilled off on an oil bath at 140°, the residue was dried with fused potassium hydroxide. The decomposition of the base in the presence of potassium hydroxide proceeds vigorously after a little warming. The distillate was washed several times with water, steam distilled and dried over
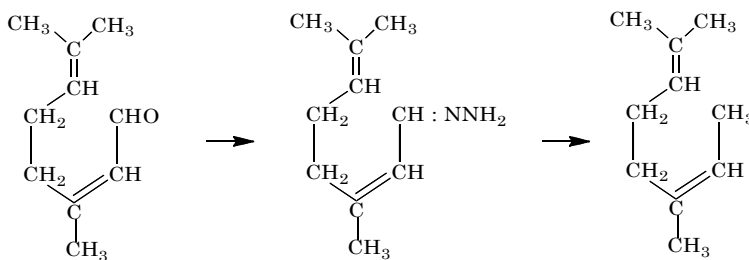

calcium chloride; yield 11 g. After boiling over sodium, the hydrocarbon boils at 164-165° at 755 mm.

... [For the characterization data, see the Supplemental material.]

If we start from the terpinolene formula for citral, the transformation of citral into the hydrocarbon $C_{10}H_{18}$ may be represented as follows: [see scheme above].

The hydrocarbon from citral is an isomer of the dihydromyrcene prepared by Semmler by the reduction of myrcene with Na and C_2H_5OH (12):

myrcene   dihydromyrcene
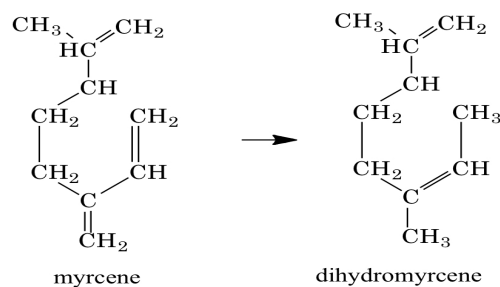
Dihydromyrcene boils at 171.5-173°; $d_{20} = 0.7802$; $n_D = 1.4501$.

Tomsk, 1 May, 1911.

Supplemental Material

An unabridged translation of this paper can be found in the Supplemental Material for the *Bulletin for the History of Chemistry* at the journal's website,

www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

References and Notes

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2. W. H. Perkin Jr. and S. S. Pickles, "Versuche über die Synthese von Terpenen," *Chem. Zentralbl.*, **1905**, *II*, 239. Abstracted article: "LXIV.—Experiments on the synthesis of the terpenes. Part II. Synthesis of Δ^3-*p*-menthenol(8), $\Delta^{3.8(9)}$-*p*-menthadiene, *p*-menthanol(8), $\Delta^{8(9)}$-*p*-menthene, and *p*-menthane," *J. Chem. Soc., Trans.,* **1905**, *87*, 639-655. Cited in the original as Cbl. *1905,* II, 239. 45,85

3. [Molecular refraction; it has the advantage that it is almost independent of the density, temperature and aggregation state of the compound, and that it can be predicted on the basis of simple addition of the of contributions from bonds, atoms or groups. We do not know why Kizhner reports R^2. See M. Born and E. Wolf, *Principles of Optics*, 4th ed. (Pergamon Press: Oxford, 1970), pp. 88-90. —translators]

4. O. Wallach, "Zur Kenntniss der Terpene und der ätherischen Oele," *Justus Liebigs Ann. Chem.*, **1908**, *360*, 26-81. Cited in the original as Lieb. Ann. **360**, 72.

5. Cited in the original as loc. cit. 74.

6. [This is the number of oxygen atoms formally added to one molecule of the hydrocarbon on complete oxidation to acetone and the potassium salt of 4-methylhexanoic acid: $C_{10}H_{20} + 2\ KMnO_4 \rightarrow C_3H_6O + C_7H_{13}O_2K + 2\ MnO_2 + KOH$ —translators]

7. I. Welt, "Contribution à l'étude des dérivés amyliques actifs," *Ann. chim. phys.*, [7], **1895**, *6*, 115-144. Cited in the original as Ida Welt. Ann. chim. phys. [7], **6**, 132.

8. The b.p. of 221° is too high if we take into account that the normal heptyl [*carboxylic*] acid boils at 222.4° at 743.4 mm.

9. V. Markovnikov and A. Reformatskii, "Issledovanie volgarskogo rozovogo masla [Investigation of the Volga rose oil]", *Zh. Russ. Fiz.-Khim. O-va.*, **1898**, *24*, 663-686. Cited in the original as Ж. Р. Ф. Х. О. **24**, 679.

10. Cited in the original as Loc. cit. 680.

11. A. Skita and H. Ritter, "Über die Sabatiersche Reduktion und ihre Umkehrung," *Ber. dtsch. chem. Ges.*, **1911**, *44*, 668-676. Cited in the original as Ber **44**, 668.

12. F. W. Semmler, *Die ätherischen Öle nach ihren chemischen Bestandteilen: unter Berücksichtigung der geschichtlichen Entwicklung*, Veit & Comp., Leipzig, 1906, vol. 1, p 356. Cited in the original as Semmler, "Die ätherischen Öle" v. 1, 356.

ICOHTEC Symposium 2016

Registration is open for the International Committee for the History of Technology (ICOHTEC) Symposium 2016, scheduled for July 26-30 in Porto, Portugal. The title of the conference is "Technology, Innovation, and Sustainability: Historical and Contemporary Narratives."

Innovation and sustainability have become key words of our everyday life, extending from political and economic discourse to teaching curricula and from the lay public to academia. However, the use of these terms is often abstract and simplistic, ignoring the density of their interrelationships in different geographic, historical and civilizational contexts, and the boomerang character of today's world.

The 43rd ICOHTEC meeting aims at addressing this complex relationship by encouraging papers that contribute to a deeper understanding of the multilayer cultural and material built meaning of innovation and sustainability and on the various roles played by technology in enabling or preventing such interplay.

Standard registration is open through May 31; late rates begin on June 1. Details at http://icohtec2016.ciuhct.org/

FROM COSMOCHEMISTRY TO FUEL CELLS: NOTES ON EMIL BAUR, PHYSICAL CHEMIST

Helge Kragh, Niels Bohr Institute, Copenhagen University; helge.kragh@nbi.ku.dk

Introduction

Few historians of chemistry will be familiar with the name Emil Baur (1873-1944), except perhaps if they specialize in the history of fuel cells. Although he has an entry in Poggendorff's *Handwörterbuch*, he is not described in either *Lexikon bedeutender Chemiker* or *Dictionary of Scientific Biography* (1). Yet Baur, a second-generation physical chemist, was far from an obscure scientist in his own time, and during his long and distinguished career in Zurich he contributed interesting work covering a wide range of the chemical landscape. From 1911 to 1942 he was professor at the Polytechnic University better known as the ETH (Eidgenössische Technische Hochschule). The only biographical accounts of Baur are two obituaries written by William Dupré Treadwell, who from 1916 to 1918 worked under Baur at the ETH Institute of Physical Chemistry and subsequently served as professor of analytical chemistry at the ETH (2).

Apart from providing some biographical information concerning Baur, this paper discusses select cases of his scientific work, including rare earth research, mineralogy, chemical

Figure 1. Emil Baur. Source: ETH Library, Zurich, picture archive.

kinetics, and his extensive electrochemical research on fuel cells. In addition, it describes his brief connection to Einstein and also Baur's views on the more general aspects of physical chemistry, including his possible anti-atomism (3).

Emil Baur, Life and Work

The German-Swiss physical chemist and electrochemist Emil Baur was born in Ulm in Württemberg, southern Germany, on 4 August 1873, the son of Adolf Baur, a merchant and civil servant, and Agnes Baur, née Adam. He was thus a fellow-townsman to the six years younger Albert Einstein. In 1905 Adolf Emil Baur (to use his full name) married Ottilia Mayer with whom he had two children, Alice born in 1908 and Arthur in 1915. The latter became a well-known author and linguist (4).

After having completed his high school (Gymnasium) education in Ulm and Baden-Baden, Emil Baur studied chemistry in Berlin and Munich. For a brief period of time he worked as an apprentice at the Arabol Manufacturing Company in New York, a

firm specializing in the production of gums, glues, and textile chemicals. He wrote his first research papers in 1897. Baur subsequently became an assistant to Friedrich Wilhelm Muthmann, professor of inorganic chemistry at the Munich Technical University. While in Munich, Baur gave a public lecture course on "chemical cosmography" to be considered below.

In 1901 Baur wrote his professorial thesis (*Habilitation*), which granted him the right to lecture at German universities as a *Privatdozent*. The subject of the thesis was an investigation of a nitrogen-hydrogen fuel cell with liquid ammonia as electrolyte. In this connection Baur also investigated the ammonia synthesis process

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 + 92\text{ kJ mol}^{-1}.$$

At the time this reaction attracted intense interest, which eventually resulted in the momentous Haber-Bosch industrial process. Apart from measuring the voltage of the cell as 0.6 V, he reported experiments on ammonia synthesis with catalysts such as platinum powder and chromium nitride, suggesting that small amounts of NH_3 might have been formed (5). Although his work did not lead to a breakthrough, it was recognized as an important part of the preparatory phase of the history of synthetic ammonia production (6).

In the winter semester 1904-1905 Baur served as assistant to Wilhelm Ostwald at his Institute of Physical Chemistry in Leipzig, and from there he went to Berlin to work as scientific assistant at the Imperial Health Bureau (Kaiserliche Gesundheitsamt), an institution founded in 1876. Two years later he accepted an offer as extraordinary professor of physical chemistry and electrochemistry at the Braunschweig Technical University. During his period in Braunschweig he published in 1907 an introductory book on spectroscopy and colorimetry, and in 1910 a book on themes of physical chemistry based on lectures given to the German Association of Engineers (7). Svante Arrhenius recommended the latter book for its excellent lecture demonstrations (8).

In October 1911 Baur was appointed full professor in physical chemistry and electrochemistry at the ETH, one of Europe's most prestigious institutions of chemistry and physics. Although founded in 1855, ETH had only recently acquired full university status, the first doctorates being awarded in 1909. The federal ETH should not be confounded with the University of Zurich, which was established in 1833 as a cantonal school. Since 1897 the Austrian chemist Richard Lorenz had served as professor of electrochemistry at ETH, but in 1910 Lorenz left Zu-

rich to take up a position at the Frankfurt Academy, which a few years later became the University of Frankfurt am Main. Baur not only succeeded Lorenz but also the German chemist Georg Bredig, who had come to Zurich in 1910 as professor of physical chemistry. However, Bredig only stayed one year after which he moved on to a chair at the Technical University of Karlsruhe (9). Baur, on the other hand, stayed in Zurich until the end of his life.

During his career as professor of ETH, Baur did research in a broad range of the chemical sciences. Although most of his papers were in photochemistry, electrochemistry, and organic chemistry, he also did much work in what today would be classified as materials science. The author or coauthor of three books and more than 160 articles, all of them in German, he was a productive scientist (10). Of the 148 papers listed in *Web of Science*, 90 had Baur as sole author and 58 were written with one or more coauthors. Most of the papers appeared in *Zeitschrift für anorganische Chemie*, *Zeitschrift für physikalische Chemie*, *Zeitschrift für Elektrochemie*, or *Helvetica Chimica Acta*.

Baur retired from his position at ETH in 1942 and passed away on 14 March 1944. During his brief period of retirement he focused on studies of natural philosophy. Following Baur's retirement the ETH chair in physical chemistry was occupied by Gottfried Trümpler, a former collaborator of and assistant to Baur.

Baur and Einstein

Not only was Baur born in the same town as Einstein, he also came to know the famous physicist during Einstein's brief stay as a professor at ETH from the summer of 1912 to the spring of 1914 (when Einstein left for Berlin). ETH was not new to Einstein, for this was the school where he had studied 1896-1900 and from which he received his diploma in physics. In his younger days he was seriously interested in problems of physical chemistry, including such topics as photochemistry, statistical mechanics, chemical thermodynamics, and the quantum theory of gases. Indeed, it has been claimed that "young Einstein was at heart a chemist" (11). Einstein's very first paper, an investigation of capillarity dating from 1901, was squarely in the tradition of physical chemistry, relying to a large extent on data from Ostwald's *Lehrbuch der allgemeinen Chemie* (12).

The Russian-born chemist David Reichinstein taught electrochemistry at the University of Zurich from 1911 to 1918 and was acquainted with both Einstein

and Baur. After World War I he returned for a while to Russia, having just become the Soviet Union, where he became professor of physical chemistry at the University of Nizhny Novgorod (13). In a biography of Einstein published in 1934, Reichinstein told how Baur came to meet the father of relativity theory: "My friend, Professor Baur, wanted to make Einstein's acquaintance. I mentioned this to Einstein and gave a description of the good qualities of my friend. … We went to a small café where Baur was expecting us" (14). According to Reichinstein, Einstein made a deep impression on Baur:

> He [Baur] was overwhelmed by Einstein's quality of emotion, by something direct which radiated from him, by his spirituality, but particularly by the ease with which Einstein produced the most intricate problems "out of his hat" so to speak. "How can he possess so much knowledge of scientific literature at this early age?"

While in Zurich, Einstein organized a series of weekly colloquia. In one of them Max von Laue presented his new theory of X-ray diffraction in crystals, the implications of which Einstein discussed. On leaving the colloquium, Reichinstein recalled (15):

> I walked beside Professor Baur and he repeated what he had said at the time of making Einstein's acquaintance at the café: "Einstein extemporizes on the most intricate problems with as much ease as if he were talking about the weather. Others need a lot of time and have to work hard to merely understand and digest every one of these problems he was talking about."

In yet another Zurich colloquium, probably on 23 July 1913, Einstein lectured on a theory of surface fluctuations recently published by the Russian physicist Leonid Mandelstam, who at the time worked in Strasbourg. After the lecture Einstein sent Mandelstam a postcard signed by, among others, Baur, Reichinstein, von Laue, and Otto Stern (16). Whereas Baur co-signed Einstein's postcard to Mandelstam, on 19 November the previous year Einstein co-signed a letter which Baur wrote to August Horstmann, the pioneer of physical chemistry and chemical thermodynamics, on the occasion of his seventieth birthday (17). Also Reichinstein and Alfred Werner, who since 1895 had been professor of chemistry at the University of Zurich, signed the letter of congratulation.

Stern, who would later receive the physics Nobel Prize for his development of the molecular beam method, had obtained his doctorate in Breslau under the physical chemist Otto Sackur. The subject of the doctoral thesis was the osmotic pressure of CO_2 in highly diluted solutions. He subsequently joined Einstein as his first assistant in Prague, and when Einstein moved to Zurich he brought young Stern with him.

Stern's *Habilitation* thesis, an 8-page essay on the kinetic theory of the vapor pressure of monoatomic solids, was evaluated by a committee consisting of Einstein, Baur, and the French ETH physicist Pierre-Ernest Weiss. While Einstein was enthusiastic, Baur was more reserved, but in the summer of 1913 the committee accepted the thesis with the result that Stern became a *Privatdozent* and could continue his collaboration with Einstein on the quantum theory of diatomic molecules. At the end of his evaluation, Baur wrote (18):

> In the eighties of the last century physical chemistry experienced a stormy development through the theory of osmotic pressure, the free ions and the phase rule. However, in the nineties a certain degree of stagnation set in. Since the previous decade, however, one observes a new growth which ultimately is based on Planck's radiation theory. It would be most desirable to have a lecture on the chemical applications of this new research area, and it seems to me that Mr. Stern has all the qualifications that are necessary for honoring this task.

Although Baur thus recognized the importance of quantum theory for physical chemistry, he did not himself contribute to this early phase of quantum chemistry. When the old Planck-Bohr quantum theory was replaced by the new quantum mechanics and in 1927 led to the Heitler-London theory of the covalent bond (work done in Zurich), Baur showed no interest. His concern was with classical physical chemistry and not with quantum chemistry or what soon emerged as chemical physics.

Philosophy of Nature

According to his biographer and collaborator William Treadwell, Baur had an "unusually broad knowledge of natural philosophy and humanist culture" (19). He may have had this interest since his youth, as indicated by a correspondence he had with the famous Viennese philosopher-physicist Ernst Mach. Baur was at the time interested in the question of whether or not life could be explained purely in chemical terms, a subject on which Mach offered his opinion. "I do not believe that the chemical laws known to us presently are sufficient to explain organic life," Mach told his young correspondent (20). On the other hand, Mach did not rule out that such an explanation would appear in the future.

Another indication of Baur's humanist interests is provided by an insightful review he wrote of a book

dealing with the relationships between science and the arts. The book was written by Felix Auerbach, a German physicist, humanist and promoter of the arts (21). In 1935 Baur published anonymously a complex and learned literary-philosophical novel, *Das Helldunkel*, in which he discussed at length his pantheistically colored view of culture, religion and nature (22). Although the book had little to say about physics and chemistry, he briefly expressed his dissatisfaction with the world view of modern physics.

There is little doubt that Baur's general view of science was strongly influenced by the ideas of Mach and Ostwald, which he much appreciated and often quoted. Neither Mach nor Ostwald before 1908 believed in the existence of atoms as physically real particles, and it is possible that Baur belonged to the dwindling minority of physical chemists sharing their view. In an interview of 1962 conducted by Thomas Kuhn, Stern recalled that when he was a *Privatdozent* in Zurich, "the professor of physical chemistry said to him that he could never have passed any of the physical chemistry exams at Zurich because he was a believer in atoms" (23). In an earlier interview of 1961, he mentioned specifically Baur as an opponent of molecular and atomic theory (24). Although Baur never explicitly denied the existence of atoms, it is remarkable that in his many works he very rarely referred to or made use of terms such as atoms or ions. In agreement with Ostwald he wanted to base chemistry on the laws of stoichiometry that do not presuppose an atomic constitution of matter (25).

In addition to stoichiometry Baur was keenly interested in reaction kinetics, a field he contributed to with several studies during the last phase of his career. Baur was fascinated by the so-called "Wegscheider's paradox," which refers to the Austrian chemist Rudolf Wegscheider, who in 1901 pointed out that the condition of vanishing reaction rate as given by chemical kinetics does not necessarily coincide with the thermodynamic equilibrium condition (26). He vaguely suggested that thermodynamics might not be applicable to all reversible chemical processes. Baur felt that a change in philosophical outlook was required if the thermodynamic concept of chemical equilibrium was to be reconciled with the one based on kinetic theory. The price to pay would be "a revision of Democritus' materialistic natural philosophy to which modern physical theory remains faithful to this day" (27). As an alternative to atomistic materialism he advocated a return to a "hylozoic" natural philosophy, the view that all matter is in some sense alive and composed of a unity of forces that extends from the simplest

molecules to living beings. Baur thought that hylozoism might be the only way to bridge chemistry not only with physics but also with biology.

According to Baur, the chemical equilibrium state might in some cases not be an ordinary dynamical equilibrium governed by the principle of detailed balance, but what he called a one-way circular reaction or circular equilibrium. Wegscheider's paradox and equilibria of the cyclical kind had earlier been discussed by the eminent American chemist Gilbert Lewis, according to whom cyclical equilibria did not exist (28). Baur's interest in circular or cyclical reactions has led Boris Yavelov to suggest that the Belousov-Zhabotinsky oscillating reaction has its origin in Baur's laboratory in Zurich. Boris Belousov graduated from ETH in 1915 and according to Yavelov, "Belousov's idea of periodical chemical reactions was prompted by Baur's works" (29). However, Baur's interest in cyclic reactions dated from the 1930s and Belousov only studied the kind of oscillating reactions named after him in about 1950 (30). For these reasons a connection is highly unlikely.

In any case, Baur thought that cases of one-way circular reactions might be realized in biochemical life processes and that they possibly violated the second law of thermodynamics (31). In his last paper, a lengthy review of chemical kinetics published shortly after his death in March 1944, he stated that his discovery of one-way circular reactions "necessitates a re-evaluation of chemical kinetics of such a range that it affects the domain of validity of the second law of thermodynamics" (32). Baur extended the apparent violation of chemical entropy increase to a cosmological scale, arguing that one-way circular reactions provided a way to prevent the so-called "heat death" of the universe caused by the continual and irreversible increase in entropy. In agreement with an older idea of Walther Nernst, who was strongly opposed to the heat death, Baur tended to conceive the universe as an eternal one-way circular process on the largest possible scale (33). Baur's somewhat unorthodox ideas of reaction kinetics did not attract much interest, but in the early 1950s they were taken up and further developed by Anton Skrabal, an Austrian chemist (34).

Rare Earths

Despite his lack of interest in quantum and atomic theories, Baur was a versatile chemist with an unusually broad interest in chemistry and its allied sciences. Together with Muthmann, his professor in Munich, he examined in 1900 the phosphorescence spectra of

lanthanum and yttrium earths. This line of research was followed up by another collaborative work, this time with his colleague at Munich, Robert Marc, which dealt with the much-discussed problem of the number of rare earth elements (35).

One of the methods of determining whether an earth metal was elementary or consisted of more elements was at the time to study the luminescence spectra of rare earths exposed to cathode rays. By means of this technique, sometimes called "phosphorescent spectroscopy," the British chemist William Crookes had suggested in 1888 that yttrium contained several "meta-elements" of different atomic compositions yet belonging to the same element (36). Crookes' claim was controversial and contested by the Frenchman Paul-Emile Lecoq de Boisbaudran, among others, who held that yttrium was not elementary but consisted of two new elements (which he designated Z_α and Z_β). Still in 1900 there was a great deal of confusion with regard to the number of rare earth elements and their place in the periodic system (37). Baur and Marc showed that pure yttrium, gadolinium, and lanthanum did not produce discontinuous luminescence spectra, and that the observations of Crookes and Boisbaudran could be explained as due to traces of the elements erbium, neodymium, and praseodymium. While ignoring Crookes' meta-elements, they concluded that Boisbaudran's suggestion of new elements was unfounded (38). Baur's early research on the rare earths was not particularly important, but it was well known among specialists in the field (39).

A decade later Baur returned to the question of the rare earths, this time in a discussion of the peri-

odic system. This was a little before X-ray spectroscopy and radiochemistry revealed the existence of the atomic number, and at a time when chemists still believed that the atomic weight was the ordering principle of the periodic system. Consequently there was a great deal of confusion with respect to the details of the system. Baur based his analysis of the periodic system on the curve of atomic volumes originally demonstrated by Lothar Meyer in 1870, but instead of plotting atomic volumes against atomic weights Baur used the logarithms of the volumes (40). In this way he found that the rare earth metals formed a zig-zag line commencing at lanthanum below barium and ending with lutetium above tantalum (Figure 2). Baur concluded that there were twelve rare earth elements. Lanthanum belonged to group III, series 8, and cerium to group IV, series 8, and the remaining elements were placed in their own group between lanthanum and cerium (Figure 3). According to Baur, it followed from his system that there could be no more elements than those already known. In this he was quite wrong, of course. Only with advances in X-ray spectroscopy and
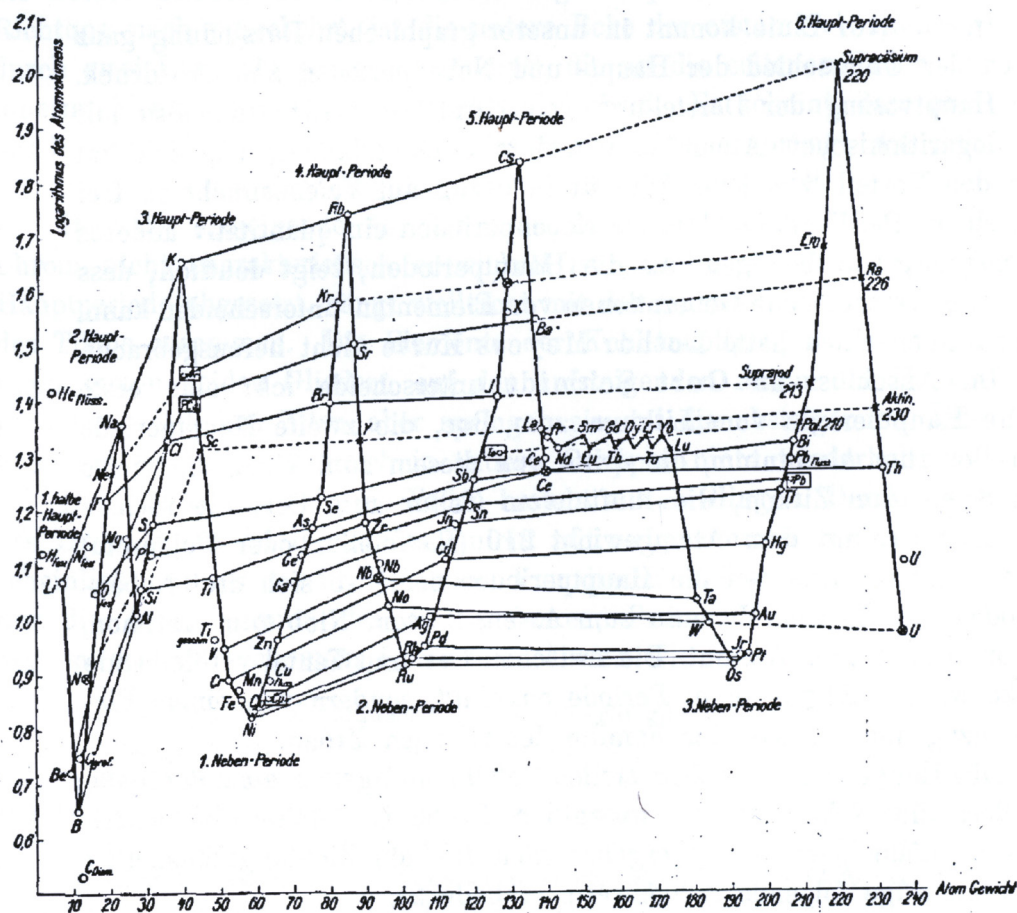

Figure 2. *Baur's semilogarithmic depiction of atomic volumes. Source: Ref. 40 (Baur), p 572.*

atomic theory was the tricky question of the position of the rare earths in the periodic system eventually resolved.

Mineralogical and Oceanographic Chemistry

As a young man Baur was seriously interested in mineralogy, geology, and geochemistry, subjects that appeared prominently in his book on chemical cosmography and on which he wrote a few scientific papers. He was a contributor to the 1915 edition of *Handbuch der Mineralchemie*. There was in the early part of the twentieth century a growing interest in applying physical chemistry to geology and mineralogy, and Baur contributed to the trend (41). In a paper of 1903 he investigated the conditions under which quartz would be formed from heating of amorphous silica (SiO_2) with potassium aluminate ($K_2Al_2O_4$) at high temperature and pressure (42). Baur illustrated his results with diagrams based on the phase rule of Gibbs and van 't Hoff, which possibly was the first mineralogical use of the rule. In the third edition of his monograph on the phase rule, the British physical chemist Alexander Findlay called attention to Baur's paper as an indication that the study of the phase rule as applied to mineral formation, although still in its infancy, gives "promise of a rich harvest in the future" (43).

It was only with the so-called "mineralogical phase rule" formulated by the Norwegian geologist and geochemist Victor Moritz Goldschmidt in 1911 that the phase rule appeared as a powerful tool in petrology (44). According to this rule the number of phases in a rock, corresponding to the number of minerals, will not exceed the number of chemical components. In a lecture to the German Bunsen Society for Applied Physical Chemistry of 1911, Goldschmidt demonstrated how the rule can be used to gain information about temperatures and pressures of silicate rock formation (45). Baur, at the time still at the Braunschweig Technical University, attend-

Das periodische System der Elemente.

Die Klammern bedeuten Anfang und Ende der Hauptperioden.

Nullte Gruppe	Erste Haupt-, Neben-gruppe		Zweite Haupt-, Neben-gruppe		Dritte Haupt-, Neben-gruppe		Vierte Haupt-, Neben-gruppe		Gruppe der seltenen Erden	Fünfte Haupt-, Neben-gruppe		Sechste Haupt-, Neben-gruppe		Siebente Gruppe	Eisen-Platin-gruppe
He	Li		Be		B		][C			N		O		F	
Ne	Na		Mg		Al		][Si			P		S		Cl	
Ar	K		Ca		Sc		Ti]				V		Cr		Mn Ni / Fe Co
Kr	Rb	Cu	Sr	Zn	Y	Ga	Zr	Ge]		Nb	[As	Mo	Se	Br	Ru Rh Pd
X	Cs	Ag	Ba	Cd	La	In	Ce]	Sn	Pr Sm Gd Dy Er Yb / Nd Eu Tb Ho Tu Lu	Ta	[Sb	W	Te	J	Os Ir Pt
Em	Supra-cäs.	Au	Ra	Hg	Akt.	Tl	Th	Pb		Supra-tantal	[Bi	U	Pol.	Supra-jod	

Figure 3. Baur's proposal of the periodic system. Source: Ref. 40 (Baur), p 583.

ed the lecture and objected to some of Goldschmidt's conclusions, which he thought lacked justification in terms of physical chemistry. On this occasion Baur did not refer to his own work of 1903 and he did not engage in public polemics with Goldschmidt. On the other hand, he got indirectly involved into a controversy between Goldschmidt and Johann Koenigsberger, a mineralogist and mathematical physicist at Freiburg University. Part of this controversy concerned the priority of the phase rule applied to minerals, which according to Koenigsberger belonged to Baur. In reply to Koenigsberger, Goldschmidt denied that this was the case: "Mr. E. Baur gives indeed an excellent description of a particular system, but he has nothing to say about the general relationship between the number of phases and the number of minerals in a naturally stable system" (46).

During the first half of the twentieth century several chemists and oceanographers tried to determine the amount of gold in seawater and, if possible, to recover the precious metal. Baur was one of them. In 1913 he was granted a British patent (BP 16898) on means of obtaining noble metals from highly diluted solutions, and in 1916 it was followed by a German patent (DRP 272654). The patents failed to attract commercial interest. At about the same time he supervised Hellmuth Koch, a graduate student who on his instigation wrote a doctoral thesis on a method to determine small amounts of gold by means of adsorption on charcoal (47). After Germany's devastating defeat in World War I, Fritz Haber and his Kaiser Wilhelm Institute of Physical Chemistry in Berlin engaged in an ambitious scheme of separating gold from seawater on an industrial scale. However, in 1927 he was forced to admit that the average concentration of gold in the oceans was too low to allow economic recovery (48).

Baur followed Haber's work closely and in 1942 he wrote two systematic reviews of the subject which

Table 1. Contents of Baur's *Chemische Kosmographie* (1903).

Chapter	Content
1	Kirchhoff's radiation laws; spectral analysis; composition of the Sun
2	Blackbody radiation; Sun's temperature; the photosphere
3	Stellar spectra; comets and nebulae; decomposition of chemical elements
4	Composition of meteorites; the stone from Ovifak; the world fire
5	Limits between gaseous-liquid and liquid-solid phases; petrographic and chemical composition of stones
6	Solidification of magma; volcanic eruptions; pneumatic mineral formation; contact metamorphosis; circuit of substances in the mineral kingdom
7	Artificial manufacture of minerals
8	Composition of the oceans; formation of oceanic salt deposits
9	Formation of oil and coal; cellulose's methane fermentation; formation of saltpeter
10	Proteins; architecture of protein molecules
11	Fermentations; structure of carbohydrates
12	Reversion of fermentative action; photosynthesis of carbohydrates; synthesis of amino acids; presence of life
13	Metabolism in animals; proteins in animal tissue; combustion of carbohydrates; fats; the source of muscular power
14	Properties and chemistry of living substances; the ideas of E. Hering and E. Mach

Chemical Cosmography

In the winter semester 1902-1903 Baur gave a series of public lectures at the Munich Technical University on what he called "chemical cosmography"—probably a term he coined for the occasion (51). By this term he meant the chemical processes in all of nature, which he divided into three groups: the chemistry of the stars, chemical transformations in the crust of the Earth, and chemical aspects of organic nature. The book was organized in 14 chapters, each corresponding to a lecture in the Munich lecture series (see Table 1). In the first lecture, dealing with the chemistry of the Sun, Baur subscribed to the hypothesis of the non-terrestrial element "coronium." In agreement with several other chemists and astronomers at the time, he assumed coronium to be lighter than hydrogen. Only in 1939 were the spectral lines of coronium identified as due to the ion Fe^{13+}.

Baur's wide-ranging and synthetic survey of chemistry, aiming to connect the chemist's laboratory with the heavens as studied by the astronomer, was in the tradition of what at the time was known as "cosmical physics" (52). The difference was that its approach was chemical rather than physical. Baur's collection of subjects included many of those dealt with by the cosmical
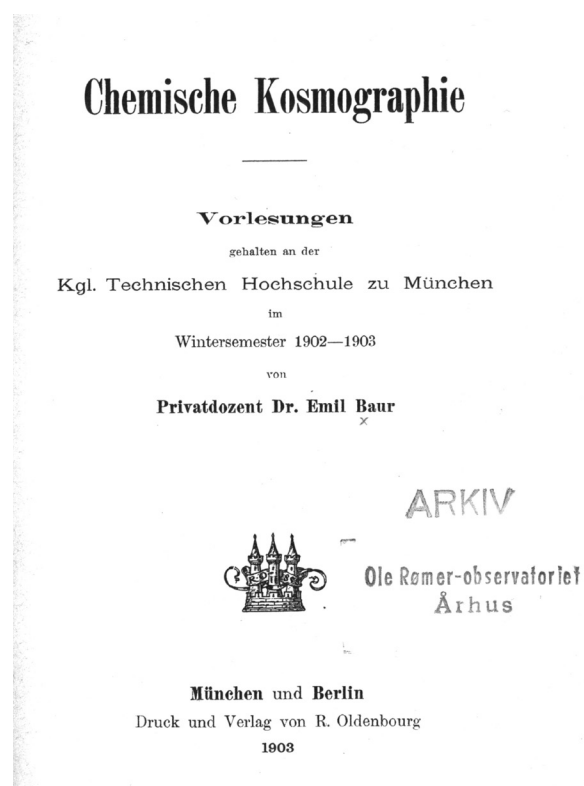
included proposals of new techniques to recover the gold (49). According to the results obtained by Baur and his collaborators in Zurich, Haber's values for the concentration of gold—on the average 0.01 mg m^{-3}—were too low. It was, they thought, too early to rule out a production of gold based on seawater. While Baur did not engage in oceanographic determinations of the content of gold, his doctoral student Walter Stark did (50). Using the measurement methods of Baur and Koch, Stark found that in some European locations the content of gold in seawater was as high as 2 mg m^{-3}.

Figure 4. Baur's Chemical Cosmography *of 1903.*

physicists, such as the constitution of the Sun, meteorites, comets, volcanoes, and the composition of sea water. On the other hand, it was even broader by covering also aspects of organic nature, including biochemistry, photosynthesis, fermentation processes, and the nature of life.

In his discussion of the temperature of the Sun, Baur introduced Max Planck's new radiation law that would soon revolutionize physics. However, to Baur and most of his contemporaries Planck's law was primarily of an empirical nature and of interest simply because it represented the spectrum of heat radiation so accurately. He did not mention the hypothesis of energy quantization, which at the time was still disputed or considered unimportant from a physical point of view. Non-quantum presentations of Planck's law were common at the time and appeared in, for example, Arrhenius' *Lehrbuch der kosmischen Physik* published the same year as Baur's *Chemische Kosmographie* (53).

At any rate, Baur's chemical cosmography was an isolated case and not an attempt to create a new framework of cosmic chemistry in the style of cosmical physics. So-called *cosmochemistry* would eventually be established as an extension of geochemistry, but this only happened some four decades later and without Baur having any share in it (54).

Research in Fuel Cells

To the extent that Baur still has a name in the history of science, it is primarily in connection with his systematic work on electrochemical processes in general and fuel cells in particular. In these areas he obtained several patents, including a German patent of 1920 with Treadwell on coal cells with solid electrolytes (DRP 325783), an American patent of 1925 on the recovery of hydrogen and oxygen by electrolysis (US 1543357A) and a Swiss patent of 1939 on a new type of solid fuel cell (CH 204347).

Like a battery, a fuel cell consists of two electrodes separated by an electrolyte, but the fuel cell is continuously supplied with a stream of oxidizer and fuel from which it generates electricity. Unlike the battery, a fuel cell does not run down and it produces electrical energy as long as fuel is supplied. The first devices that converted parts of the chemical energy from fuel and oxidizer (hydrogen and oxygen) into electricity were constructed in the late 1830s, independently by William Groves in England and Christian F. Schönbein in Germany. These early studies were part of the extensive controversy concerning the origin of voltaic electricity, where the chemical theory was confronted by the contact theory (55). Over the next many decades a variety of fuel cells, some of them based on liquids and others on solid electrolytes, were studied, but few of them had any practical applications (56).

Baur's studies of electrochemistry were diverse—they included a model of the electrical organs of fish (57)—but it was only with his and his assistants' work on fuel cells that an extensive and coherent research program was established. As mentioned, as early as 1901, Baur had investigated a nitrogen-hydrogen fuel cell. While at the Braunschweig Technical University he supervised the doctoral dissertation of Itzek Taitelbaum, a Polish student, who studied fuel cells with molten NaOH as electrolyte, various carbon compounds as reactants, and a diaphragm of porous MgO (58).

The ETH laboratory for physical chemistry began research in fuel cells in 1912, when Baur and H. Ehrenberg reported experiments with, for example, molten silver as oxygen cathode and a carbon or iron rod as anode (59). As electrolyte they used various molten salts heated to 1000°C, including KOH, NaOH, $KNaCO_3$, and NaB_4O_7. Over the next two decades Baur and his assistants tried a large number of modifications of fuel cells, claiming in 1921 that they had shown that it was technically feasible to construct stable and powerful cells with electrolytes of molten carbonates (60). However, at the time it was more wishful thinking than reality and it would remain so for
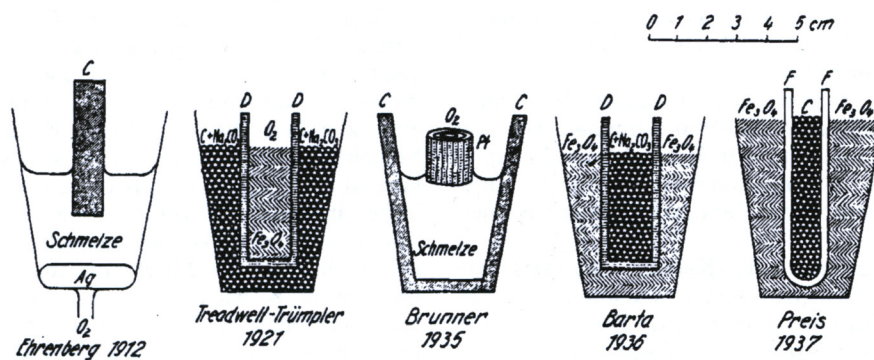

Figure 5. *Various types of coal fuel cells developed in Baur's laboratory. C = coal, D = diaphragm and F = solid state conductor (Festleiter). Source: Ref. 61, p 726.*

decades. Indeed, in his last publication of the subject, a brief review from 1939, Baur admitted that the desired goal, a cell that delivered electric energy with a high efficiency from the heat of combustion, had not been attained. Yet he ended the review in an optimistic tone: "Even when in the end only 50% of the combustion energy of the fuels could be delivered as electric energy at the switchboard of the fuel cell power plant, it would be a revolution in the energy economy of the world" (61).

By the mid-1930s Baur had become convinced that efficient fuel cells must be completely dry. This was one of the conclusions that he reached in a collaborative study with Ronald Brunner on various kinds of cells based on solid conductors (62). In another important paper of 1937, this time in collaboration with Hans Preis, the two ETH chemists reported on a series of experiments on fuel cells with solid electrolytes in the form of ceramic materials with a relatively high conductance (63). They found that the best, if not entirely satisfactory material was a zirconia ceramic with 85% ZrO_2 and 15% Y_2O_3. A substance of this composition is known as the "Nernst-mass" because its conducting properties were first discovered by Nernst, who in the late 1890s used it as a glower in the so-called Nernst lamp (64). Baur and Preis used the Nernst-mass electrolyte or modifications of it in the form of a crucible, and used iron and magnetite (Fe_3O_4) as anode and cathode, respectively. With a stack of eight such cells they constructed a test battery, but although the battery worked, its current output was too low to be of practical significance. Nonetheless, they estimated that the volumetric power density (as measured in kW m^{-3}) was competitive with that of conventional steam power plants.

In spite of not being commercially useful the Baur-Preis cell was an important advance that attracted much attention by later researchers. The paper has received 84 citations in the scientific journal literature (Web of Science), which makes it the most cited of Baur's many papers. Of the 84 citations, 63 date from after 1990. Today zirconia-yttria and zirconia-ceria electrolytes of the kind first studied by Baur and Preis are widely used in fuel cells. Baur and his group at ETH were pioneers in two of the types of fuel cells that currently attract most attention, namely what is known as SOFC (solid oxide fuel cells) and MCFC (molten carbonate fuel cells). These types of high-temperature fuel cells are generally considered the best candidates for the stationary power generation of the future.

Conclusions

Emil Baur was a well-known, respected and productive physical chemist during the first four decades of the twentieth century. Although he was never himself nominated for a Nobel Prize, he nominated several scientists (Table 2). His successful nomination of Francis Aston for the 1922 chemistry prize was particularly important, since it was directly responsible for Aston's prize. Aston's sole nomination for the chemistry prize came from Baur in Zurich, whose motivation was "the discovery of isotopes of ordinary chemical elements by means of the mass spectrograph constructed by F. W. Aston" (65). Several other nominees, including Theodor Curtius, Gustav Tammann, S. P. L. Sørensen, and Georges Urbain, had considerably more support from nominators (66). In 1922 two Nobel prizes were awarded in chemistry, the other to Frederic Soddy who received it for the year 1921. Incidentally, Aston received three nominations for the 1922 *physics* prize.

Table 2. Baur's nominations for the Nobel Prize. Aston was the only one of Baur's nominees who received the prize.

Year	Subject	Nominee	Nationality
1915	chemistry	Eugen Herzfeld	Germany
1922	chemistry	Francis W. Aston	Great Britain
1929	chemistry	Otto Warburg	Germany
1933	physics	Friedrich Paschen; Arnold Sommerfeld	Germany
1934	chemistry	Carl Neuberg	Germany
1939	chemistry	Hermann Staudinger	Germany

Despite his recognition among contemporary scientists, today Baur has fallen into oblivion. The present account of his life and work is naturally limited by existing sources, which seem to be largely missing when it comes to Baur's personal life in particular. Thus I have been unable to find information about his citizenship during his long stay in Switzerland, although I suspect he remained a German citizen. Despite these and other lacunae it is possible to give a picture of the scientific contributions and views of a major player in interwar European physical chemistry. The picture reminds us that a large part of physical chemistry in the period, both in Europe and abroad, was relatively uninfluenced by the new theories of quantum and atomic physics. Classical physical chemistry in the tradition of Ostwald, van 't Hoff and Nernst was still very much alive, but it is a subject that has received little attention by historians of science.

Acknowledgment

I am grateful to Karl Grandin, the Royal Swedish Academy of Science, for providing me with a copy of Baur's nomination for the 1922 Nobel Prize in chemistry. I also want to thank Christian Joas and Susan Splinter for help with archival material, and Quazi Hasan for having stimulated my interest in Baur.

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THE HISTORY AND STRUCTURE OF STANTIENITE (1)

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Abstract

Organic materials have a long history of cultural importance as gemstones. The best known such minerals are amber and jet. For almost 150 years, stantienite has been considered to be a rare structural variation of Baltic amber, which is a fossilized product of plant resins. Spectroscopic examination, however, demonstrates that the material is a variety of jet or coal, which is a fossilized product of the woody portions of plants. A Turkish material called Oltu stone or black amber has similar spectroscopic characteristics to jet and stantienite and also is a coal derivative rather than a resinous product that could be called amber.

Introduction

Following the history of a mineral can be a fascinating chemical enterprise. Amber from the Baltic Sea has been important to European culture for thousands of years. Amber is a gemstone but differs from almost all other such materials in being composed of organic constituents. It is formed from ancient plant resins, exuded millions of years ago and subjected to structural changes during the ensuing geological eras (2-8). The raw resins are composed of numerous terpenes, a class of compounds that evolved within plants to provide, *inter alia*, physical protection from the ravages of damage, disease, or drought. The original plants were either coniferous (gymnosperms) or flowering (angiosperms). The cultural importance of Baltic amber began in the early Neolithic period (up to about 10,000 years ago). Its importance increased through Classical Egyptian, Greek, and Roman times, as trade routes developed. During the Medieval period, amber was a popular material for the construction of rosary beads. The ancient trade routes from the Baltic and North Seas to the Mediterranean Sea were known commonly as the Amber Road (9).

From prehistorical to modern times, the major European source of amber was the Samland coast in the current Kaliningrad Oblast of Russia just north of Poland. The region was reconstituted after World War II but historically was the Königsberg area of East Prussia, where up to 90% of extracted amber in the world market has been derived. By the late Middle Ages, the Baltic amber sources were controlled by the Order of Teutonic Knights. When the Protestant Reformation decreased the demand for amber rosary beads, the Order transferred control of the trade to the Koehn von Jaski merchant family of Danzig (Gdańsk today, in Poland) in 1533 (6). In 1642, the Great Elector of Prussia bought the rights from the merchants. The Prussian monopoly of the amber trade continued until 1811, when private individuals were allowed to purchase the right to collect and market amber. Amber was transported from its sources to Danzig by ship. Channels for the ships needed to be dredged, and this process created more amber sources. In 1870, the private firm of Stantien & Becker contracted with the

Prussian government for the exclusive right to mine for amber. In their first years, they harvested about 10,000 lb (4500 kg) per annum. The company's new mine in Palmnicken (today's town of Yantarny in Kaliningrad; *yantar* is the Russia word for amber or resin) enabled extraction of 450,000 lb (200,000 kg) of amber in 1875. By 1885, production was nearing a million pounds (450,000 kg), and the peak of 1.2 million pounds (550,000 kg) occurred in 1895. At this point the Prussian government reclaimed control of amber production and founded the Royal Amber Works of Königsberg (later the Preußische Bergwerks- und Hütten AG).

Large scale production continued until World War I, but post-war production dropped precipitously during the 1920s and 1930s (6).

Friedrich Wilhelm Stantien (1817-1891) had businesses in the old Lithuanian towns of Klaipėda and Rumpiškės, including a fishing ship, a restaurant, and a windmill (10). From 1852, he had searched for amber in his holdings, and in 1854 he obtained the rights to deepen the shipping channel of the Curonian Lagoon and extract amber (Figure 1; Yantarny is just off the map, to the left or west, and Danzig is farther down the coast in the same direction). Moritz Becker (1830-1901) was a merchant from Danzig who joined Stantien in 1858 to establish the firm of Stantien & Becker. Continuous extraction of amber was begun in 1862 in the northern part of Juodkrantė (today in Lithuania), now known as Amber Bay. At its height, the company employed 500-600 people in three shifts, operated seven steamboats, utilized 19 steam dredgers, and built dams to keep the sea back. Stantien sold much of his holdings in 1868 for two million marks, and in 1870 the company moved its offices to Königsberg. Becker sold the firm to the state in 1899. During this time, the

Figure 1. *Map of the amber-rich region on the border of Kaliningrad and Lithuania. This map is based on "Curonian Spit and Lagoon," is licensed under CC BY-SA 3.0 via Wikimedia Commons—http://commons.wikimedia.org/wiki/File:Curonian_Spit_and_Lagoon.png#mediaviewer/File:Curonian_Spit_and_Lagoon.png.*

fishing village of Juodkrantė became a resort. The company built the harbor, supported a school and a doctor, and even presented an organ to a new church (10). The company's name lived on as a producer of flare pistols at least until World War I.

Varieties of Baltic Amber

During the mining of amber in Juodkrantė and elsewhere, rare and unusual resinous varieties were recognized that merited scientific investigation. These materials differed from common Baltic amber in appearance and properties. Whereas Baltic amber normally has a yellowish orange appearance, a brown variety was known by the workers as *Braunharz* (brown resin) or *das Braune* (the brown), and a black variety as *Schwarzharz* (black resin) or *das Schwarze* (the black) (11). The black material, actually brownish black, was shiny, opaque, and brittle and cleaved conchoidally, as amber tends to do, whereas the brown material, actually gray-brown, was matte in appearance and rarely cleaved conchoidally.

The first scientific comparison of these varieties, vis-à-vis true Baltic amber, was reported by Pieszczek (12) in 1880 and was abstracted the following year in the English literature. He found that the brown material dissolves in a wide variety of organic solvents, but the black material is generally insoluble. He failed to find succinic acid, which is a hallmark of Baltic amber and is reflected in its mineralogical name of succinite (from the Latin word *succus* for juice). He determined the ash content (respectively none, 4.5%, and 3.4% for succinite, brown resin, and black resin), the specific gravity (variable, 1.126, and 1.175), the carbon content (77.73-78.96%, 67.86%, 71.02), and

the hydrogen content (9.01-10.51%, 8.56%, 8.15%). On the basis of these differences, he concluded that the three materials are distinct minerals. He proposed the name *stantienite* for the black resin and *beckerite* for the brown resin, to honor the two men largely responsible for the expansion of amber production and trade. These minerals joined the nineteenth century proliferation of mineralogical materials related to amber: ajkaite (ajkite), ambrite, burmite, cedarite (chemawinite), copaite, delatynite, gedanite, gilsonite (uintahite), glessite, goitschite, hachetite, jaulingite, jelinite, kochenite, kranzite, ozokerite (ozocerite), ozonite, rosthornite, rumanite, schraufite, siegburgite, simetite, and walchowite. These terms have served primarily to identify geographical origin of the materials and were not based on any knowledge of their chemical structure. Beckerite and stantienite differ from most of these in that they were varieties found in the sands along the Baltic Sea along with succinite and are not geographically distinct from succinite.

Beck et al. (11) reexamined the case of beckerite, carried out critical new diagnostic experiments involving infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies, and concluded that this putative class of fossil amber is not a distinct mineral but rather contaminated succinite. Beck's analysis of the early literature called into question the original conclusions of Pieszczek (12). The low proportion of succinic acid, Beck noted, was not an independent result but had been inferred from the weight of precipitated barium salts. Klebs (13) already had pointed out that there are several dark-colored Baltic resins and that Pieszczek's single sample may not have been representative. Indeed, brown resin samples identified as beckerite are very heterogeneous (14). Schubert (15) concluded that the brown color of beckerite comes from the presence of decomposed wood and insect excrement known in German as *Frass* (from the German *fressen*, to eat). When Schubert examined the resinous portions of beckerite, with the exclusion of *Frass*, he found that the morphology of the resin canals was the same as present in succinite. He concluded that "there is no longer any justification to consider beckerite as a distinct resin with respect to its [botanical] origin." This conclusion falls short of saying that beckerite and succinite are structurally different. Beck and his co-workers (11) spectroscopically analyzed a dozen samples of alleged beckerite, most of which had come directly from Schubert, notwithstanding the 25 year hiatus between the two studies. They found that both IR and carbon-13 (^{13}C) NMR spectra showed no differences between the beckerite samples and control samples of succinite. Since the spectroscopic signals are proportional to relative amounts

of materials, the low concentrations of *Frass* compared with resin failed to provide observable signals. Moreover, the carbonyl regions of the ^{13}C NMR spectra were identical for beckerite and succinite, including the peak at δ ca. 170 indicative of the presence of succinic acid, contradicting the nineteenth century conclusions from ambiguous chemical isolation. Beck and his co-workers (11) concluded that beckerite is succinite contaminated with woody materials and insect detritus and should not be considered to be a distinct mineralogical material. The insect-altered wood (*Frass*) may not undergo the same process of fossilization as resin during geological aging.

Possibly due to its rarity, little scientific study has been carried out on stantienite, the other mineral described and named by Pieszczek (12). He recognized the most defensible difference from succinite and beckerite in the latter's lack of solubility in all solvents he studied. The Expert Commission on Qualification of the International Amber Association (16), based in Gdańsk, Poland, listed and described fossil resins that accompany Baltic amber in its deposits: gedano-succinite, gedanite, Baltic stantienite, Bitterfeld stantienite, glessite, and siegburgite (which the Commission spelled "zigburgite"). This list of amber is incomplete, in that it focuses on materials found in Baltic and Bitterfeld deposits, ignoring all other European materials (as well as Asian, African, Pacific, and American) but including the very different siegburgite. This material, found in Germany and New Jersey (USA), is fossilized polystyrene rather than amber, which is composed of terpenoid polymers. The Bitterfeld deposits are located near the town of Bitterfeld-Wolfen in the state of Saxony-Anhalt in the former East Germany. Amber deposits have been known there since the seventeenth century but were kept secret during the Communist period, under suspicion of association with uranium deposits (17, 18). Originally assigned to the lower Miocene period (ca. 22 Mya) and then to the Oligocene (23-34 Mya), Bitterfeld amber also has been considered to be contemporaneous with Baltic amber (35-50 Mya) (19). Although the Bitterfeld coal seams are from the Miocene or Oligocene, the amber-bearing portions may have been redeposited and are more difficult to date. As a result, the Bitterfeld deposits may be considered part of the Baltic amber complex. These conclusions are based largely on the similarity of the insect inclusions in both materials and are not universally accepted. The Expert Commission (16) provides the following descriptions: "the extremely rare black stantienite, which produces very good sheen (the 'black amber') … is confused with jet coal," and "other 'soft' and 'hard' black resins, occurring in somewhat greater

amounts in the Bitterfeld deposit, differing in hardness from stantienite." Materials from both sources have been referred to as stantienite, but it is better to maintain the distinctions of Baltic stantienite and Bitterfeld stantienite, entirely on geographical considerations.

In the only modern study of stantienite, Yamamoto et al. (20) examined a single sample of Bitterfeld stantienite by gas chromatography/mass spectrometry, in conjunction with analogous examination of two succinites, two glessites, and one goitschite from Bitterfeld. Whereas the glessites contained triterpenoids characteristic of angiosperms and the succinites and the goitschite contained mono-, sesqui-, and diterpenoids characteristic of gymospermous precursors, the stantienite produced a chromatogram predominantly of an unresolved, complex mixture of esters and diesters, indicative of waxes from higher plants. The observed carbon preference index (21) corresponded to the rank of bituminous coal. The authors did not, however, conclude that stantienite was a form of coal. Rather, they always referred to stantienite as an amber. They concluded that "peat/coal surrounding the stantienite may have contaminated the amber over geological time," and "The resin was deposited initially in a peat layer, diagenetic changes occurred continuously at the early stages, with absorption and inclusion of leaf waxes, biopolymers and triterpenoids from the surrounding peat." This study did not include Baltic stantienite, so any molecular differences between the Bitterfeld and Baltic materials remain to be defined.

NMR Spectra of Stantienite and Baltic Amber

Because beckerite proved to be mineralogically identical to Baltic amber, the distinct properties of stantienite suggested that further study of this variant also should be advantageous. During more than 35 years of sample acquisition, we have managed to obtain three samples of stantienite, which we now have examined by ^{13}C NMR spectra. Stantienite is insoluble in all solvents, so spectra were recorded on the bulk solid, rather on solutions, using magic angle spinning techniques (22). We compared the spectra of the three samples of stantienite with those of one sample of standard Baltic amber and two samples of jet.

1) Sample 34 of stantienite was provided in 1981 by the late Prof. Curt W. Beck (Vassar College) from his personal collection. He obtained it from the Paris Museum of Natural History, sample 100.1369, from Baltic sources.

2) Sample 1391 of stantienite from Palmnicken (now Yantarny, Kaliningrad) was originally from the collection of Prof. Jean H. Langenheim (University of California, Santa Cruz) via Laurie Gough (Polytechnic of the South Bank, London, (now London South Bank University)) and Prof. Royal H. Mapes (University of Iowa, Iowa City, now Ohio University, Athens, OH).

3) Sample 1538 of stantienite was from the collection of Mr. Teruhisa Ueno (Kyushu University, Fukuoka, Japan) in 2014. It came from the Goitzche mine, Bitterfeld, Sachsen-Anhalt, Germany.

4) Sample 1657 of Baltic amber was from Palmnicken (Yantarny), Kaliningrad, provided by the National Museum of Natural History, Washington, DC.

5) Jet sample J-10 was from Port Mulgrave, North Yorkshire, England, provided by Helen Muller, Bramhope, Leeds, England.

6) Jet sample J-14 was from Utrillas, Teruel (Aragon), Spain, provided by Ramón Requeixo-Rebón, Santiago de Compostela, Galicia, Spain.

Figure 2 contains the ^{13}C spectrum of sample 1657, Baltic amber from the Yantarny region of the Kaliningrad Oblast, taken on powdered, bulk material. The lower spectrum was recorded with normal decoupling of all hydrogen nuclei. As in all other such spectra, the dominant resonances occur in the region of saturated (aliphatic) carbon atoms, between δ 10 and 60 (23). These resonances are from CH_3, CH_2, and CH groups and quaternary carbon atoms. This particular pattern is repeated in all spectra of Baltic amber. In addition, weak resonances of unsaturated carbons between δ 100 and 150 are present. Characteristically, there are clear resonances from exomethylene groups (C=CH_2), with the unsubstituted carbon at about δ 150 and the methylene resonance at about δ 105. In addition, weak resonances occur in the carbonyl (C=O) region between δ 160 and 220, the peak at δ 173 being diagnostic for succinic acid. The upper spectrum was recorded with dipolar dephasing (also called interrupted decoupling). This procedure employs a delay period that allows all carbons to relax except quaternary carbons and a few rapidly moving methyl carbons. It is employed to provide a second ^{13}C fingerprint. Only two peaks remain in the saturated region. These spectra are typical for Baltic amber, which constitutes NMR amber Group C (mass spectrometric Class Ia) (24) and are very similar to the spectra of samples from the large NMR Group A (Class Ib). Both these materials derive from a similar conifer

origin. Samples from elsewhere in Europe (Romania, Sicily, France, and so on) belong to Group A. In contrast, amber from Groups B and D have an angiosperm (flowering plant) origin but have many aspects of their NMR spectra in common with Groups A and C (25, 26).
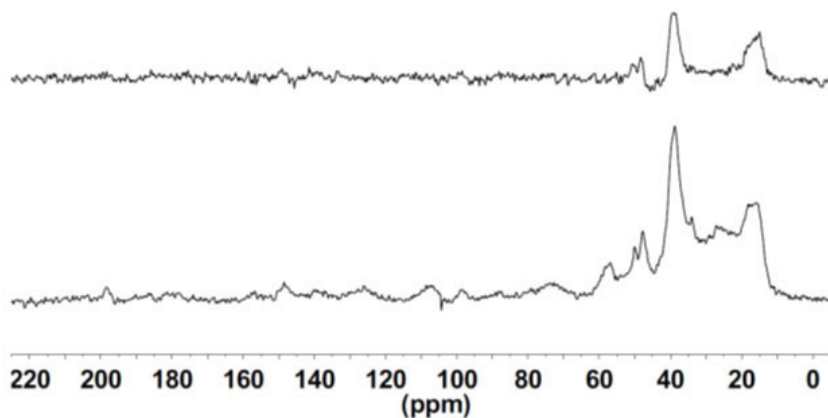
Figures 3-5 present the ^{13}C spectra for the three stan-

Figure 2. The ^{13}C NMR spectra of amber from the Yantarny region of the Kaliningrad Oblast, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1657).

tienite samples, which we will designate by the names of their donors, respectively Beck, Mapes, and Ueno. The Beck and Mapes samples are from the Baltic Sea and the Ueno sample from Bitterfeld, Germany. The spectrum in Figure 3 was recorded at a time when only complete decoupling was available. The other two figures contain spectra for both types of decoupling. All three spectra contain two broad peaks. The peak from saturated or aliphatic carbons has a maximum at about δ 33, with two side peaks at about δ 16 and δ 20 in all three spectra. The peak from unsaturated carbons (aromatic and possibly double bond or alkenic) contains a maximum at about δ 130. There is an additional peak at about δ 138, which is a shoulder in Figures 3 and 5 but larger in Figure 4. These peaks are from carbons with different substitution patterns. The broad peaks at about δ 80 and 180 in Figures 4 and 5 are artifacts of spinning the sample. Called spinning side bands, they appear equally spaced on either side of the main peak for highly anisotropic environments, as found with unsaturated but not saturated carbons. Figure 3 was taken at a higher spinning rate, so that they moved out of range. With dipolar dephasing (Figures 4 and 5), the saturated carbon peaks are largely reduced, and the unsaturated carbon peaks have lost much of the portion centered at δ 130, leaving predominantly the portion at δ 138. The latter

represent fully substituted unsaturated carbons (bearing no hydrogen atoms). The surviving saturated carbon resonances probably are from rapidly moving methyl groups. The important point is that the Baltic (Figures 3 and 4) and Bitterfeld (Figure 5) spectra of stantienites behave very similarly with dipolar dephasing.

These spectra differ fundamentally from the terpenoid patterns of amber, not just those of Baltic amber (Figure 2) but those of all types of amber (24). Spectra of terpenoid resins are dominated by the resonances of saturated carbons, have numerous, more defined peaks in that region, and have very weak peaks from unsaturated carbons. The spectra in Figures 3-5 of stantienite closely resemble those of coal and can be termed examples of carboniferous materials. Coal spectra contain a large, nearly undifferentiated resonance from saturated carbons and a very large resonance from unsaturated carbons. Of the coal spectra illustrated by Fyfe (22), those of lignite and subbituminous coal most closely resemble the present spectra of stantienite. Spectra of bituminous coal have stronger unsaturated than saturated peaks, spectra of anthracite lack unsaturated peaks entirely, and spectra of peat exhibit stronger saturated peaks. Resonances from phenolic carbons are found in the spectra of less matured lignite, e.g., Onakawana lignite, but are absent
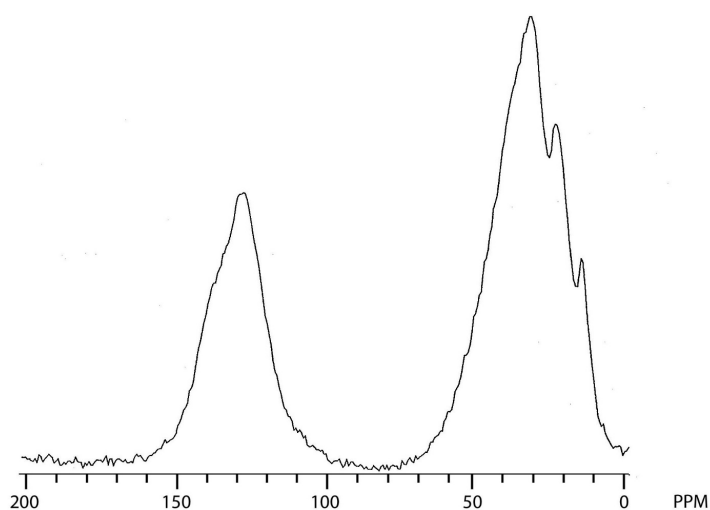

Figure 3. The ^{13}C NMR spectrum of stantienite from the Baltic Sea, donated by Curt W. Beck, with decoupling of all hydrogen nuclei (sample 34), adapted from Figure 9 of Ref. 30.
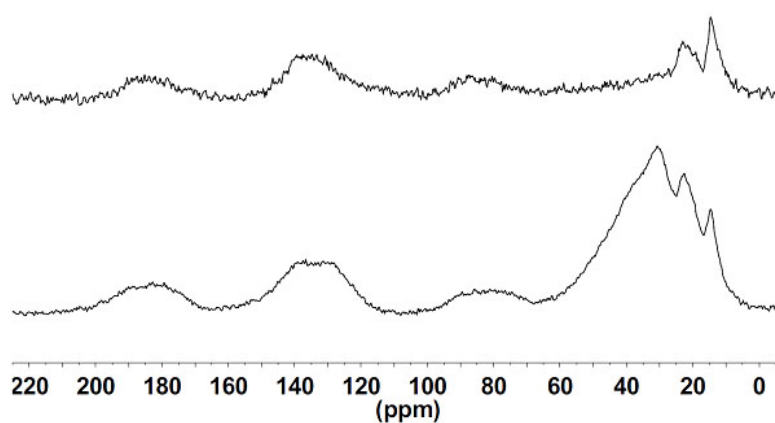
Figure 4. The ^{13}C NMR spectra of stantienite from Yantarny, Kaliningrad, donated by Royal H. Mapes, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1391).
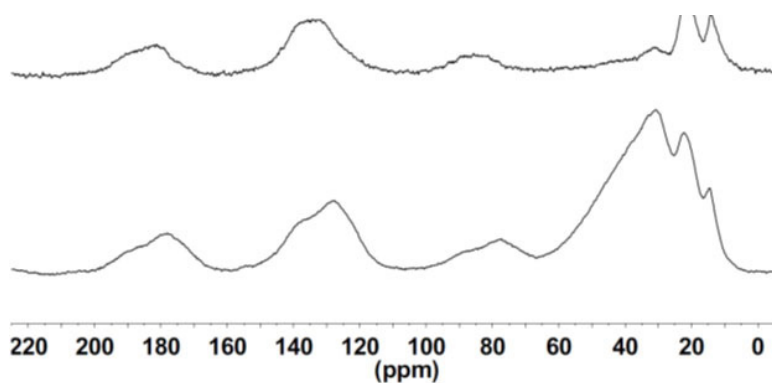

Figure 5. The ^{13}C NMR spectra of stantienite from Bitterfeld, Germany, donated by Teruhisa Ueno, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1538).

from the spectra of more matured lignite, e.g., lignite A, in Fyfe's examples. Phenolic peaks, which would occur at about δ 150, are absent in Figures 3-5. Subbituminous coal samples vary from spectra exhibiting nearly equal saturated and unsaturated peaks to spectra with much stronger unsaturated than saturated peaks. Stantienite reproducibly exhibits stronger saturated peaks, more similar to lignite. Thus we identify stantienite as a type of coal or carbonaceous material of rank most closely resembling more highly matured lignite.

Comparison with NMR Spectra of Jet

Jet, like amber, is considered to be an organic gemstone (27). Its shiny, black appearance has been appealing for jewelry and other purposes since Neolithic times, but particularly during the Victorian period in England for mourning decoration. Jet, unlike amber but like coal, derives from woody material that has been compressed under anaerobic conditions over geological times. Lambert, Frye, and Jurkiewicz (28) inferred from the solid state ^{13}C NMR spectra of several samples that the rank of jet is between those of lignite and subbituminous coal. Figures 6 and 7 show respectively the ^{13}C spectra of jet samples from England and Spain. They illustrate typical carbonaceous spectra, with the two peaks from aromatic and aliphatic carbons. The spectrum in Figure 6 from Port Mulgrave, which is nine miles (15 km) northwest of Whitby, a famous Yorkshire source of jet, closely resembles those of stantienite in Figures 3-5. In particular, the saturated resonances in both materials exhibit the shoulder peaks at about δ 16 and 20 (compare Figures 3-5 with Figure 6). In both cases the integral of the aliphatic peak is greater than that of the aromatic peak. For the Spanish sample (Figure 7), the aromatic resonance is slightly larger than the aliphatic resonance, and the shoulder peaks on the low frequency side of the aliphatic resonance are absent. Both jet spectra exhibit a spinning side band at about δ 240. In contrast to the stantienite spectra, the jet spectra exhibit clear phenolic resonances at δ 155, a diagnostic characteristic.
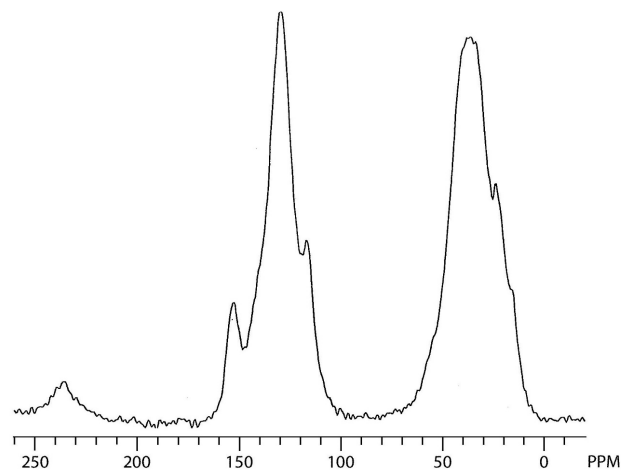
Figure 6. The ^{13}C NMR spectrum of jet from Port Mulgrave, North Yorkshire, England, donated by Helen Muller, with decoupling of all hydrogen nuclei (sample J-10).
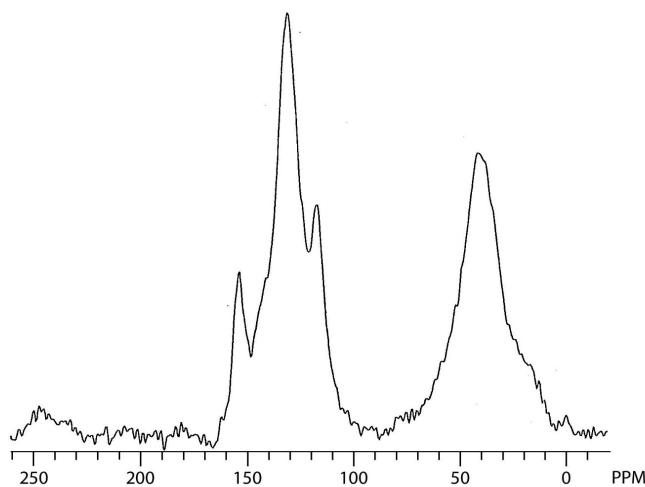
Figure 7. The ^{13}C NMR spectra of jet from Utrillas, Teruel (Aragon), Spain, donated by Ramón Requeixo-Rebón, with decoupling of all hydrogen nuclei (sample J-14), adapted from Figure 4 of Ref. 28.

Other mineraloids (noncrystalline mineral-like materials) resemble stantienite and jet, including Oltu stone from Turkey (29). Oltu stone has been found in coal mines in the Turkish province of Erzincan. Commonly called black amber, it has been worked, particularly in the Turkish city of Erzurum, for the production of jewelry and other decorative objects, We have obtained samples from two sources (Sezai Adıl of Erzincan University and Serap Mutun of Abant Izzet Baysal University) and examined their carbon spectra in the solid (Figure 8). They are nearly identical to the spectra of jet in Figures 6 and 7, so that this organic gemstone, like stantienite, may be considered a variety of jet.
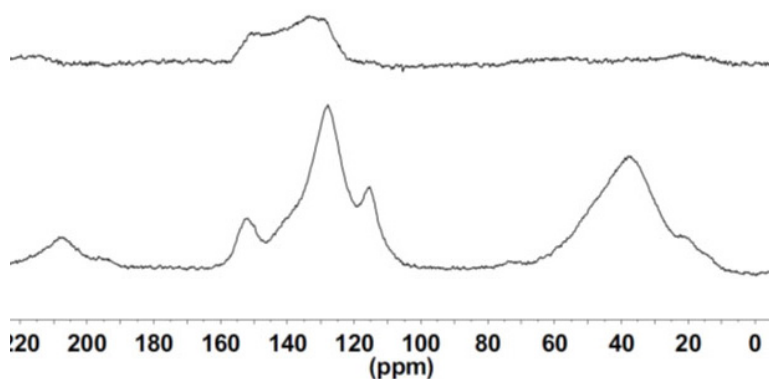
Figure 8. The ^{13}C NMR spectra of Oltu stone, donated by Sezai Adıl, Erzincan University, Erzincan, Turkey, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1666).

There is no evidence that amber degrades to a carbonaceous material. As amber matures or fossilizes (from comparison of Eocene to Cretaceous materials) (30), the saturated resonance broadens but the unsaturated region does not grow. As carbonaceous materials mature (lignite to anthracite), the unsaturated region becomes increasingly dominant. Amber in its form known as resinite is found as transparent, shiny inclusions within coal seams, the resin surviving as distinct material within the woody host during the progress of degradation.

Conclusions

The solid state ^{13}C NMR spectra of three samples of stantienite, two from the Baltic Sea and one from Bitterfeld, Germany, indicate that this mineraloid is a carbonaceous material of coal rank approximating that of mature lignite. The spectra bear no resemblance to those of amber of any variety, which are dominated by aliphatic resonances and contain very weak alkenic resonances and none from aromatic carbons. Spectra of stantienite are very similar to those of jet from England and Spain, although the latter exhibit modest phenolic resonances. Stantienite closely resembles jet in appearance and in lack of solubility. Oltu stone from Turkey also proved to be a carbonaceous, rather than a resinous material, very similar to jet.

In the mass spectral study by Yamamoto et al. (20) of Bitterfeld stantienite, the authors powdered and sonicated the single sample three times in 1:1 dichloromethane:methanol and examined both underivatized and silyl-derivatized materials by mass spectrometry. Because of the low solubility of stantienite in comparison with their other study samples, the extracts of stantienite must have represented only a minor portion of the bulk. The ^{13}C NMR method examines the entire bulk material in a powdered form. Nonetheless, Yamamoto et al. were able to draw valuable conclusions that are not in contradiction with our results. The other Baltic materials in the Yamamoto study predominantly exhibited distributions of terpenoids in their mass spectra, whereas stantienite exhibited unresolved, complex mixtures of esters, with only minor amounts of terpenoids not found in the other Baltic materials. They interpreted these results as indicative of waxes from higher plants with a carbon preference index corresponding to bituminous coal. They did not revise the structure of stantienite, however, maintaining that it is a type of amber (despite the low content of

terpenoids) that had been contaminated by surrounding peat or coal.

It is clear from the ^{13}C NMR examination of bulk, solid stantienite that it is not an amber but rather a carbonaceous material resembling lignitic coal in structure and resembling jet in structure and appearance. Oltu stone from Turkey follows the same pattern. They should not be considered varieties of amber ("black amber") and do not merit distinct mineralogical designations.

Acknowledgments

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Proceedings of IWHC2015

Proceedings of the 2015 International Workshop on the History of Chemistry, held March 2-4, 2015 at the Tokyo Institute of Technology are available online at

http://kagakushi.org/iwhc2015/proceedings

The title of IWHC2015 was "Transformation of Chemistry from the 1920s to the 1960s." The proceedings are edited by Masanori Kaji, Yasu Furukawa, Hiroaki Tanaka, and Yoshiyuki Kikuchi.

TOOLS FOR CHEMISTS: THE DESREUX-BISCHOFF VISCOSIMETER

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Summary

This particular tool was of use, during the heyday of polymer chemistry, in determining the molecular weight of a macromolecule. Arguably, "name" pieces of glassware for the chemical laboratory are landmarks in the history of chemistry and they thus deserve notice. The so far unacknowledged contribution of the glassblower, who actually built this apparatus, is put on record.

Introduction

The previous paper in this series was devoted to the so-called Dean-Stark trap, used to remove water from a solvent or a solution (1). The name of the glassblower, Mr. Demuth, who actually made the apparatus, was absent from the roster of authors, even though his contribution was acknowledged at the end of the article.

This was not an oversight. As a rule, glassblowers, and technicians more generally, were not included in print. It was a social class distinction. Laboratory technicians, during that period of the 1920s, were like blue-collar workers in industry. They were deemed mere manual workers. Authorship of scientific publications was reserved for scientists, typically those with a Ph.D. degree, whose contributions were recorded in a laboratory notebook, prior to possible transfer to journal pages (2).

Such an inferior status of technicians endured into the 1950s, as the present paper will showcase. Another glassblower, Mr. Wenig, was the "invisible man" in the paper I am about to describe and comment upon (3). Since I was professionally acquainted with this gentleman, this article also draws on personal recollections.

The Apparatus

The apparatus worked in what was then the standard way to measure the viscosity of a liquid, by timing how long a given volume took to flow through a glass capillary. Leo Ubbelohde, in Berlin, had both patented and published such a device towards the end of the 1930s (4). The diagram from his US patent is shown in Figure 1. The Ubbelohde viscometer—the two accepted spellings are *viscometer* and *viscosimeter*—which Desreux and Bischoff (3) used as their template, was of the "suspended level type," viz. referring to the air-liquid interface existing in the feeding bulb before the liquid flows through the capillary. This innovation obviated the need to correct for surface tension. Another correction is necessary in principle for the kinetic energy of the solution as it flows through the capillary tube. In order to minimize this second correction, one has to decrease the rate of the flow, which can be done either by a very narrow capillary tube—but then dust particles may affect the determination—or by reducing the hydrostatic pressure driving the flow.

Desreux and Bischoff opted for the latter solution (Figure 2), achieved by placing next to one another the two containers for the liquid solution, at departure into the capillary and arrival from it. The bulb that fed the
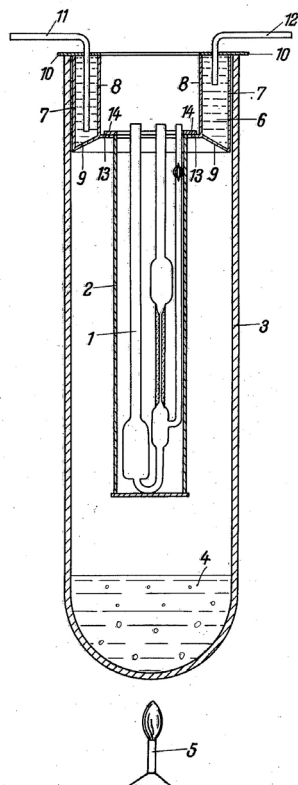
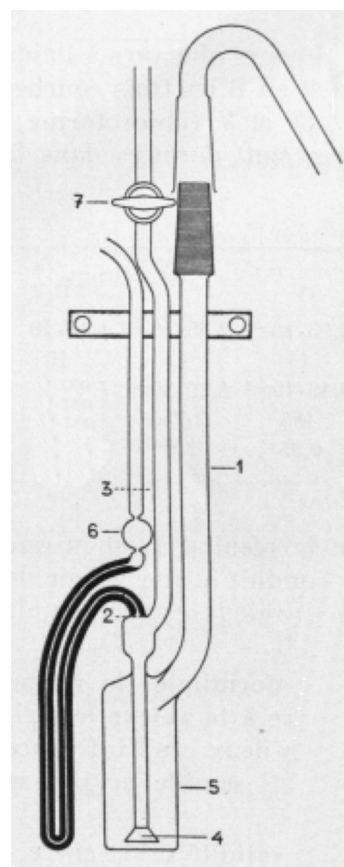*Figure 1*. Diagram of viscosimeter from Leo Ubbelohde's US patent (Ref. 4a).

Figure 2. Diagram of viscosimeter Desreux and Bischoff's paper (Ref. 3).

The Plastics Era

1950, when this paper was published, besides marking the mid-twentieth century, was also a pivotal date marking the switch from a broad swath of natural products to synthetic materials made of polymers, which to a large extent were petrochemicals (5). There is a long list of such substitutions, of which I need mention only Plexiglas® for glass windshields; acrylates for wool and cotton; nylon and other polyamides for silk; synthetic elastomers for natural rubber; PVC for ceramic tiles, wooden floors and lead tubing; styrene-butadiene foam rubber for sponges; Formica® laminate from melamine resin (1938) for wood; polyethylene for glass in bottles; PVC-covered fabric for leather; polymeric substitutes for horn in combs; … Indeed, such a list could go on for pages and pages (6). In 1950, it did not take the gift of prophecy to herald a triumphant Age of Plastics, as polymers became known popularly. To the historian, the justifiably famous line written by Buck Henry for the movie *The Graduate* (1967), "One word: plastics," the career advice given to the young Benjamin played by Dustin Hofmann, was late by a quarter-century.

capillary (labeled 6 in the figure) had a fixed and known volume between 0.5 and 1 mL. The diameter of the capillary they used was 0.25 mm. Its length varied between 10 and 20 cm depending upon the viscosity to be measured, and the hydrostatic pressure driving the flow was kept to a 3 cm height of liquid above the capillary racetrack. 40 mg of polymer dissolved in about 7 mL of solvent was sufficient for a series of viscosity measurements, which translated into a determination of its molecular weight. Both filtration of the solution and serial dilution could be done within the apparatus. Filtration was accomplished by drawing the solution through fritted glass (labeled 4) and dilution by introducing solvent via the sidearm (labeled 1). The whole determination could be done in a couple of hours (3).

Polymer Chemistry and Physical Chemistry in 1940

Hermann Staudinger (1881-1965), was the founding father of polymer chemistry, who had staunchly defended the revolutionary concept of macromolecules until it gained acceptance. In 1930, Staudinger proposed the simplest of correlations between the observable viscosity and the unknown molecular weight, a simple proportionality (7, 8).

During the late 1930s, American chemists burst upon the scene of polymer chemistry and they stole the show. A genius, Wallace H. Carothers (1896-1937), synthesized polyamides. The company he worked for, DuPont de Nemours, successfully began marketing stockings made from the new material, nylon, thereby replacing silk.

If there was a single scientist who carried forward Staudinger's and Carothers's work, developing the physical chemistry of polymers and the precise dependence of viscosity on molecular weight, he was Paul J. Flory (1910-1985). Other polymer physical chemists active in the field and who carefully studied the relationship between the viscosity of solutions and the molecular weight of the polymer were Herman F. Mark (1895-1992) and Werner Kuhn (1899-1963).

A student and a coworker of Carothers, Flory seems to have inherited from him the shuttling between industry and academia, between practical results and conceptual advances that was the distinctive mark, at least at some times, of the Experimental Station of DuPont, in Wilmington, Delaware. After a few years at DuPont, Flory started his academic career at the University of Cincinnati (1938-1940). He would return to industry from 1940 to 1948, when he again came back to academia.

While in Cincinnati, Flory investigated the relationship of viscosity to the length of a polymeric chain. He did so both empirically and theoretically, from first principles. Staudinger had been intuitively right, but factually mistaken. The intrinsic viscosity of polymers in solution is proportional to the 0.64 power of the molecular weight, rather than to its power unity (9).

Polymer Chemistry and Physical Chemistry in 1950

In the late 1940s-early 1950s, the main subcultures of chemistry, in an academic setting, were organic, inorganic, physical, analytical and biological. Before university expansion reached full bloom in the United States, led by research universities funded by government grants, a predominantly post-Sputnik development, industrial laboratories were the main employers of university-trained chemists, at both the B.S. and Ph.D. levels (10). Pharmaceutical companies and dye manufacturers hired organic chemists, producers of commodities hired inorganic chemists, biological chemists found positions in government laboratories and specialized niches, such as breweries. Industry of all kinds had a need for analytical chemists, to run their spectroscopy apparatus in particular. Physical chemists to some extent enjoyed pride of place: industry looked to them for managerial positions, as group leaders, not only as specialists in instrumentation (11).

With the rise of petrochemicals and polymers, a new need arose in the aftermath of World War II for chemists trained in the brand-new polymer science. One such scientist, the head of a whole school of polymer chemists, was the previously named Paul J. Flory. Let me briefly remind the reader of his post-Cincinnati career, it will help to put into context the invention of the Desreux-Bischoff viscosimeter.

As Flory wrote in his Nobel autobiography (12)

In the Spring of 1948 it was my privilege to hold the George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University. The invitation on behalf of the Department of Chemistry had been tendered by the late Professor Peter J. W. Debye, then Chairman of that Department. The experience of this lectureship and the stimulating associations with the Cornell faculty led me to accept, without hesitation, their offer of a professorship commencing in the Autumn of 1948. There followed a most productive and satisfying period of research and teaching. *Principles of Polymer Chemistry*, published by the Cornell University Press in 1953, was an outgrowth of the Baker Lectures.

It was during the Baker Lectureship that I perceived a way to treat the effect of excluded volume on the configuration of polymer chains. … It became apparent that the physical properties of dilute solutions of macromolecules could not be properly treated and comprehended without taking account of the perturbation of the macromolecule by these intramolecular interactions. The hydrodynamic theories of dilute polymer solutions developed a year or two earlier by Kirkwood and by Debye were therefore reinterpreted in light of the excluded volume effect. Agreement with a broad range of experimental information on viscosities, diffusion coefficients and sedimentation velocities was demonstrated soon thereafter.

In short, measurement of the viscosity of polymer solutions was a very important piece of data at the beginning of the 1950s, when Desreux and Bischoff published the apparatus they had devised. Their publication (3) mentioned only the Staudinger proportionality, ignoring the 1940 correction by Flory.

The Belgian Context

Victor Desreux, when he designed this new tool for polymer chemists, was a professor of physical chemistry at the University of Liège, in Belgium. Given the lead Flory and others had taken in polymer chemistry, one might have expected for this invention to have occurred in an American institution. Thus, a word of explanation is needed, concerning Belgium and chemistry in Belgium, during that period of the beginning of the 1950s.

With a population then of 8.6 million people, this small country had four universities. They reflected a careful political balance. Two were private, so-called Free, universities; the other two were State universities. The Free universities were the Catholic University in Louvain (Leuven), which had existed for many centuries as a gem of the Catholic Church. To counterbalance its influence, Brussels housed the officially atheistic Free University, rumored to be under the influence of Freemasons. As for the officially non-ideological State universities, one was located in Ghent (Dutch-speaking Flanders), the other in Liège (French-speaking Wallonia). At that time (1950), French speakers made up the political, administrative and educational elite of the country. Of these four universities, the Catholic university in Louvain was the most prestigious and was known the world over.

During World War II and their occupation of Belgium, the Nazis had played on the linguistic split between the Flemish and the Walloons. They deemed the former legitimate Aryans and the latter degenerate Latins. After Germany lost the war, the Flemish were again under the political rule of French speakers. Only several decades later would they come out on top, on the strength of their more prolific demography. Since World War II has been mentioned, let me note for future reference that Belgium acquired, as part of war reparations, a significant number of German prisoners. They were put to work in the coal mines, located predominantly in the Walloon part of the country.

Belgium, previously part of the Netherlands, gained its independence in 1830 and was set as a buffer state, between Holland, England, Germany and France. It was the second region in Western Europe, after England, to have undergone the Industrial Revolution, drawing on its coal mines. Hence, Belgians remained keenly aware, in the aftermath of World War II, of the economic importance of industry to their prosperous well-being. Even though Belgium was a small country, its industrial exports, then greater than those of the Soviet Union, were in 1950 among the industrial giants in the world. At that time, Belgium was also a colonial power. Its possession of the Belgian Congo gave it enormous mineral wealth (13).

In terms of the chemical industry, Belgium was home to the Solvay corporation, started by Ernest Solvay (1838-1922) in 1863, that had thrived on exploitation and exportation of the Solvay Process. By 1950, it became the biggest producer of chemical commodities in Belgium, including polymers such as PVC (14). Belgian academic chemists, proud of the industrial achievements of their country, felt very close to the concerns of their industrial counterparts.

Thus, even though their number was small, they did not feel inferior to their British, Dutch, French and German colleagues. In mentality, because Belgium was such a new country, because World War I had been fought to a significant extent on its territory, because the United States had intervened in both World Wars to liberate it from the Germans and had helped afterwards in its reconstruction, and because of its Swiss-like prosperity relative to adjoining countries, Belgians were Americanophiles and their affluent lifestyle was very much American-like.

Victor Desreux, the Senior Author

The senior author, Victor Desreux (1910-2004) was born and educated in Ghent. He earned a doctorate in chemistry at the University of Ghent in 1934, when the French language was still tolerated there—only a year before full Flemishization was imposed in 1935-36—in Frédéric Swarts's (1866-1940) laboratory, devoted to fluoro-organic molecules (15). A co-worker of Desreux, Ms. Yvonne Désirant, achieved the first preparation of hexafluorobenzene.

During the ensuing years, Desreux had outstanding training. He followed a path worthy of a student in Early Modern times, with study in no fewer than four institutions of higher learning in three different countries outside of Belgium. It covered a wide diversity, not only of topics, but of sub-disciplines of chemistry as well.

His first postdoctoral stay was in 1935 with Professor Georges Dupont (1884-1958)—an organic chemist

whose specialty was terpenes, with applications to perfume chemistry—at the École *normale supérieure*, in Paris. Half-a-dozen publications resulted from that stay (16). For instance, Desreux and Dupont made a chiral allene, taking advantage of the acetylene-to-allene rearrangement. On to Utrecht, where he spent the year of 1936 in Professor Hugo Rudolph Kruyt's (1882-1959) laboratory, devoted to the physical chemistry of colloids. Then, with a fellowship from the American-funded Commission for Relief in Belgium, from 1937 to 1939 Desreux went on to Cambridge, Massachusetts, where he was a postdoc in Louis F. Fieser's (1899-1977) laboratory at Harvard. He worked on carcinogenic aromatic hydrocarbons, synthesizing derivatives of 20-methylcholanthrene (17). During his stay, Desreux presented a seminar on his doctoral work and organofluorine chemistry (18). In 1938-39, Desreux moved to Princeton, New Jersey, where the Rockefeller Institute—later upgraded to a University—was then located. He joined the protein laboratory of John H. Northrop (1891-1987), Nobel prizewinner in 1946, where he worked on the enzyme pepsin, and its preparation as a pure protein. Three publications ensued from Desreux's work at Princeton (19).

Only then, after spending four years abroad, did Desreux return to Belgium—and the onset of World War II, with Nazi Germany occupying Belgium. He received a teaching position in 1941 at the University of Liège, as *chargé de cours* (lecturer). He was able to resume physico-chemical studies of polymers in 1945, after the war ended. He gained a full professorship, in physical chemistry, in 1946. Belgian universities copied the German faculty system. Full professors came in two categories. An *ordinarius* professor was full-time and had to reside locally. An *extraordinarius* professor was a visiting, part-time faculty member. Desreux became an *ordinarius* professor.

As for his coworker J. Bischoff, he was a graduate student who acquired his doctorate working under Desreux's supervision on polymer chemistry (20) and who left his laboratory, presumably for an industrial position, by the mid 1950s. In the meanwhile, he was a postdoc in Professor Arthur V. Tobolsky's (1919-1972) laboratory in the Department of Chemistry at Princeton (21). (Tobolsky and I were colleagues there during the ensuing decade, in the 1960s).

Finding the Invisible Man

In the aftermath of World War II, the city of Liège reverted to its former life, cultural, social and economic.

The local bourgeoisie, French-speaking, proud of institutions such as the University, the music conservatory and symphonic concerts, a theater and an opera, thrived on the proceeds of geography. Liège, on the river Meuse with important barge traffic, was well located between Brussels, Antwerp, Maastricht and Aachen, by road or rail. Trade was thus a major factor in its prosperity. Another was manufacturing.

Engineers were a significant part of the city elite. Liège, rather comparable in that respect to the Pittsburgh I have depicted in the previous paper in this series, was blessed with a natural resource—coal rather than petroleum. Nearby coal seams, within the French-speaking Walloon area, fed into the dominant industry in Liège, siderurgy. The iron ore came by rail, via Luxemburg, from Lorraine in France.

Coal mining is hard work, and it is also dangerous. Hence, the Liège bourgeoisie imported the needed workforce. At first, it resorted to the Flemish. But after their Belgian fellow-citizens organized themselves as efficient agriculturalists, via the Boerenbond organization, and prepared themselves to rival French speakers for running the whole country—as we saw, an early symptom was their take-over of the University of Ghent starting in 1930—there was a need to replace them in coal mines. Thus, Poles and Italians were imported as coal miners and steelworkers (22). This population of immigrants settled in the suburbs of Liège.

With the end of World War II, a yet cheaper source of labor could be tapped, German war prisoners. As part of the war reparations, Belgium was able to secure an abundant supply of slave labor from Germany. Abundant? No fewer, than 60,000 German prisoners were obtained from the Allies. They were coerced into coal mining, under subhuman conditions that violated both international (the Geneva Conventions) and national (the Belgian social legislation) laws. Their working and living conditions were so severe that 4,000 Germans tried to escape. 23 were shot and killed in the attempt. This resort to slave labor, Germany being repaid in its own currency, lasted between 1945 and the spring of 1948 (23).

During that period, at the beginning of 1947, Professor Desreux and his colleagues from the Institute of Chemistry, Louis D'Or and Georges Duyckaerts, needed a glassblower for their Institute. Desreux had an idea: surely, there must be among the German prisoners some who had been trained as glassblowers in their earlier, civilian life. Before the war, Germany, factories in Jena

in particular, had enjoyed a reputation as world leaders in glasswork of every kind.

The Liège chemistry professors advertised their offer to this large captive population, a competition would be held at the University of Liège for a glassblower, who accordingly would be liberated from his brutal coal mining duties. Three young Germans, with the proper credentials, were selected (24). After he won the competition, Mr. Heinz Wenig started work at the Chemistry Institute on May 15, 1947.

One might have expected him to have returned to Germany during subsequent years. However, he met a local Belgian woman whom he married, they started a family, and he continued working for the University of Liège, heading a small glassblowing workshop with three or four coworkers at the Chemistry Institute until his retirement, aged 60, on July 1, 1984. During the intervening decades, Professor Desreux remained the administrative supervisor for the glassblowing shop (Figure 3).

Figure 1. Heinz Wenig, the glassblower (left), and Professor Victor Desreux (right). A picture from the late 1970s or early 1980s.

As a personal note, I was acquainted with Mr. Wenig for almost my whole time as an *ordinarius* professor of chemistry at the University of Liège, 1970-1986. (I became *extraordinarius* from 1986 until 1995 when I returned to the *ordinarius* status, until 1999 when I retired.) As a craftsman, I found Mr. Wenig to be superb. He told me he enjoyed the challenge of the most intricate tasks. As a person, he was very congenial, friendly without being obsequious and he spoke French with a melodious German accent. He and I also had a connexion because of the tragedy that befell him. A couple years after I started teaching in Liège, I had his son as a student, a freshman

in biology. A few weeks into the semester, the young Wenig was killed in a car accident.

Laboratory Technicians

Universities in Belgium, such as the University of Liège, are representative of European universities in the way they treat laboratory technicians. In mid-twentieth century, at the time Desreux and Bischoff published their design of a capillary viscometer, someone like its craftsman, Heinz Wenig, enjoyed a well-recognized status, a position guaranteed for years, even though the salary was meager (25). At least during the first two decades, he had to clock in and out, like a factory worker. Even though he did not sign the publication, I surmise that Mr. Wenig contributed to the design of the apparatus he built.

During the second half of the twentieth century, technicians with permanent appointments were viewed as an asset for European academic scientists, Belgians in particular. Their American colleagues were envious, they did not enjoy the same privilege. American universities maintained an alternative organization, in a tradition going back to Justus von Liebig's laboratory in Giessen (26). Graduate students did the technical work, and thus had to be trained anew in these ancillary technical tasks every few years.

Named Glassware

Even though the new device was described in a relatively obscure chemical journal, it was nevertheless adopted by a number of laboratories, in polymer chemistry predominantly—this is no surprise—all over the world. The paradox is that by publishing a description of this little device, Desreux and Bischoff achieved immortality—of sorts. It became known henceforth as the Desreux-Bischoff viscometer. Looking up these words with Google Scholar, yielded 242 hits on February 19, 2014.

It is in good company. To think of it, quite a few other pieces of glassware bear the names of their progenitors. I have often toyed with the idea of teaching a history of chemistry, anchored by such devices. It would provide quite a different narrative from the more usual, geared to Nobel prizewinners. Just as there are name reactions, there are also name (or named) pieces of laboratory apparatus, more often than not part of the glassware. They vouch for the permanence of glassware in both chemistry stockrooms and laboratories.

Even a short list would need to include several dozen named pieces of glassware, such as, in alphabetical sequence (the) Abderhalden drying pistol / Allihn condenser / Bennert vacuum gauge / Buchner flask / Buchner funnel / Dean-Stark trap / Dewar flask / Drechsel bottle / Eppendorf tubes / Erlenmeyer bulb / Erlenmeyer flask / Florence flask / Friedrich condenser / Gay-Lussac pycnometer / Gooch crucible / Graham condenser / Hempel, Oldershaw, Snyder and Vigreux distillation columns / Hirsch, Powder and Filter funnels / Hopkins reflux condenser / Imhoff cone / Kipp's apparatus / Kitasato flask / Kofler bench / Liebig condenser / Liebig *kaliapparat* / McCarter sublimer / Ostwald viscometer / Pasteur pipettes / Petri dishes / Schlenk flask / Schott bottle / Soxhlet extractor / Thiele tube / Ubbelohde viscometer / West condenser.

Naming pieces of glassware, in like manner as with name reactions (27), pays homage to their inventors. Which shows, again in like manner as with key transformations, the central importance of designers of novel glassware to chemical history.

Conclusion

Thus we end this microhistory with the notion of the importance of those scientists and technicians having devised a tool for the laboratory, at least in the form of glassware. One of the virtues of a microhistory is to resurrect otherwise anonymous persons, Mr. Heinz Wenig in this case. That chemists are history-conscious is well established; the popularity of chemical genealogies partakes of the same spirit as the naming of reactions and of glassware instrumentation. Why such an acute consciousness of past achievements and achievers? Because chemistry, in addition to being a science, is a craft. To this day, its knowledge, theoretical and practical both, is passed on as master-to-apprentice. At least in that aspect, chemists are the heirs to alchemists.

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About the Author

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

A PIONEERING COURSE IN PHYSICAL ORGANIC CHEMISTRY: J. W. BAKER'S 1942 THIRD-YEAR LECTURES TO UNDERGRADUATES

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Introduction

Physical organic chemistry is a creation of the twentieth century in which the techniques used in physical chemistry were introduced to the study of structure, properties and mechanisms of organic molecules. As Tidwell has pointed out (1):

> Thus by 1925 the experimental basis of the subject existed in a form very recognizable today: the major reactive intermediates, namely carbocations, free radicals, carbanions, and carbenes had been formulated, and the first three were even known as long-lived species; kinetic investigations of reaction mechanism were being applied; and the key factors influencing the structure-reactivity relationships were being considered such as stereochemistry, steric effects, and electronic substituent effects.

This new field came to be known as physical organic chemistry with publication of Louis Hammett's book of the same name in 1940 (2). In the five years preceding the publication of Hammett's book several British authors had written works which had a physical organic orientation, which attests to the interest in this newly developing area of investigation in Great Britain. Among these works are ones written by Watson (3) and Waters and Lowry (4). One must also acknowledge the 1934 *Chemical Reviews* article by Ingold, "Principles of an Electronic Theory of Organic Chemistry" (5), which would have been available to many American chemists either directly or in libraries.

These were advanced texts and likely were not used as texts for courses for undergraduates, but rather for reference and for keeping up with the latest developments in this new field of organic chemistry. The emphasis in instruction was still very much oriented to descriptive organic chemistry and its application to synthesis and elucidation of structure of natural products.

The person who had the greatest influence internationally on the development of physical organic chemistry was Christopher Kelk Ingold (1893-1970) (6). His appointment as Professor of Organic Chemistry at Leeds University in 1925 allowed him to initiate a revolution in the way organic chemistry was to be taught. Instead of rote memorization, understanding by examination of structure and mechanism became the emphases of Ingold's revolution. When Ingold left Leeds in 1930 to become professor of organic chemistry at University College London, his former student and collaborator John William Baker (1898-1967) continued the course of lectures given to students in their third and final year of their B.Sc. degree course. In the three ten-week terms in the British academic calendar, third-year students would attend lectures in advanced topics chosen by the lecturers and which reflected generally their interests. Thus it was quite natural for Baker to continue the Ingold course and to continuously update it with new discoveries in the burgeoning field of physical organic chemistry (7).

The new system of Ingold was given the name the "English school" to denote its origins and its difference

from traditional organic chemistry in the period up to 1950. In the United States this new way of connecting structure and mechanism did not make much of an impression. In the preface to his *Electronic Interpretation of Organic Chemistry*, published in 1943, A. E. Remick writes (8):

> Another objective, shared by all advanced courses which are "frontier courses," is to give the student such knowledge as is necessary to follow future developments in the field by reading the research literature. It is partly for this reason that the symbolism and language of the English school have been introduced, despite the fact that they are not popular in this country at the present time.

The basis of this paper is the set of notes taken by Donald Vincent on Baker's course in the second term (mid-January to Easter) of the academic year 1941-1942 at Leeds University (9). Several of the topics covered will be discussed in the context of the work of Ingold as summarized in the 1953 first edition of his *Structure and Mechanism in Organic Chemistry* (10). The opportunity to present the George Fisher Baker Lectures at Cornell University in the fall semester of the academic year 1950-1951 was the incentive to produce the first edition of this book. This book summarized the work of Ingold and his collaborators at University College London and included much research done by other physical organic chemists.

Major Topics Covered in the Lectures

The following is a list of the subject areas covered in the course of lectures at Leeds. Since the course notes do not have dates so as to gauge the amount of time devoted to each topic, they are listed in the chronological order as found in the notes.

•The modern electronic theory of valency (14 pages)

•Application of principles: electrophilic and nucleophilic aromatic substitution (14 pages)

•Tautomerism (24 pages)

•Substitution at saturated carbon (8 pages)

•Elimination reactions and addition reactions (13 pages)

I will discuss in detail three of the subjects that are most associated with Ingold and the so called "English school." These are the modern electronic theory of valency; orientation effects of substituents in electrophilic aromatic substitution; and mechanisms of nucleophilic substitution at saturated carbon as well as elimination reactions. For the three subjects discussed in detail I shall make comparisons with the 1953 first edition of Ingold's *Structure and Mechanism in Organic Chemistry* (henceforth SMOC) to show how advanced this course was for undergraduate instruction in 1942.

The Modern Electronic Theory of Valency

The lectures begin with a review of covalent bond theory and proceed to electronic displacements by the inductive effect and other modes of electron displacement. The terminology used is pure Ingoldian such as inductive, inductomeric, mesomeric, and electromeric, and also + and − signs to note excess and deficiency of charge. In deference to Ingold's longtime rival Robert Robinson
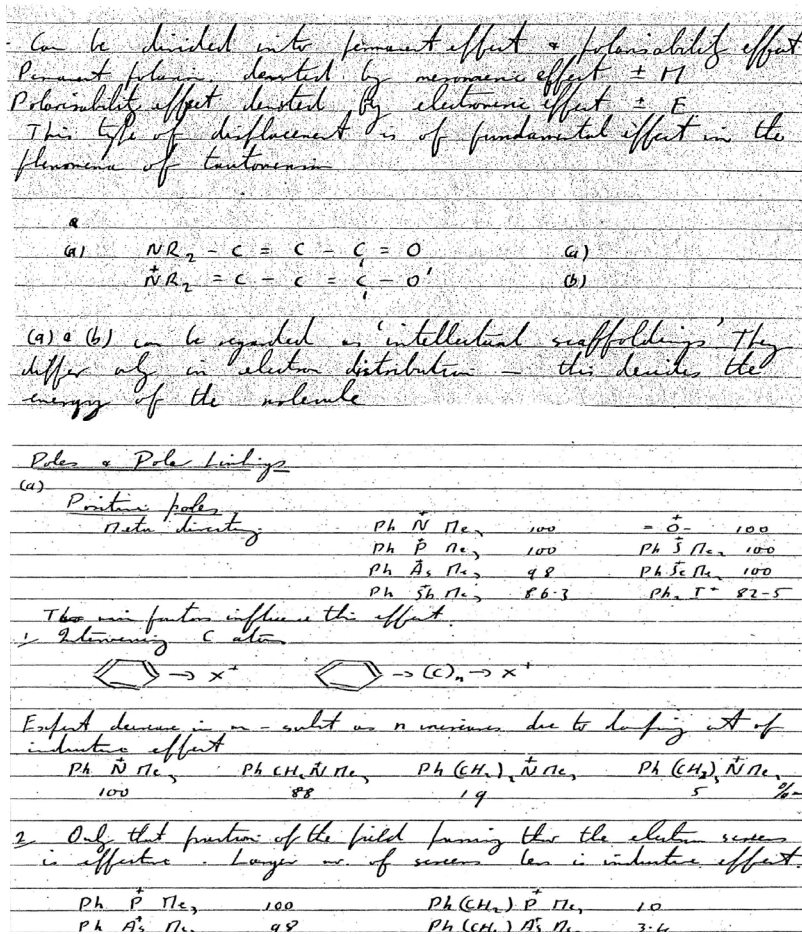
***Figure 1**. Illustrations of the various types of electron displacement*

the curved arrow to show movement of electron pairs is also included. Coupling of these effects is also discussed in terms of where they work in tandem with each other or in opposite directions. Baker's concept of hyperconjugation, for which he is probably best known, is offered as the best explanation for understanding the effect of alkyl groups. The important role played by poles and polar linkages as well as the position of these groups in molecules is illustrated.

Ingold devotes 32 pages in Chapter 2 of SMOC to the material covered in this first section of introductory lectures presented by Baker. Shown below is a typical entry from this first part of the course which illustrates various electron displacement effects as well as the resonance (mesomeric) effect.

TABLE 18-1.—EFFECT OF SIDE-CHAIN LENGTHENING ON PERCENTAGES OF META-DERIVATIVES FORMED IN MONONITRATION OF AROMATIC AMMONIUM IONS.

Substituent Effects in Electrophilic Aromatic Substitution
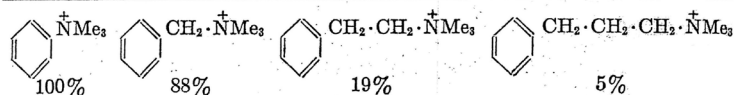
Figure 2. Aromatic substitution results from Baker's course (above) and from Ingold's SMOC (below).

Orientation effects of substituents in aromatic systems had been the subject of much empirical investigation in the late nineteenth and early twentieth centuries. Experimental results from reactions such as nitration of monosubstituted benzenes had led to tables which gave guidance, by extrapolating back to the collected data, on what might happen to systems that had not been investigated. However a rationale for why certain groups direct ortho and para and others meta was not known. Ingold was a pioneer in this field. He not only used his own insight but relied in the beginning of these investigations on ideas presented by his contemporaries Arthur Lapworth (1872-1941) and Robert Robinson (1886-1975). The explanations given by Ingold are summarized in Baker's lectures and these are the ones that are found in any introductory textbook today.

After reviewing the history of the various structures proposed to explain the properties of benzene and why the Kekule structure was the best, Baker then discusses some of the conclusions that one can reach from experimental observations that had been made by various investigators. These general observations include the effect both electron-donating and electron-withdrawing groups have on orientation. Next specific examples are given concerning the effects of poles and polar linkages. The importance of position and charge in terms of orientation

effects is reviewed. Much of the data presented by Baker can be found on pages on 231-243 in SMOC.

After considering the effects of alkyl groups and the role of hyperconjugation as well as inorganic substituents he then discusses the evidence for his theoretical presentation. Baker discusses the transmission of electrical effects by various classes of substituents using the letters I and T for inductive and tautomeric effects and + and – to signify changes in electron distribution that occur in the course of reaction. Shown below (Figure 3) is an excerpt of the notes from Baker's course as well as the table found on page 247 in SMOC.

Baker then discusses the role of inductive effects in electrophilic aromatic substitution. According to Baker ortho, para substitution may possibly arise from the following:

a) Increase in ortho, para activation with decrease in meta activation;

b) Increase in ortho, para activation leaving the meta activation unchanged;

c) Increase in ortho, para activation with smaller increase in meta activation.
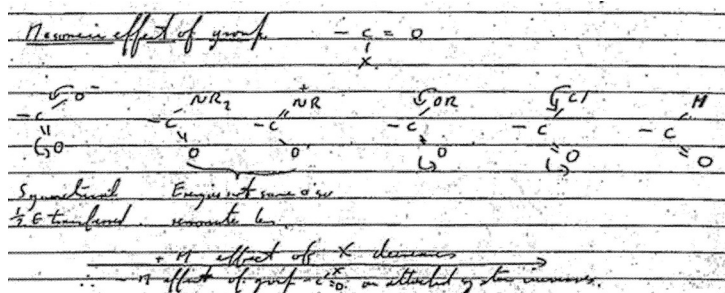
Ingold: Structure and Mechanism in Organic Chemistry 1st Ed.

TABLE 19-3.—CLASSIFICATION OF ORIENTING SUBSTITUENTS.

Type	Electronic mechanism	Examples	Effect on	
			Orientation	Reactivity
(1) +I	Ph←R	Ph—CH₃	ortho-para-	Activation
(2) −I	Ph→R	Ph—CO₂Et	meta-	Deactivation
(3) −I+T	Ph→R	Ph—SMe₂⁺	As in (2)	
		Ph—Cl	ortho-para-	Deactivation
		Ph—OMe	As in (4)	
(4) +I+T	Ph←R	Ph—O⁻	ortho-para-	Activation

Figure 3. *Inductive and tautomeric effects in electrophilic aromatic substitution from Baker notes (above) and SMOC (below).*

Data from experiments involving the competitive nitration of benzene and toluene was used to determine the correct scenario. In this study the ratio is 23 for toluene as compared to benzene and the o : m : p ratios are 58.4 : 4.6 : 37.2. This supports the interpretation that (c) is the best explanation. Continuing in this vein Baker discusses what happens in the case of a combination of inductomeric and electromeric effects and how this leads to a large increase in the activation of the ortho, para substitution. The inductive effect of electron withdrawing groups has the greatest effect at the ortho, para positions and by default increases the amount of meta substitution.

The unusual activity of the halogens is explained in terms of the conflict between resonance displacement and the inductive effect which leads to an overall deactivation of the molecule. This favors meta substitution. The final portion of the lectures in this section deals with the question of how the attack by reagent molecules occurs in aromatic substitution. The conditions for nucleophilic aromatic substitution are discussed by analogy to electrophilic aromatic substitution.

Substitution at Saturated Carbon and Elimination Reactions

The two last topics are nucleophilic substitution reaction at saturated carbon as well as elimination reactions. These two types of reactions are the ones chemists most associate with the so-called Ingold or English school. Most of Baker's lectures deal with the nucleophilic substitution reactions. He introduces the distinction between S_N1 and S_N2 reactions and the two types of elimination reactions are briefly mentioned in the context of how they can compete with S_N processes. An alkyl group that favors the release of electrons will favor the release of X as an anion in alkyl halides.

According to Baker there exists a continuum of substitution reactions depending on the conditions. Five possible ways for changing bimolecular to uni-molecular and six for the reverse are presented. Some of these factors are:

•Strong electron affinity of X will favor ionization.

•Weak nucleophiles or low nucleophile concentrations hinder attack on the substrate.

•Factors favoring ionization include having a solvent with a high polarity.

•Temperature changes as they apply to the energy of activation.

Applications of these ideas are discussed with specific examples of reactions that had been investigated. An example of this comes from the work of Hughes, Ingold and Shapiro (11) on the hydrolysis of alkyl halides. This is shown below in the form of a graph which summarizes the arguments in his lecture (Figure 4). A similar graph can be found as Figure 24.1 in SMOC (Figure 5).
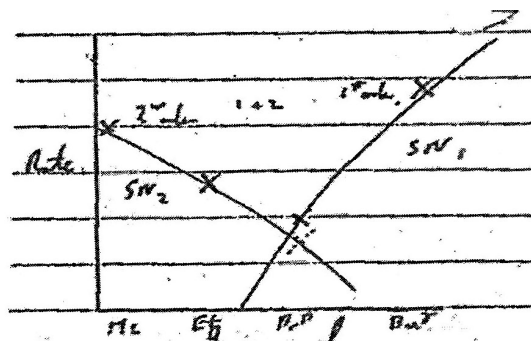

Figure 4. *Schematic illustration of how mechanism, kinetic order, and rates change as shown by Baker (1942).*
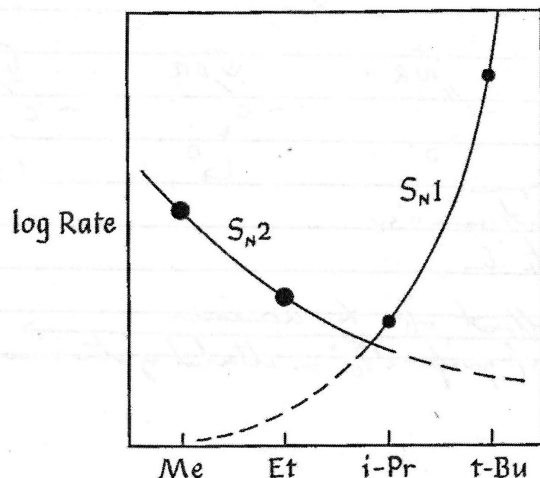
V   NUCLEOPHILIC ALIPHATIC SUBSTITUTION

FIG. 24-1.—Schematic illustration of changes of mechanism, kinetic order, and rate, in a nucleophilic substitution, Y+AlkX=AlkY+X, with variable groups Alk arranged in order of increasing electropositivity.

Figure 5. Schematic illustration of how mechanism, kinetic order, and rates change as shown by Ingold (1953).

A brief section is devoted to the discussion of the mechanisms of elimination reactions and their relationship to substitution reactions. Due to their similarities a duality exists as far as the mechanisms are concerned. Baker points out that the electronic character of the leaving group is not the key factor in the removal of the β hydrogen atom in the E2 mechanism. In the case of the E1 reaction he draws attention to the similarity to the S_N1 reaction in terms of the rate determining ionization step.

Baker's lectures identify actors in the ratio of S_N2 versus E2 in terms of the basicity of the attacking reagent. Using the series Br^-, OAc^-, OPh^-, OH^- as an example, it is shown how the increasing basicity favors the S_N2 over the E2 reaction. This is due to the nature of the attack on carbon versus that on hydrogen. As the basicity decreases the ability to attack carbon increases and causes a rise in S_N2.

The ionizing power of solvents is next considered in elimination versus substitution reactions. The key to the ratios of S_N versus E is the charge distribution in the transition states of these reactions. In the transition state for elimination there is a wider distribution of the charge as compared to substitution. Four scenarios are shown in the diagram below (Figure 6) for bimolecular reactions. In each pair the two transition states are shown and the effect of solvation shown. Table 33-2 on page 457 in SMOC (Figure 7) is more detailed but in many ways similar.

Conclusions

This set of notes offers a unique snapshot in time between leading edge research and its transfer to the advanced undergraduate classroom of the day. These lectures show how advanced undergraduate students in the course discussed in this paper were exposed to a whole new way of thinking about organic reactions. For a student to understand the new insights that Ingold and collaborators brought to the study of mechanism and structure would have required extensive reading of the primary literature. This would have been a daunting task for an undergraduate or post graduate student especially in the United States. As illustrated by the detailed

Figure 6. Solvent effects in substitution and elimination reactions from Baker notes.

Figure 7. Solvent effects in substitution and elimination reactions from SMOC.

examples given above, students in Baker's course were exposed to data and interpretations considered worthy of inclusion in a specialist monograph a decade later. Moreover, the treatment of that material has become standard even in introductory organic chemistry half a century later.

We have previously examined a course in physical organic chemistry given by Paul Bartlett (1907-1997) at Harvard in the spring semester of 1938 (12). This course is much more oriented to the application of physical chemistry in organic chemistry than the approach of Ingold which emphasized structure and mechanism. Baker's course of lectures to advanced undergraduates in this time period may have been possibly unique and we can only answer this question if more material is found from this era.

The significance of the work of Ingold and his collaborators which is discussed by Baker as part of his lectures was so important that Remick devoted a whole chapter to it in his 1943 text (8) which was written for an American audience assumed to be unfamiliar with it. By contrast, the 1953 first edition of SMOC contains many references to the work of a new generation of American chemists. Many of them had spent time in Ingold's laboratory as Fulbright Fellows in the immediate post war era such as J. F. Bunnett (13). American chemists would soon become the leaders in physical organic chemistry in the post war era.

Acknowledgment

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About the Author

Martin D. Saltzman is Professor of Natural Science at Providence College. He is currently working on a study of the state of chemical knowledge in the United States from 1846-1876 as found in *Scientific American*.

A COMPELLING EXAMPLE OF SCIENTIFIC INTEGRITY

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Introduction

In recent years, much evidence for fraud and other faults in the conduct of science has appeared. A classic example is *Betrayers of the Truth* (1), in which a critical view is taken of the level of integrity in the scientific enterprise over many centuries and reasons for the failures are assessed. Another, recent example is "Misconduct Accounts for the Majority of Retracted Scientific Publications" (2). This paper in the *Proceedings of the National Academy of Sciences* focuses on the biomedical literature, where the incidence of fraudulent activity seems to be most severe. News accounts in the popular press and in scientific publications such as *Science, Nature*, and *Chemical and Engineering News* supply reports of fraud in science (3). Revelations of misconduct in science would naturally tend to cause the public as well as scientists to lower their estimations of the integrity of all scientists.

Because of the conventions about reporting scientific results, it is almost impossible to find clear-cut examples of high levels of integrity being exhibited by scientists. Such examples cannot be found by reading the journals because scientists are inhibited by literary convention and scarcity of journal space from telling the full story about how a project evolves. The majority of scientists sustain high standards without making this practice known explicitly in their papers or in other ways. This silence is regrettable, especially in the face of all the questioning of integrity in science. There is a critical need for positive examples.

Scientists who receive funding from the National Science Foundation and the National Institutes of Health are required to give instruction in ethics to student and postdoctoral researchers. Such presentations are principally admonitory in that they tell about proper scientific ethics and give negative examples of fraudulent work. Largely unavailable is an inspiring component that leads young scientists to high standards of conduct through reading about work done with obvious integrity. Our paper provides a compelling example of a high level of scientific integrity. We hope that publication of this paper on scientific integrity might encourage other examples of exemplary ethical behavior to be brought forward, which could also be used inspirationally in ethics courses. IWL knows of this need from direct experience in teaching ethics courses at the NIH. Through consultation with scientific colleagues we have confirmed this need.

Having in our files and in the Archives of Oberlin College an outstanding example of a case of notable integrity in the practice of science, it seems timely to report about it. The example dates back to the time around 1980 and concerns a topic of great interest at the time.

Experimental Background

First, we recall the circumstances that led to the example. While NCC was on a year's leave in 1978-79 in IWL's laboratory at the National Institutes of Health, we reexamined the literature on the vibrational spectroscopy of the two isomers of diazene (HN=NH), also named di-imide. Many studies had been published about the

infrared and Raman spectroscopy of the trans isomer, even though its short lifetime at room temperature made such studies difficult. Most of the studies were with matrix-isolation methods at very low temperatures, where the reactive trans isomer was stabilized. A few questionable claims of spectroscopic evidence for the cis isomer also existed. The cis isomer was of great interest because it was regarded as the key intermediate in converting atmospheric nitrogen (N_2) to ammonia with the nitrogenase enzyme, as subsequent work has confirmed (4,5). At Oberlin College, we had done a full study of the vibrational spectra of the isotopologues of *trans*-methyldiazene ($CH_3N=NH$) (6), and we had succeeded in converting the trans isomer into the cis isomer by photolysis of frozen material at liquid nitrogen temperature (7). Observing *cis*-methyldiazene was the closest anyone had come to finding direct information about *cis*-diazene. The reinvestigation of the diazenes involved developing a convincing assignment for the six vibrational fundamentals of the trans isomer, based on published matrix-isolation spectra. Normal coordinate calculations using empirical force constants based on the vibrations of the isomers of methyldiazene and *trans*-diazene led to predictions for the vibrational spectrum of *cis*-diazene. These calculations also reinforced the difficult assignment of two close-lying modes of *trans*-diazene, which were separated by less than 30 cm^{-1}. These modes were the antisymmetric in-plane NH bending mode, ν_6, at 1317 cm^{-1} and the out-of-plane NH torsion mode, ν_4, at 1288 cm^{-1}.

High-resolution Infrared Spectroscopy at the NRC

The revised vibrational assignment for *trans*-diazene and the predictions for the elusive cis isomer appeared in the *Journal of Chemical Physics* in July 1979 (8). Within a short time of this publication, a letter came from Dr. John Johns at the National Research Council (NRC), the premier laboratory for the physical sciences in Canada. A copy of his letter (Figure 1) follows. Hallin, Johns and Trombetti had done heroic experiments on the high-resolution infrared spectroscopy of *trans*-diazene. They had succeeded in observing the spectrum of this unstable species in the gas phase in a flow system and had assigned *2400* rotational lines in the entangled spectrum in the region where we had assigned the two controversial bands observed in condensed matrix phases. The gas-phase spectrum was made especially complex by a strong
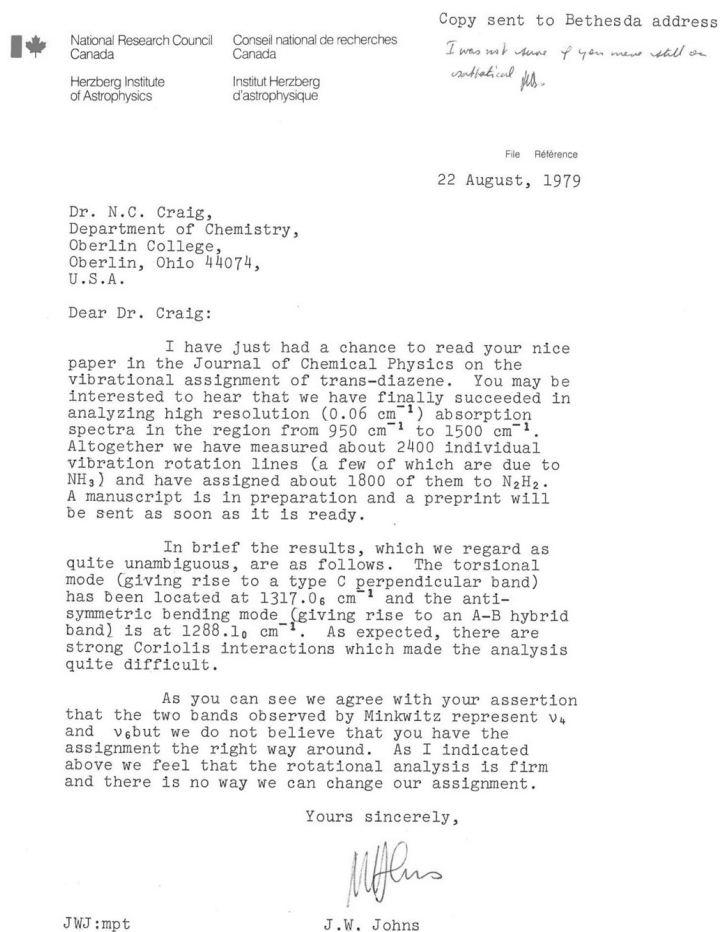

Figure 1. Letter from Johns to Craig pointing out a difference in assigning vibrational modes in trans-*diazene (9)*.

Coriolis interaction between the two bending modes and rotational states. Upper rotational states were severely mixed between the two bands. From their analysis of all the rotational structure, Hallin et al. had made an assignment of the two close modes that was opposite to ours. Johns wrote, "…we feel that the rotational analysis is firm and that there is no way we can change our assignment." "A manuscript is in preparation and a preprint will be sent as soon as it is ready" (9).

The evidence for the correct assignment of the two fundamentals from the analysis of the rotational structure seemed superior to what we had done with the various low-resolution spectra and normal coordinate calculations. Even though we had confidence in our analysis, we could do nothing but wish the NRC group well. A copy of our response is in Figure 2 (10).

September 4, 1979

Dr. J. W. Johns
National Research Council
Herzberg Institute of Astrophysics
Ottawa, Canada
K1A OR6

Dear Dr. Johns:

Thank you for your letter telling me of your elegant results on the high resolution infrared spectrum of _trans_-diazene. Of course, the detailed analysis of the vibration-rotation spectrum gives a definitive assignment. While I was pleased that your results support in general our reinterpretation of the various low resolution infrared and Raman experiments, I am disappointed that we were unable to get ν_4 and ν_6 in the correct order. No doubt this means that a frequency difference of 29 cm^{-1} is too close to call with the harmonic oscillator approximation applied through the product rule or through normal coordinate calculations to experimental frequencies that include condensed phase values. It is interesting to note that our original prediction of 1326 cm^{-1} for the torsional frequency of _trans_-diazene, which was based on the unambiguous assignment for the NH flapping mode in _trans_-methyldiazene, was so close. Although the ab initio calculations of Peric et al predict a high frequency for the torsional mode of about 1520 cm^{-1}, the value is too imprecise to be of use.

I look forward to seeing the preprint of your paper on _trans_-diazene. Do you have plans to study the high resolution spectrum of the $\underline{d_2}$ species?

Since your letter reached me after I got back to Oberlin, I am sending a copy of it and of this letter to Ira Levin at the NIH.

Sincerely yours,

Norman C. Craig
Professor of Chemistry

NCC/md
cc Ira W. Levin

Figure 2. *Response from Craig to Johns thanking him for sharing the results of their analysis of the* trans-*diazene spectrum (10).*

A Complete Revision

Fifteen months passed, and nothing was heard from the Johns group. In November 1980, Johns sent another letter, as seen in Figure 3. In this letter he reported that he had developed doubts about their analysis and had redone the assignments of the multitude of rotational lines (11). The consequence was a much better fit of the data and a reversal in the order of the assignments of the two modes. Having subsequently done rotational analyses on high-resolution IR spectra of less complicated systems a number of times, NCC testifies to the breath-taking significance of the decision to redo an analysis that must have taken many months. This renewed effort was far from merely tying up loose ends. The paper of K-E. J. Hallin, J. W. C Johns and A. Trombetti had the title, "The Infrared Spectrum of Di-imide near 7.6 mm" (12).

In the paper, there is only one place that hints at the strenuous path leading to the final result. In the section on rotational analysis on p 666, the paper says

Figure 3. *Letter from Johns to Craig reporting a reanalysis of the* trans-*diazene spectrum (11).*

At this stage we were unable to extend the initial analysis into the region where the asymmetry doubling was resolved. After some time it was finally realized that the vibrational assignment of the two bands could have been made incorrectly because the effect of the strong Coriolis interactions on the selection rules had not been fully realized.

Our response, which is in Figure 4, was muted but congratulatory (13).

It is not hard to imagine a different outcome for these studies. Had the paper from the Johns laboratory appeared first, it is unlikely that anyone would have challenged the conclusion about the proper assignment of the two bending modes of *trans*-diazene. We would certainly have been hesitant about our results. An incorrect assignment of the two fundamentals is likely to have remained in the literature for years.

We emphasize that we bring this compelling example of scientific integrity forward not because we

National Research Council
Canada

Conseil national de recherches
Canada

Herzberg Institute
of Astrophysics

Institut Herzberg
d'astrophysique

File　Référence

19 November, 1980

Dr. N.C. Craig,
Department of Chemistry,
Oberlin College,
Oberlin, Ohio 44074,
U.S.A.

Dear Dr. Craig:

You will no doubt have wondered what had happened to my paper on trans diazene (di-imide). The truth is that I became suspicious of our results and was finally able to show that they were incorrect. This has entailed a complete re-analysis of the data with results that leave me much happier. The big change is that my assignment of the vibrational levels ν_4 and ν_6 now agrees with yours. The new assignment involves different rotational assignments for most of the lines involving values of K_a lower than 3. The resulting parameters are now much more reasonable and they give rise to a fit to the observed frequencies that is almost an order of magnitude better.

For your interest I enclose a preprint of the paper which I have just submitted to the Canadian Journal of Physics.

With best wishes,

J.W. Johns

JWJ:mpt
Enc:

found the correct assignment of the two bending modes of *trans*-diazene. We bring it forward to demonstrate how science takes place at the highest levels of probity. Note that Johns and coworkers undertook their laborious revision in the absence of external motivations such as either compelling evidence or vocal disagreement on our part. We bring it forward because we were privy through correspondence to the high-level path of an investigation in another laboratory.

Another reason for reporting this exceptional example of scientific integrity is to underscore the need for examples of this type. Such material would strengthen instruction in scientific ethics now mandated by the NSF and the NIH. Examples of such material would lift the sights of young scientists. Yet another reason for this report is to encourage scientists to include brief reviews of the evolution of a research project as part of the introduction to a paper.

Acknowledgment

We will be forever grateful to Dr. John Johns for his forthright report of the progress on the analysis of the high-resolution spectrum of *trans*-diazene in his laboratory. He has agreed to the publication of the exchange of letters. Attempts to reach Professor Agostino Trombetti in Italy failed.

Figure 4. *Response from Craig to Johns commending the reanalysis of the* trans-*diazene spectrum (13).*

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About the Authors

Norman C. Craig is Emeritus Biggs Professor of Natural Science in the Department of Chemistry and Biochemistry at Oberlin College, Oberlin, OH, 44074. He has published papers in the *Bulletin* and elsewhere on Charles M. Hall, the inventor of the process for refining aluminum metal. He has also published a paper on Hall's older sister, Julia B. Hall, in *Chemical Heritage*. He has written about the history of chemistry at Oberlin for the *Bulletin*.

Ira W. Levin is a retired Senior Scientist and Scientific Director of the Intramural Research Program of the National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD, 20892. As Scientific Director, he was directly involved with teaching biomedical ethics courses and in leading ethics seminars and discussions for all levels of the scientific staff in his Institutes' program.

HIST Elections 2016

Nominations are open for several posts within the Division of the History of Chemistry (HIST).

If you would like to nominate a HIST member for any of the positions listed below, please contact one of the members of the Nominations and Elections committee by August 1, 2016. Self-nominations are welcome.

Elections will be held later in 2016 for the following positions:

* Chair-Elect (2017-2018), to be Chair in 2019-2020 and immediate past chair in 2021-2022;

* Secretary-Treasurer (2017-2018);

* Councilor (2018-2020 term);

* Councilor (2017-2019 term);

* Alternate Councilor (2018-2020 term);

* Alternate Councilor (2017-2019 term)

The positions and duties are described in HIST bylaws, available at http://www.scs.uiuc.edu/~mainzv/HIST/bylaws/bylaws-oct1995-HIST.pdf

One must be a member of ACS AND of HIST to be eligible for any of these positions.

To make a nomination (including a self-nomination) or an inquiry about any of these positions, please contact the chair (Ned Heindel, ndh0@lehigh.edu) of the Nominations and Elections committee by August 1, 2016.

Thank you for your interest and membership in HIST!

Vera Mainz, Sec/Treas HIST
for Ned Heindel, Chair of the Nominations and Elections Committee

A REVERIE
KEKULÉ AND HIS DREAM:
AN INTERVIEW

Richard E. Rice, P.O. Box 1210, Florence, MT 59833, charrice@juno.com

Editor's Note: A folded typescript of this interview on A4 paper was found in a copy of *The Kekulé Riddle*, which the editor of this manuscript purchased several years ago from a bookseller at abebooks.com. The interviewer (A^2) has not been identified beyond information on the bookplate, which features an alembic and the symbol "A^2" as the book owner. In addition to the typescript, there was also a single folded sheet of the same size paper with a handwritten letter, which is reproduced in the Postscript. —RER

Interviewer's Note: Friedrich August Kekule von Stradonitz (1829-1896) was Professor of Chemistry at the University of Ghent from 1858 to 1867. From there he moved to the University of Bonn, where he remained for the rest of his life. He is best known for the hexagonal ring structure of benzene and for his other early contributions to structural organic chemistry. The following interview took place in a small parlor off the lobby of the Hotel Ouroboros at Berlin's Schlangeplatz on 11 March 1990, the 100th anniversary of the Benzolfest. *The only restriction imposed by Kekulé was that no photographic or audio recording equipment could be used during the interview. Instead, a stenographer was present and provided a verbatim transcript from which this manuscript was prepared. Both of us spoke in English, and we sipped some well-aged Cognac as we conversed by the fireside.*

Interviewer (A^2): Professor Kekulé, first let me express my appreciation to you for agreeing to this interview. I know you have been upset by the controversy that has arisen about your famous—some would say *infamous*—dream of the snake biting its own tail, but until now you have remained silent. Thus, all of us in the scientific community look forward to hearing what you have to say in response.

August Kekulé (AK): I thank you and the esteemed editor of this learned journal for the opportunity to express my views. I can tell you that I agreed to this interview because I could no longer tolerate all the nonsense and ridiculous *Halbwahrheiten* that have been bandied about concerning my dream and my remarks at the *Benzolfest* here in Berlin so many years ago.

A^2: One hundred years ago today, to be exact.

AK: Yes. I wish that I could say that it seems like only yesterday, but it does not.

A^2: With your permission, Professor Kekulé, I'll begin by summarizing the recent controversy about your dream and your speech at the *Benzolfest*.

AK: No, I do not care to dignify my critics and their silly pronouncements by refuting them point by point. Though I easily could. Instead, I wish to make known my views about science and the creative process. Most especially about my own creative process as it pertains to science.

A²: However you wish to proceed.

AK: Let me begin with the facts. That is indeed where science begins. But that is hardly where it ends. You know, it is not only the naive and gullible public that misunderstands science and thinks that the only currency we scientists deal in is facts. Even though nothing could be further from the truth, many scientists themselves also labor under this same illusion. According to this mistaken view, we scientists do not even need to think, let alone to dream. Instead, we march into the laboratory and single-mindedly gather facts.

A²: But you certainly wouldn't deny that scientists do need to gather facts?

AK: Of course not. Facts, facts, and more facts. They are an essential part of science, but at the same time they are perhaps the least interesting part of science.

A²: I'm sure that everyone would agree about their importance, Professor Kekulé, but what do you mean by "the least interesting"?

AK: Let me explain. What are facts? My friend Ernst Mach would say that a fact is a description of some immutable pattern in time and space. Something that all rational people can agree on. For instance, the sun rises each morning and sets each evening. Who could disagree? Man has observed such phenomena through time and space for eons.

A²: So you're suggesting that our familiarity with such facts makes them uninteresting?

AK: Not at all. Let me ask you this. Does the sun, in fact, rise each morning? There is no question that we see the same phenomenon every day. But to say that the sun "rises" means that we see it move relative to us, to the earth. It means that we have adopted a geocentric point of view. But in fact, we know that this diurnal movement of the sun is only apparent and actually results from the rotation of the earth on its axis. So even such a simple "fact" as the rising sun must be interpreted by the theory within which it is evoked.

A²: But isn't the "rising" of the sun merely an instance of our everyday language?

AK: Certainly, but I would not say "merely." After all, our everyday language has grown out of certain beliefs. In this case, out of the earlier belief that the earth is at the center of the universe. That particular theory was discarded centuries ago, but it lives on in our everyday language.

A²: But you're not saying that facts are whatever beliefs we happen to accept at the time.

AK: Of course not. Facts cannot be whatever we might want them to be. But neither does science consist only of objective facts within a vacuum. Facts provide us with evidence for our hypotheses, and they must be accounted for by our theories. There is a certain circularity between fact and theory.

A²: Ah, there's an appropriate figure of speech for you.

AK: But, as you know, facts do not produce theories by themselves. The human mind does that.

A²: So you're saying that science results from the interplay between facts and the human mind.

AK: Broadly speaking, yes. That was certainly the case with me, but I am hardly unique in this regard. Science has always arisen from this interplay ever since there has been scientific observation and thinking. The first instance we know of is in the 6th century B.C., when Thales developed his theory that water represents the ultimate reality of the material universe. Of course, some people today point to this as an indication of the misdirection of Ancient Greek science. I point to it as an indication of the interplay of facts—the ubiquity and importance of water—with the human mind.

A²: And you would claim this to be a hallmark of science ever since.

AK: Consider some examples. Copernicus and his heliocentric universe. Newton and his inverse square law. Lavoisier and his oxygen. Dalton and his atom. Mendeleev and his periodic table. Watson and Crick and their double helix. And may I be so bold as to add myself to this most impressive list, Kekulé and his benzene ring.

A²: These are truly some of the greatest achievements of science.

AK: And you will notice that each of them is a creation of the human mind, consistent *with* the known facts and also predictive of new facts, but none of them consists *only* of facts. The inverse square law, the benzene ring, the double helix, these things do not exist in the world as scientific entities for us to behold and examine like a flower growing in the field or the sun rising in the morning.

A²: I find it curious, Professor Kekulé, that you include the DNA double helix since that discovery occurred half a century after your death.

AK: I do not know Watson and Crick—they are both still alive, of course—but this is an episode about which I do have some personal knowledge.

A²: You do?

AK: No doubt you have read *The Double Helix*, Watson's striking account of his and Crick's discovery of the helical structure of DNA. This story particularly interests me because it bears certain similarities to my own discovery of the ring structure of benzene. In the case of DNA there were essentially two groups of investigators looking for the structure. I purposely omit Linus Pauling as he is irrelevant to my point.

A²: Maurice Wilkins and Rosalind Franklin at King's College London, as well as Watson and Crick at the Cavendish in Cambridge.

AK: Exactly. And I hope you are aware that Miss Franklin was a most excellent scientific worker. I have had many fascinating discussions with her about x-ray diffraction, in which she was an expert. This technique did not exist in my day of course, but it is interesting that Wilhelm Röntgen discovered x-rays at Würtzburg shortly before my death. In fact, his first public lecture on x-rays was in January 1896, only a few months before I died.

A²: But Rosalind Franklin was born nearly a quarter century after that.

AK: She was, but we all try to pass the time pleasantly in eternity with interesting discussions. It is possible to tolerate only so much shuffleboard and bridge.

A²: That sounds like a topic for another time.

AK: Miss Franklin is a lovely woman, and I can tell you that Watson's unflattering portrait of her in his memoir is very inaccurate, very biased, very shallow. He tried to get himself off the hook with that pathetic apologia at the end of the book, but it fails utterly.

A²: So there were two groups looking for the DNA structure.

AK: Yes, a lovely girl, and first-rate in the laboratory. But . . . what I mean to say is . . . she and Wilkins both lacked a certain creativity . . . the imaginative impulse, even playfulness, which Watson and Crick possessed to an extraordinary degree. In some way, Miss Franklin seemed to expect the DNA structure to leap out at her from the x-ray data that she accumulated.

A²: So you're saying that facts are not enough.

AK: I am saying that they are definitely not. They were not enough for Miss Franklin. They were not enough for Watson and Crick. What were Watson and Crick doing at the Cavendish? That is, besides terrorizing Bragg and the rest of the old guard waiting to retire. I believe that I am not breaking any confidences if I tell you that Bragg still complains about Crick and his booming voice. Poor Bragg, he fears the day when Crick . . .

A²: You asked what Watson and Crick were doing at the Cavendish.

AK: Exactly. Watson knew nothing about x-ray diffraction. He knew no structural chemistry, as he himself admits. No, no, as he himself *brags*. It is your 20th-century custom of running yourself down, so that when you succeed, everyone finds your success all the more amazing. And should you not succeed. Well, then you have already explained the reason for your failure.

A²: One thing Watson and Crick were doing was building models.

AK: Yes, they were doing that, but more importantly they were daydreaming. They were thinking of other things. Crick of foreign films, Watson of Cambridge popsies, as he termed them. These were the surface events in their lives, but their work on DNA continued unabated underneath.

A²: In the unconscious.

AK: Please. Do not get me started with that kind of terminology. Sigmund Freud is an excellent bridge partner, but we do not discuss science even though he still mistakenly regards himself as a man of science.

A²: You were saying, under all the surface events of their lives.

AK: And the answer eventually came to the surface through the models they constructed. After Watson had been wrong more than once, he had that flash of insight—prepared for by a structural chemist, I might add, in addition to his own daydreaming—in which he saw the pairing of the bases and the way they fit together between the sugar-phosphate chains. There was his true creative genius.

A²: In seeing the relationships.

AK: Exactly. The facts were essential, but rather uninteresting. They were there to be seen by anyone. Various distances extracted from the x-ray patterns. The amount of water present in the sample. The structure had to be consistent with them, of course. But what those

facts implied was of paramount importance, not the facts themselves. So it was with me and benzene as well.

A²: The problem simmering under the surface.

AK: I was engaged in many activities on the surface—my laboratory work, my teaching. I was writing my *Lehrbuch*. I was courting my Stephanie.

A²: Your *Lehrbuch der organischen Chemie*.

AK: But underneath those surface events there was always benzene. That clear, odorous liquid from the London gas lines. The great Michael Faraday himself sent me a sample, which I kept in a glass vial on my mantelpiece.

A²: Where you could see it every day.

AK: Where it plagued me every day. Especially as I worked in my rooms in the evening. Whenever I looked up, there it was, hiding its structure like the unseen skeleton of a skyscraper under its outer skin. Many chemists thought that the molecule had a linear diallene structure, but how could that be? The known facts about benzene did not fit such a structure.

A²: Such as the equivalence of all six hydrogens.

AK: That particular evening I was having some trouble making progress on my *Lehrbuch*. What it was, I do not remember anymore. I poured myself some brandy. I lit myself a cigar. And I sat in front of the dying fire and stared at the benzene. Simple. It *had* to be simple.

A²: I need to ask you, Professor Kekulé, whether you actually dozed off or were merely daydreaming? The German word you used was *Halbschlaf*. Literally, that means "half-sleep" in English, but the exact translation isn't clear.

AK: No translation is ever exact. However, your inexact meaning of the German word is sufficiently correct to describe the state I was in. My landlady had prepared a most excellent meal for me. I had a good cigar and a little too much brandy. A very comfortable armchair. The warmth of the fire. The fingers of leaping flame played on my imagination. I passed into that state between sleeping and waking, and it was there that I saw the snake grasp its own tail in its mouth.

A²: Did you make the connection of this snake to the ring structure of benzene as soon as you woke up?

AK: Even before. The flash of insight occurred to me as I saw the snake whirl before my eyes. But I would tell everyone, including my critics, so they understand,

that I also knew this to be my fancy, my reverie, while in the *Halbschlaf*. The comparison—or analogy—of two things does not make them the same thing. My fancy was not science. The science of chemistry does not permit the theory of whirling snakes. [*laughs*]

A²: How then did the snake in your dream, in your reverie, become science?

AK: It is extremely important to distinguish between science as it is done and science as it exists. The former is the creative impulse of the individual scientist, and it must be unique to each scientist, just as each individual is unique in his own thoughts and ideas and knowledge and way of doing things. But the simple addition of all these individual contributions is not science. If they were, science would be as muddled as sociology or—God forbid—Freudian psychiatry.

A²: Luckily, not many social scientists are likely to read this interview.

AK: In fact, we can appeal to a famous social scientist—the economist Adam Smith—for a way of seeing how these contributions do become science. Science as it exists—as a structure that is always *becoming*—consists of the essences of those individual contributions, stripped of the idiosyncrasies that accompanied or even enabled their discovery.

A²: The economist Adam Smith?

AK: The unseen hand that directs and coordinates all these contributions as no individual or group of individuals could. The free market of ideas where the fruitful contributions survive and the barren ones perish.

A²: Are you suggesting that an "unseen hand" transformed your snake into the benzene ring?

AK: Of course not. I did that myself. I saw the analogy even before I awoke. But then when I did awake, I quickly realized the scientific consequence of the snake biting its own tail. Joining the linear molecule's terminal carbon atoms together eliminated the problem of the two extra valences. They simply vanished. With that realization, I wondered how I did not see it before. How Couper, Loschmidt, all of them did not see it before.

A²: So you actively transformed the snake into a carbon ring structure.

AK: I actively transformed my reverie into a scientific description devoid of fancy, a description that could compete on its own merit in that free market of scientific ideas. And other scientists determined my idea to be

sound. Once I dressed my idea up in suitable scientific garb, it mattered nothing to science that the idea had originated from a whirling snake. Though it has obviously mattered to some scientists of your time.

A²: You're suggesting that your critics have a fundamental misunderstanding of how science operates.

AK: I know they have when they say that science consists only of going into the laboratory and gathering facts. Facts by themselves have little or no meaning. Their meaning arises only in connection with some hypothesis or theory from the human mind. The illustrious Sir Francis Bacon himself collected hundreds of facts about heat, but they never progressed beyond "natural history," as he termed his work, because he had no theory to recast all those facts into something more than just individual bits and pieces.

A²: We've covered a lot of ground, Professor Kekulé, from Thales to DNA, then to the benzene ring, and now to Francis Bacon and heat. We are just about out of time. But before we conclude this interview, is there some final point you'd like to make?

AK: By all means. My critics make one charge that I would like to address directly. They have impugned my honesty by saying that I did not mention my dream of the snake in my speech at the *Benzolfest*, that I added it afterwards in the published account. There is no credible evidence to support such a charge because it is not true. I would add that I believe this whole episode reveals more about my critics than about me though I will leave it to others to make that judgment. The honesty of each scientist in his work and in reporting his work to others is crucial to the success of science as a worldwide enterprise. If scientists do not trust each other in what they say and do, the structure of science will collapse. I know that it has become fashionable toward the end of your century to try to find the feet of clay of every person of stature and accomplishment. It was not so in my time. We respected people then for their great deeds in science or politics or art or whatever field of endeavor in which they excelled, and for that I am glad not to be living in your time. I do not hesitate to place my honor behind what I have said, both publicly and privately, as well as behind the science I have tried to do.

A²: [*stands and shakes Kekulé's hand*] Professor Kekulé, on behalf of all scientists and readers of this journal, I thank you for granting this exclusive interview and for setting the record straight.

AK: [*also stands*] I am extremely grateful for the opportunity to do so. Especially since I am not able to publish on my own anymore.

Postscript

My dear Maura,

In all the years you have been my editor (nearly 25!), I have never been more mystified and disappointed than I was by your recent rejection of my interview with Professor Kekulé. You seem to have 2—perhaps 3—major objections: the topic is too narrow, the 'facts' have already been thoroughly discussed, and this interview brings nothing new to the discussion. I must disagree with each of these.

It is true that the 'facts' about his dream of the snake have been laid out more than once though there is not necessarily agreement on what they actually are. In Professor Kekulé's own words (translated from the German), it appears that his 'dream' was more of a daydream or a reverie in that state between waking and sleeping. (I believe that the technical term for this state is 'hypnagogia'.) He specifically mentions the vision of atoms in his 'mind's eye,' suggesting that he was partly awake, not sleeping. But his harshest critics deny the existence of any (day)dream of a snake seizing its own tail because none of the contemporaneous newspaper accounts of his speech at the Benzolfest mentions such a vision, so therefore he must not have mentioned it himself. Such an argument would seem to have little merit. Presumably, none of the newspaper accounts mentioned his waistcoat either; is that omission evidence that he wasn't wearing one?

Thus his critics leap to accuse him of scientific fraud, claiming that he later invented the story of the snake to avoid having to share any credit with earlier scientists who had made vague proposals toward some kind of ring structure for benzene. Professor Kekulé's structure went far beyond those earlier proposals, and yet he graciously admitted in his speech that his views had 'grown out of those of my predecessors and are based on them. There is no such thing as absolute novelty in the matter.' Tellingly, none of those predecessors that he referred to ever disputed his claim of priority to the benzene structure.

At the very least, an exclusive interview with the very individual at the center of this controversy is an incredible coup for the magazine. Nowhere else has Professor Kekulé ever taken on his critics, not directly by arguing point by point, but by doing exactly what he discussed in the interview, i.e., placing the facts within

the context of his own imaginative processes. That is surely the addition of something new to the discussion.

Nor does he stop with the interplay of facts and imagination in the case of his discovery of the benzene ring structure. He expands his ideas to the discovery of the DNA helical structure and discusses the x-ray data of Rosalind Franklin (whom he knows in the hereafter) in connection with the model building of Watson and Crick. Her x-ray data was critical to revealing the helical structure, but would it have ever been enough by itself? Not without some kind of imaginative leap, just the sort of leap that Watson and Crick made. Thus, Professor Kekulé broadly considers the interaction of facts and creativity, providing insight into his own attitudes about the nature of the scientific method. Contrary to the statement of one of his critics that chemists do not 'operate by dreaming up things,' Professor Kekulé would assert that indeed they do, though not in a vacuum, but rather in conjunction with known facts.

I feel certain that today's historians of science would find all of Professor Kekulé's statements in complete agreement with the currently accepted historical record of these events.

It is unfathomable that you would pass up such an interview, but since you have made it absolutely clear that you will not publish it and that you will not change your mind, I shall seek its publication elsewhere, a necessity that I very much regret.

I assure you that I remain yours sincerely, etc.

Editor's Note: Unfortunately, the letter bears neither a signature nor date. —RER

Further Reading

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About the Author

Richard E. Rice is retired from teaching chemistry and the history of science. Besides chopping wood for the long Montana winters, he enjoys reading, writing, research, and travel.

BOOK REVIEWS

The Limits of Matter: Chemistry, Mining, and Enlighten-ment, Hjalmar Fors, University of Chicago Press, 2015, 248 pp, ISBN: 9780226194998, $40.

Hjalmar Fors's *The Limits of Matter* is an erudite and absorbing book. Its general, ambitious aim is that of tracing and delineating a major transition in early modern European culture: the construction and establishment, in the first half of the eighteenth-century, of the "modern notion of materiality." By the term "materiality," Fors identifies a wide intellectual territory, generally comprising sets of beliefs, worldviews and theories about the nature of matter. This is of course a daunting task, which Fors wisely approaches by considering the case of Sweden, in the period between the end of the seventeenth-century and the first half of the eighteenth-century. Moreover, Fors describes this major transition focusing on a specific group: the intellectuals, natural philosophers and chemists who founded and led the Royal chemical laboratory of the Bergskollegium, or Swedish Bureau of Mines.

The Limits of Matter opens on the fascinating figure of Urban Hiärne, head of the chemical laboratory at the Bureau between 1683 and 1720. Hiärne occupies a central position in Fors's argument. For Fors, Hiärne represents the epitome of the curious, inquisitive late seventeenth-century virtuoso and natural philosopher. Hiärne was a complex figure, belonging contemporarily to several and different worlds. A Cartesian by formation while a student at the university of Uppsala, he turned subsequently to Paracelsian doctrines. Fors's discussion of Hiärne is intriguing, and thoroughly shows how the Paracelsian worldview well adapted to the popular beliefs on trolls and the other invisible entities populating Swedish and European mines and forests. While at the Bureau of Mines, Hiärne transformed the role of the

chemical laboratory from that of a pharmacy into the leading institution for the study of chymistry in Sweden and a "showpiece for the Swedish state" [49]. Hiärne's efforts brought to the institutionalization of chymistry in Sweden as a useful and profitable discipline. Most of all, thanks to Hiärne, the laboratory and the Bureau of Mines established themselves as a cultural "contact zone" (a notion that Fors derives from the work of historian Kapil Raj), where artisanal knowledge about matter was "transformed into the knowledge of high-status mining officials" [52].

A crucial section of the book is dedicated to the practices through which the Bureau gathered new knowledge. Again, Hiärne was instrumental in establishing many of these procedures. In particular, young officers of the Bureau were sent abroad to acquire new skills. This was the case of Hiärne's trusted disciple, Erich Odhelius. Fors reconstructs Odhelius's travels through Europe in order to learn an array of useful disciplines, including "practical and theoretical chymistry, medicine, and pharmacology, mining crafts such as smelting and assaying, as well as administrative skills" [53]. Odhelius's task was that of learning, and also passing newly acquired knowledge to his teacher. For instance, during his stays in Saxony and in Freiberg, Odhelius became conversant with assaying and mining, a familiarity Hiärne himself lacked. Most importantly, thanks to Hiärne's efforts, the Bureau of Mines institutionalized this type of training system for its young officials: if in the first half of the seventeenth-century the Bureau's officials were mainly immigrant artisans from Germany, by the end of the eighteenth-century thy were fully trained directly by the Bureau, according to Hiärne's principles. Additionally, contacts abroad brought a steady flux of skilled and knowledgeable assistants, especially from the mining districts of Saxony. Fors's account does

not follow the conventional scheme of peripheries versus centers of knowledge production, and emphasizes instead the European character and the international interactions of late seventeenth- and eighteenth-century mining.

The new generation of officers at the Bureau brought a strongly different approach. Fors characterizes this moment as the passage from an age of "curiosity" to one of "ingenious knowledge." This new, strongly utilitarian character developed in parallel with the adoption of markedly mechanistic worldviews. In this process, "mechanical project making" took the place of chymistry as the mainstream form of expertise at the Bureau. Christopher Polhammar (ennobled Polhem) was certainly the most important figure of mechanical projector at the Bureau. Of humble origins but a gifted mechanic, Pohlem had a swift and striking career there. The creation of a new Laboratorium Mechanicum in 1697 (at the same time a laboratory, a school and a permanent of exhibition of mining machines) fully represented this change of direction in the Bureau's policies.

The move from the chymical to the mechanical paradigm did not regard only projects. The start of the eighteenth-century saw a concomitant move toward the "mechanization of chymistry," according to the example of Herman Boerhaave. The passage from Paracelsian chymistry to "useful" mechanical chemistry, together with the emphasis on assaying and natural history, brought about a new mineralogical chemistry, based on the notion that metals constituted the "basic species of nature," "building blocks from which the world of matter was composed" [100]. In fact, a central chapter of *The Limits of Matter* ("Elements of Enlightenment") is devoted to the historical reconstruction of this research program, culminating in Axel Fredrich Cronstedt's mineralogical classification system. Fors convincingly argues that this research was fully integrated into the industrial requirements and interests of the Swedish state. Elemental, pure metals were the sought-after commodities of the mining industry. The classification of minerals in terms of constituent metals was then not only a natural philosophical research program—but the necessary theoretical component of an "integrated system of production," the goal of which was "to increase the revenues of the mining business" [117] .

One of the major merits of *The Limits of Matter* is its eclecticism. As its author states, among other things, this is a book about "witches, trolls, angels, premoni-

tions, transmutative chymistry, mechanical philosophy, and utilitarian, patriotic science" [147]. It is certainly the account of the establishment and growth of a scientific institution. It is also a concrete case study of the obliteration of chymistry and the Enlightenment repudiation of chrysopoeia. In Fors's book, these two narratives are intertwined: the rise of mechanical and mineralogical chemistry (a "cameral science at the service of the state" [148]) mirrors the growth of the Bureau of Mines as a center of scientific and economic power. The history of the Bergskollegium and the redefinition of the disciplinary notions of matter are a major concern of the book. Fors's discussion is rich and nuanced, and "invites not only chemists into the debate, but also assayers, miners, mineralogists, and alchemists" [2].

However, *The Limits of Matter* is far from being just an exercise in the history of chemistry. Fors is careful not to delimit his narrative in too narrow disciplinary perspectives. Complementary to his analysis of institutions and disciplines is a very engaging discussion of folk and popular culture on issues of materiality and spirituality. Borrowing the notion of "boundary work" from sociologist of science Thomas Gieryn, Fors delineates the slow cultural and rhetorical processes through which disreputable popular beliefs on materiality became marginalized among the learned as superstitions and were replaced by acceptable and newly sanctioned views. This phenomenon regarded "a small group of well-educated men belonging to the middle and upper classes," involved in natural philosophy, industry and manufacture [148]. By no means, Fors suggests, we should assume that these new skeptical and rationalistic approaches were diffuse and widespread in society. At the same time, the redefinition of the limits of materiality brought about by social environments like the Swedish Bureau of Mines meant a major reshaping of the intellectual landscape of the European savants. Trolls and kobolds inhabiting mines could still raise the curiosity of Paracelsian natural philosophers of the seventeenth century, but became irrelevant fantasies for the new generations of Enlightenment experts concerned with utilitarian chemistry and efficient means of industrial production. Slowly, they fell off the edge of the map.

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Medical Monopoly: Intellectual Property Rights and the Origins of the Modern Pharmaceutical Industry, Joseph M. Gabriel, University of Chicago Press, 2014, 328 pp, ISBN: 9780226108186, Cloth $35.

In September 2015, a little known drug company called Turing Pharmaceuticals suddenly leapt into the public eye. In a matter of days its CEO, a young Wall Street trader named Martin Shkreli, caused widespread outrage as newspapers and social media flooded with stories about what some saw as hitherto unparalleled greed. The cause of this furor? Shkreli's company had purchased the marketing rights to a drug called Daraprim—a front-line treatment for the parasitic disease toxoplasmosis—and raised the price per pill from roughly $15 to $750. For many commentators, this story reflected the worst side of a drug industry that too often puts profits before people. In a short matter of time, Shkreli could legitimately make a claim on being the "most hated man in America." A quieter, but still prominent minority, defended Shkreli's decision, suggesting that he was merely operating within the rules of the system, and that such tactics are necessary to fund the development of new, patentable drugs.

In *Medical Monopoly*, Joseph M. Gabriel brilliantly traces "the moment when the pursuit of profit and the advancement of medical science were first linked to one another." He pursues this history of the pharmaceutical industry through an in-depth examination of intellectual property rights and marketing policy. Through a close reading of collections from more than two dozen legal and pharmaceutical archives, Gabriel charts the evolution of trademark and patent law and its relation to medicinal drugs from the pre-Civil War era up until the eve of the First World War.

At the heart of the book is an absolutely remarkable transformation, almost unthinkable by those of us living in the age of Shkreli and the Daraprim debacle. Prior to the Civil War, as Gabriel adeptly describes, the patenting of drugs was seen as an uncouth corruption of scientific and medical ethics. Such an attitude was pervasive among physicians, pharmacists, and pharmaceutical producers themselves. Trademarking a medicinal substance was squarely the domain of quacks, charlatans, and others whose quest for financial gain was seen as both illegitimate and incompatible with good medical practice. By contrast, proper drug manufacturers rejected the concept of monopoly over chemical wares. Instead, they framed themselves as benevolent partners, working alongside physicians and pharmacists, in the gradual pursuit of medical science. In this context, the free circulation of knowledge—without patent or trademark—was

paramount. In Gabriel's words, "scientific progress and monopoly" were understood as "mutually opposed categories." Thus, in the dominant narrative of the pre-Civil War era, pharmaceutical producers closely followed on the heels of scientific developments, patiently waiting for researchers to explore the value of a plant or chemical before transforming it into a sellable, medicinal substance. In short, marketing should only proceed once efficacy and knowledge had been established.

Whereas general attitudes in the early American republic were noteworthy in their distaste for monopolies, shifting understandings of capitalism and the free market eventually eroded opposition to proprietary rights over medicinal drugs. While on the one hand, pharmaceutical producers (many of whom were physicians themselves) were responding to broader social shifts, Gabriel adroitly demonstrates that these companies were also active participants in bringing about corporate forms of capitalism. This change began to unfold in the period after the Civil War, when pleas in favor of trademarking and patenting medicines became louder. In short, those involved in the production of drugs had to make the case that profit and scientific advancement were not mutually exclusive; rather, they could be pursued simultaneously. Although the consequences would produce substantial financial gain, new arguments in favor of monopoly were not only formulated in terms of boosting profits. For instance, early defenses of pharmaceutical patenting noted that consumers would consequently gain access to safer medications, since the patenting process required the disclosure of ingredients. A move towards legitimizing monopoly would deal a fatal blow to nostrum producers, whose secret recipe cure-alls were notoriously popular among, and dangerous to, the public.

The book concludes on the eve of the First World War; by this time, the situation had changed dramatically. The modern form of drug nomenclature had solidified itself (the dual-naming system whereby drugs are called by both their brand and generic name) and proved a crucial step in ensuring that trademark holders could maximize their financial gain. Meanwhile, the notion that large profits were necessary so that they could be reinvested in further research was also gaining steam. New products of immense therapeutic value, like Adrenalin and Salvarsan, were made widely available through partnerships between researchers and industry. In short, a growing consensus suggested that "the promotion of medical science and the pursuit of corporate profits were deeply intertwined projects." In other words, the modern pharmaceutical industry had been born.

In truth, this book could, and perhaps should, have been a dry read; navigating legal history is often an overly complex affair. The need to track minute changes to law can result in necessarily dense prose. Thankfully, Gabriel's book possesses nothing of the sort. He writes in an accessible and enjoyable style. The key arguments are plainly stated and convincingly argued. Although aimed primarily at fellow historians of medicine, the book could be easily read by a wide audience. Concepts that are intuitive to fellow drug historians, such as why it is important that drugs came to have both branded and generic names, are clearly laid out for non-experts. Thus, students would have no problem understanding the text's most important points.

Historical accounts of drugs and their marketing have become familiar fixtures within the world of medical history. Well researched and well written monographs and articles cover innumerable aspects of twentieth-century pharmaceutical history, including drug invention and discovery, the prescription system, fears over social and individual dependency, and drug advertising. By focusing on the issue of intellectual property rights, Gabriel's book serves as a very useful enhancement to virtually all of these studies, thoroughly enriching the discussion and debate over why pharmaceutical products came to play such a central role in the lives of North Americans over the last 150 years.

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Science History: A Traveler's Guide, Mary Virginia Orna, Ed., ACS Symposium Series 1179, American Chemical Society, Washington, DC, 2014, distributed in print by Oxford University Press, 384 pp, ISBN 978-0-8412-3043-9 (paperback), $49.95.

This extremely detailed and meticulously referenced volume originated in a symposium held at the 237th National ACS Meeting in Salt Lake City, the content of which has been greatly expanded to include many additional sites. In Chapter 1, "Science History on the Road: An Overview," an introductory chapter outlining the rationale, goals, and content of the book, including practical helpful information about its use, Mary Virginia Orna reveals the origins of this volume about travel to places with scientific content. In 2009, she decided that it was time to "go public" about the tours discussed in this book, and the ACS invited her to organize the talks into an ACS Symposium Series volume. The study tours that she had conducted had as one of its goals learning science through travel to sites where the science actually happened.

The book is broadly scientific but also deals with areas other than chemistry. However, where appropriate, chemistry is the highlighted science. The book is also organized on the "base city" principle whenever possible: certain cities are hubs from which the traveler can branch out to other venues of interest. The second part of the book consists of four chapters on the sites in the British Isles: London and environs, including Oxford, the Royal Institution, Cambridge, and Scotland. The book's third part contains eight chapters on sites in continental Europe moving from north to south and then west to east. The final two chapters encompass the archaeology of Israel and fanciful journeys to Asia, Africa, and North and South America. The authors all have first-hand knowledge and in many cases, professional expertise, with respect to the history of the sites.

Chapter 2, "A View from the Cockpit: A Mid-Summer's 'Flight' through Chemical Europe," by Leigh Wilson, is an attempt to reproduce the unique atmosphere of the late John Wotiz's summer-long flying trip through historically important chemical sites in Europe. Chapter

3, "Scientific Scotland," by Robert G. W. Anderson, claims that Scotland "punches above its weight" when judged by its rich scientific, technological, and medical heritage. In European terms, it is a relatively small country, with a proportionately small population and a modest gross national product and has frequently felt itself in contention with its larger and wealthier English neighbor. Scottish universities, once having a distinct pedagogic system, became more closely uniform with those in England from the middle of the 19th century.

According to Chapter 4, "London as a Center of Science," by Peter J. T. Morris, London's centrality in science can be attributed to the fact that it is the seat of government, site of the headquarters of many learned societies, center of a seafaring empire for several centuries, a flourishing commercial center, and the nexus of the country's major institutions of higher education. This chapter is an introduction to every scientific facet of this city in the form of a gargantuan walking tour.

In Chapter 5, "Displaying Science in Context at the Royal Institution of Great Britain," by Frank A. J. L. James, states that over the last two centuries the Royal Institution has been home to eminent scientists whose discoveries have helped to shape the modern world. It has also shared this work with a wide public audience and continues to encourage people to think more deeply about the wonders and applications of science.

According to Chapter 6, "Science in Cambridge," by Gary Patterson, Cambridge University is world-renowned in a multitude of disciplines. This chapter introduces the scientifically minded reader or traveler to its rich scientific heritage as exemplified in its famous colleges and those who taught and did research in them. In Chapter 7, "Paris: A Scientific 'Theme Park,'" the book's editor, Mary Virginia Orna, states that there is more science, some of the most remarkable discoveries, including the discoveries of ten elements, radioactivity, stereochemistry, etc., concentrated in one small area of Paris than perhaps in all of the rest of France. In Chapter 8, "Scientific Florence," Marco Fontani reports that of the 72 museums in Florence, eight are scientifically oriented and there are two historic points of interest. This chapter tells where they are, how to get there, and the importance of the stories that they tell in the history of science and natural history.

In Chapter 9, "Rome and Northern Italy: Scientific Highlights," Orna returns to point out that Italy is not only the home of the artistic Renaissance, but it also gave rise to a scientific rebirth as the famous names of Avogadro,

Volta, Galileo, and Galvani testify. The chapter explores the scientific treasures of Rome and of the Northern Tier of Italy from Milan to Venice. In Chapter 10, "Wonderful Scientific Copenhagen," David A. Katz reminds us that Tycho Brahe and Niels Bohr are Copenhagen's scientific stars. The sites where they worked can be visited today as diversions from the other major attractions in this beautiful city. According to James L. Marshall and Virginia R. Marshall in Chapter 11, "Northern Scandinavia: An Elemental Treasure Trove," more elements have been discovered in Sweden than any other country. An exploration of these elemental sites includes Norway and Finland, whose elemental work was closely associated with Swedish academia.

In Chapter 12, "The Auer von Welsbach Museum," Roland Adunka discusses Carl Auer von Welsbach (1858−1929), a brilliant scientist and inventor who revolutionized the use of light and fire. A museum dedicated to his life and works exhibiting the inventions that sparked the growth of the gas industry and the electric industry opened in 1998 in Althofen, Carinthia, Austria. In Chapter 13, "Scientific Wanderings in Southern Germany and Austria," Janan M. Hayes explores the scientifically unique contributions to the culture, economy, and history of southern Austria and Bavaria. Salt is the unifying focus, centered on three major salt production areas that surround Salzburg and that have made a significant contribution to this city's political and economic development. Iron, mined in Althofen, in Austria's southernmost province, Carinthia, from prehistoric times, and rare-earth elements, are relatively recent developments on the mining scene.

In Chapter 14, "Points East: Selected Science Sites of Central and Eastern Europe," Roger Rea and Jiří Jindra give the scientifically curious visitor a taste of what can be found in some eastern European countries, most of which were once part of the communist bloc. The first two sites are in Vienna, the gateway to the east. Then the lure of Prague, Budapest, and Saint Petersburg are next. In Chapter 15, "Scientific Study Tour of Ancient Israel," Zvi C. Koren considers more than a dozen scientific techniques have been applied for the study of archaeological artifacts excavated from various sites of Ancient Israel by an international field of researchers. The results of the analyses performed with these methods on artifacts found in four representative archaeological sites in Israel, travelling from north to south, over a 450 km stretch of land, are presented. The science tour of Ancient Israel, which can be employed for the study of any region with a rich ancient history, shows how advanced scientific

analyses of archaeological artifacts are essential for understanding the life and times of ancient societies. In Chapter 16, "Flights of Fancy: World Heritage and Other Sites in Egypt, China, Peru, and Mexico," Carmen J. Giunta outlines possible itineraries for four countries on four continents outside of Europe: Egypt, China, Peru, and Mexico. This chapter imagines study tours in the history of chemistry based on chemical technologies and their artifacts.

I heartily recommend this modestly priced volume to chemists and persons in general who are interested in the travel aspects of science around the world.

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GDCh Mitteilungen

The History Group of the German Chemical Society is proud to announce that its journal "Mitteilungen" is now online and openly accessible. The content of all back issues from 1 (1988) to 24 (2014) is available from the Group's homepage:

https://www.gdch.de/netzwerk-strukturen/fachstrukturen/geschichte-der-chemie/mitteilungen-der-fachgruppe-online.html

In this way the GDCh History of Chemistry Group hopes to improve its service, and to strenghthen its ties, to the international community of historians of chemistry. Most articles in the "Mitteilungen" are of course in German, but contributions submitted in English will also be considered for publication.

Christoph Meinel, Managing Editor

Chemistry at the Three Societies Meeting

This year's Three Societies Meeting brings together three organizations dedicated to the study of the history of science, technology, and medicine: the British Society for the History of Science (BSHS), Canadian Society for the History and Philosophy of Science (CSHPS), and the History of Science Society (HSS). The Eighth Joint Meeting of the BSHS, CSHPS, and the HSS will take place in Edmonton, Alberta, Canada, June 22-25, 2016. The theme of the meeting is 'Transitions'. For details, see

https://uofa.ualberta.ca/arts/research/3-societies-meeting

The HSS Forum for the History of Chemical Sciences (FoHCS) will sponsor a session on "Chemistry at the Guillotine" that examines chemistry and politics in the context of early nineteenth-century Europe, following the political upheavals of the American and French Revolutionary Wars.

Instructions for Authors

Articles of 4-20 pages, double-spaced (excluding references) should be submitted electronically by email attachment to the Editor, giunta@lemoyne.edu, at Le Moyne College. The title of the article should be of reasonable length (up to 15 words); a subtitle may be included if appropriate. Authors should strive to make the title descriptive of the specific scope and content of the paper. Preferred file formats for submissions are .doc, .docx, and .rtf.

Subheadings within the paper are often appropriate to enhance clarity. Authors should bear in mind, however, that the format of an article in history of chemistry (order and content of sections) is not the same as the format of an article in chemistry. Recent issues of the *Bulletin* should serve as a guide. Detailed text formatting (paragraph justification, for example) need not be imitated, however; such text formatting will be applied at the layout stage. *The ACS Style Guide*, (3rd ed., Anne M. Coghill and Lorrin R. Garson, Eds., American Chemical Society and Oxford University Press, 2006) is also a useful resource for names, terms, and abbreviations appropriate for writing about chemistry.

In addition to scholarly articles, readers are encouraged to submit short notes or letters to the Editor. We would welcome hearing from those who have an interest in refereeing papers and/or preparing book reviews.

Before publication, a signed transfer of copyright form will be required, but this is not required as part of the initial submission.

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