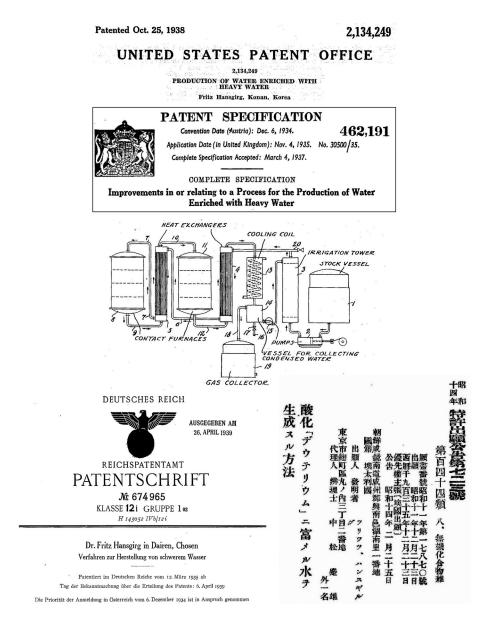
BULLETIN FOR THE HISTORY OF CHEMISTRY

Division of the History of Chemistry of the American Chemical Society

VOLUME 45 Number 2



Heavy Water Patents, 1930s



2020

BULLETIN FOR THE HISTORY OF CHEMISTRY VOLUME 45 CONTENTS

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The Cover... Fritz Hansgirg and Heavy Water (p 101)

LETTERS TO THE EDITOR

Jack Sylvester Hine 1923-1988

Jack Hine was an outstanding physical organic chemist. His Ph.D. was with Roger Adams and he did his post-doctoral work with John Roberts who regarded him highly. He was the author of about 170 papers and three books: *Divalent Carbon, Physical Organic Chemistry* [2 editions], and *Structural Effects on Equilibria in Organic Chemistry*. He was Regents Professor of Chemistry at Georgia Tech before moving to Ohio State. The purpose of this letter is to express my surprise that I have been unable to find a proper biographical account of Prof. Hine. I would have expected to see a plethora of obituaries in the standard journals and in C&EN. I can find almost nothing. Perhaps your readers can help?

E. J. Behrman, Prof. Emeritus, Chemistry & Biochemistry, Ohio State University, behrman.1@osu.edu

More on Jack Baldwin

I very much enjoyed reading your *Back Story* about Sir Jack Baldwin in the recent issue of the *Bulletin* (1). Seeing the picture of Jack in what appears to a ca. 1986 Austin Mini City E in front of the Dyson Perrins Laboratory reminded me of a day I spent with Jack in 2009 as I was in the UK for my Robert Robinson Award lecture series. I visited Jack, and he proudly exhibited his Ferrari 599. The attached photo will reveal his love of red, seen vividly in the on-line version of your *Back Story* and also in the on-line version of my photograph. Clearly Jack had graduated from the Mini to the Ferrari.

Jack already owned a Ferrari when he was teaching at MIT before he was called to the Waynflete Professorship at Oxford in 1978. But that Ferrari was a more modest model. He blew up Barry Sharpless's Corvette



(Left) Jack Baldwin in a car that most certainly did not fit his oversized personality. He was better known for his fast motorcycles and his even faster Ferrari (Right). Left photograph courtesy Jeffrey I. Seeman, right courtesy Scott Denmark.

racing down Memorial Drive in Cambridge, but that's another great story of this unique man.

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1. J. I. Seeman, "The Back Story: Sir Jack Baldwin," *Bull. Hist. Chem.*, **2020**, *45*, 64.

Citation for Chemical Breakthrough 2020 Awardees

The term "breakthrough" refers to advances that have been revolutionary in concept, broad in scope, and long-term in impact. Plaques, to be placed in the hallways outside the office or laboratory where the break-throughs were achieved, are presented to the departments and institutions at which these breakthroughs occurred. Jeffrey I. Seeman, then Chair of HIST and creator of the award, in 2006 said that the award is intended to "celebrate great scientific accomplishments and motivate, through shared pride of achievement. We hope that all who walk by and see the plaques will say, 'Wow! That was done here!""

The 2020 awardees are:

Imperial College London for William Henry Perkin, "Producing a new Coloring Matter for Dyeing with a Lilac or Purple Color Stuffs of Silk, Cotton, Wool, or other Materials," Great Britain Patent 1984, August 26, 1856.

The Royal Institution, London, and University College London for Lord Rayleigh and William Ramsay, "Argon, a New Constituent of the Atmosphere," *Philosophical Transactions of the Royal Society A*, **1895**, *186A*, 187-241.

The University of Manchester for Henry G. J. Moseley, "The High-Frequency Spectra of the Elements," *Philosophical Magazine* [Ser. 6], **1913**, *26*, 1024-1034.

New York University for Robert S. Mulliken, "The Assignment of Quantum Numbers for Electrons in Molecules. I," *Physical Review*, **1928**, *32*, 186-222.

HIST Election 2020 Results

Chair-Elect (Term 2021-2022); Chair (Term 2023-2024): Arthur Greenberg

Secretary/Treasurer (Term 2021-2022): Vera Mainz

Councilor (Term 2021-2024) Mary Virginia Orna

Alternate Councilor (Term 2021-2024) Christopher Heth

Congratulations to winners and to all the members who stood for election and were willing to serve.

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FROM "BLUE PILLS" TO THE MINAMATA CONVENTION: MERCURY, A SINGULAR METAL

Liliane Catone Soares, Federal University of Ouro Preto, Ouro Preto, Brazil, liliane.catone@ufop.edu.br

Abstract

Mercury is a singular element, which was employed in the past as both a medicine and a medium to carry out the death penalty. These purposes are apparently contradictory, but they rely on a single property: its high toxicity. Mercury toxicity was already known when its compounds were used as medicine in past centuries for the treatment of various diseases, mainly bacterial infections. The most common knowledge related to mercury toxicity is the Minamata disease and the "mad hatter syndrome." However, throughout history, whether through accidental or intentional poisoning, mercury has made countless victims from murders, unsuccessful medical treatments, occupational diseases, accidents and environmental crimes. Instead of discussing the most famous and popular cases involving mercury contamination, we seek to report and discuss different uses of mercury compounds in the treatment of diseases, as well as peculiar and little-known cases of mercury poisoning over the 19th and 20th centuries. To conclude, it will be shown that even today there are cases of deaths due to mercury poisoning in mining, homes and even schools. Thus, there is currently a global effort, represented by the Minamata Convention, to minimize the damage caused by mercury to the environment and human health.

Introduction

The singular properties and famous toxicity of mercury make it a unique element: it is the single metal that is liquid at normal pressure and room temperature; it is a highly toxic heavy metal with the ability of bioaccumulation and biomagnification in the environment; and also, it is considered a global pollutant. This element, which has aroused scientists' curiosity for centuries, is connected to relevant events in history and is part of popular knowledge. Minamata disease, the expression "mad as a hatter," the antiseptic brand names Mercurochrome and Merthiolate: all these mercury-related terms may be and have been found in the present or recent past.

Mercury was employed in the past both as a medicine and in carrying out the death penalty. These purposes are apparently contradictory, but they rely on a single property: its high toxicity. Mercury made countless victims throughout history through both accidental and intentional actions: murder, unsuccessful medical treatments, occupational diseases, environmental crimes and accidents.

Famous scientists such as Sir Isaac Newton, Blaise Pascal and Michael Faraday, who suffered intensely from their pathologies, may have been victims of mercury poisoning because of their scientific work (1). Furthermore, when speaking about occupational poisoning in science, the tragic death of renowned American researcher Karen Wetterhahn in the late 20th century has shaken the scientific community.

Here, we present a review of some issues that make the study of mercury so fascinating, starting with its unique properties, and some aspects about the chemistry of mercury culminating with its toxicity. We present different uses of mercury compounds in disease treatments, as well as peculiar and little-known cases of mercury poisoning illustrated through medical reports from the 19th and 20th centuries. To conclude, lest the reader think that mercury poisoning and contamination are problems of past centuries, it will be shown that even today there are cases of deaths due to mercury poisoning in mining, homes and even schools (including children). Thus, there is currently a global effort, represented by the Minamata Convention, to minimize damages caused by mercury to the environment and human health.

Mercury: Sources and Properties

Mercury is released by a variety of natural sources, such as volcanoes and other geothermal phenomena (as fumaroles and hot springs (2)); biomass burning and weathering of rocks and soils; anthropogenic processes, such as burning of fossil fuels; ore processing; chlorine; soda industry; incineration of temperature and pressure measuring devices, and electrical and electronic materials (3). Methylmercury compounds were used in the United States and Europe as fungicides, because they were economical and highly efficient (4). But in other places in the world, mercury is still currently used in pesticides and fungicides (5). Almost 50% of mercury anthropogenic release into the atmosphere comes from Asian sources. Nowadays, artisanal and small-scale gold mining (ASGM) and coal burning are the main anthropogenic sources of mercury emissions (5).

Once emitted into the atmosphere, elemental mercury is retained for long periods. Consequently, this element can be transported over large distances and is therefore characterized as a global pollutant. Atmospheric transport is particularly important for mercury. The same is not true for other metals, for which the aqueous medium is the main means of transport (5, 6).

In nature, mercury occurs mainly in the form of cinnabar, a mineral of mercury (II) sulfide, HgS, due to the strong interaction between mercury and sulfur, soft acid and base, respectively. HgS was used in China a thousand years before Christ, as a red pigment, and in the Greco-Roman world for the same purpose, when Hippocrates and Galen recognized their toxicity (7).

Metallic mercury has a melting point of -38.83 °C (8). It is the only metal that appears in the liquid state under normal pressure and room temperature. This characteristic has been explored in important applications throughout history, such as its use in thermometers and

amalgam formation for the extraction of precious metals. The ability of mercury to form amalgams with other metals has been known for a long time. In about 500 BC, in the Mediterranean region, amalgamation of noble metals and subsequent heating was already employed to extract these metals (9).

The characteristic of presenting itself in liquid state at room temperature was also responsible for the naming and representation of the chemical element. The symbol \forall used by alchemists in the 17th and 18th centuries is a reference to the god Mercury's caduceus. The modern symbol (Hg), introduced by Swedish chemist Berzelius, comes from the Latin word *hydrargyrum*, which means "liquid silver." The earliest written reference to mercury was made by Aristotle, who referred to the metal as "silver fluid" (10). Why is mercury the only metal that appears in the liquid state at normal pressure and room temperature?

Mercury also shows other singular properties. It has the highest density of all liquids under normal conditions, 13.546 g cm⁻³, at 20 °C (8). It has low electrical and thermal conductivities, and it is the only metal that does not form a diatomic molecule in the gaseous state (9, 11). Compared with gold, for example, its neighbor in the periodic table, mercury shows very different properties (Table 1).

Table 1. Some physical properties of mercury and gold under normal conditions (9)

Property	Mercury	Gold
Melting Point (°C)	-38.83	1064
Density (g cm ⁻³)	13.53	19.32
Enthalpy of fusion (kJ mol ⁻¹)*	2.30	12.8
Conductivity (kS m ⁻¹)	10.4	426

*Fusion entropies, on the other hand, are very similar, 9.81 and 9.29 J K^{-1} mol⁻¹, for mercury and gold, respectively.

Since the 1970s, the anomalous behavior of mercury has been explained by strong relativistic effects (9). However, only in 2013 the hypothesis was demonstrated by a group of researchers from Massey University of New Zealand. Employing quantum models, Calvo and collaborators (11) showed that, ignoring the relativistic effects, mercury's melting point would be 82 °C. On the other hand, including relativistic effects, the calculated melting point of mercury was very close to tabulated values. This hypothesis has just been demonstrated because, until then, computers could not complete the complex calculations performed by the group (11). According to the authors, their study shows that relativistic effects on chemical bonding drastically change the thermodynamic state of mercury (11).

To sum up, a few factors contribute to mercury being liquid: the 6s orbital is relativistically contracted and filled. In mercury, the two 6s electrons do not contribute significantly to the metal bond; the Hg–Hg bond is predominantly van der Waals, and, therefore, weak. This also explains the low electrical conductivity of mercury compared to that of gold: in mercury, the two 6s electrons are more localized and thus do not contribute to electrical conduction. For further details, the works by Norrby (9) and Calvo *et al.* (11) are recommended.

Mercury as a Medicine: Cases of Illness Treatments

In this section, we will show several medical cases from the 19th and early 20th centuries that report the use of mercury as a medicine. Note that some terms used in past centuries to designate chemical substances or units of measurement are not so usual today. For example, for mercuric chloride (Hg₂Cl₂), the term "perchloridum hydrargyri" (12) or "perchloride of mercury" (13) was used, as well as "corrosive sublimate" or "mercury bichloride." As for mercurous chloride, it was referred to as "protochloridum hydragyri" (12), "calomel" or "blue pill." About measurement units, for example, Dudgeon (13), reports "I then gave him 1/16 grain (gr.) of perchloride of mercury in 10 c.cm. of normal saline." Grain (gr) is an old unit of mass, which is equivalent to 64.799 mg and "c.cm" is short for cm³.

In the 19th century and early 20th century, the lack of specific treatment for many acute infections resulted in the preparation of different formulations. Different mercury compounds had already been used in the treatment of a wide range of diseases, such as cases of anuria (failure to pass urine), eye diseases (e.g., conjunctival lesions and corneal opacity), and erysipelas (a skin inflammation), as reported by Hall (14). In fact, mercury had an important role in medicine, in the words of Professor William Brande at a chemistry lecture (12):

The next metal on our list is mercury, which is an important metal in many respects, but especially on account of its extensive use as a medicine. [p 168]

It is likely that one of the most important uses of mercury in medicine has been in the treatment of syphilis. After the Black Death, which decimated about a third of the European population in the 14th century, Galen's

medicine was discredited, and medical novelties were desired. A century and a half later, when syphilis became epidemic in Europe, mercury was adopted as the standard drug for treating the disease, although Galen had already recognized its toxicity (15).

Paracelsus was one of the first to propose the use of mercury for treating syphilis; based on the diuretic properties of mercury salts: at the time, it was believed that by promoting diuresis and salivation, the causative agent of syphilis could be eliminated from the body (16).

Sarsaparilla, introduced by the French physician Nicholas Monarde in the 16th century, became popular in Europe because of the belief that syphilis had been brought from Asia by Columbus's sailors and that any native disease of a country could be cured by a native plant (15). Although sarsaparilla was most beneficial, mercury had been the major antiluetic for about 500 years and continued to be used until the development of penicillin in 1940 (16). The popularity of sarsaparilla probably decreased, because the treatment had to be done concomitantly with a month of confinement in a hot room over forty days of abstinence from sex and wine (15).

Treatment of diseases such as syphilis and gonorrhea were performed by administering pills and intravenous or intramuscular injections of mercury salts. To illustrate the use of mercurous chloride for the treatment of syphilis, referred to as "blue pills" by Abernethy, in a lecture at St. Bartholomew's Hospital (17):

I believe that mercury, to a certain extent, will counteract the progress of the specific malady, and as some sores are doubtful, as you cannot exactly decide whether they are specific or not, I should advise you to give mercury. Tell them to take the blue pill, but take it mildly. If the sore be syphilitic, it will heal under the administration of mercury, and if it be not syphilitic it will do no harm, but frequently promote the healing of the sore. [p 165]

According to Dudgeon (13), intravenous injections of mercuric chloride in the treatment of syphilis and gonorrhoeic rheumatism were employed, for example, by Baccelli in 1907.

The first case of septicemia which I treated with perchloride of mercury occurred in 1918 in the Balkans. The patient, a soldier, was suffering from an acute illness which was diagnosed on clinical evidence as malignant malaria.... I then gave him 1/16 grain (gr.) of perchloride of mercury in 10 c.cm. of normal saline [(18)], intravenously, which was repeated about 12 hours later as no improvement had occurred. After the second injection the temperature fell rapidly from 105 °F; to 100 °F; and then to normal, and the patient made a complete and rapid recovery. The only ill effects were a sharp attack of diarrhea and mercurial stomatitis, both of which responded to treatment. [p 170)]

Vecki (19–21) employed intravenous and intramuscular injections of calomel, sublimate, and mercury salicylate. He advocated the use of mercury in the treatment of syphilis, including another medicine, salvarsan, an arsenic compound introduced in 1910 by Paul Ehrlich:

It is very hard to judge of the relative value between salvarsan and mercury. Salvarsan surely has its charms and allurements. But, plainly speaking: if I had to abandon one of the two remedies it surely would not be mercury. [(21), p 372]

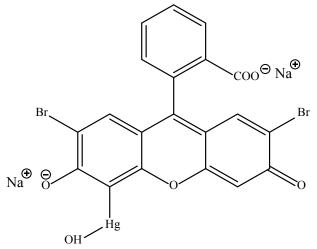
We know now that intramuscular injections of insoluble mercurial salts can be given with absolute safety, that when the proper preparation is used in the right way, the patient is never in any danger, that even calomel, the most powerful of all mercurial compounds, can be injected, the disadvantage of causing abscesses avoided and the ensuing pain reduced to a tolerable minimum. [(20), p 359]

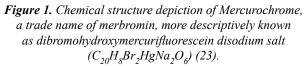
In 1919, Young, White and Swartz introduced a new drug for the treatment of bacterial infections, particularly for treatment of genital-urinary tract infections: Mercurochrome 220. According to the authors (22):

In synthesizing a drug for local use as a urinary antiseptic, it was sought to combine the following properties: 1) ready penetration of the tissues in which the infection exists; 2) lack of irritation of the drug to tissues; 3) high germicidal activity; 4) ready solubility in water and stability of the solution; 5) freedom from precipitation in urine, and 6) sufficiently low toxicity to avoid systemic effects from the small amount of the drug that may be absorbed.

Dudgeon (13) reports the use of perchloride of mercury or Mercurochrome (Figure 1) (23) (Mercurochrome 220) or both in numerous cases of acute bacterial infection. The author reports that 330 patients underwent treatment with these drugs. Mercury perchloride was the treatment for 200 cases of acute bacterial infection, including puerperal fever (24), infections caused by Staphylococcus aureus, hemolytic and non-hemolytic streptococci and Bacillus coli. (13)

Chemically it is the di-sodium salt of dibromoxymercury fluorescin. It is readily soluble in water and normal saline and is unaffected by moderate heat or exposure to air. It contains about 26 per cent of mercury, and even 1 per cent of this preparation does not form a precipitate with hydrocele fluid. The wide range of application of the drug in urinary and many other septic processes is fully recognized, but it is only the intravenous use of this preparation which is now under consideration. [p 170]





The use of mercury for treating syphilis was widely publicized and advocated, and some physicians extended its use to other diseases. This practice was not unanimous among physicians, since the toxicity of mercury compounds had been known for centuries. The following text, taken from a lecture by Dr. Astley Cooper from Guy's Hospital, on mercury treatment of venereal diseases, illustrates his indignation at the practice for gonorrhea patients (25).

At the present time, however, a surgeon must be either grossly ignorant, or shamefully negligent of the duty which he owes to the character of his profession, and to the common dictates of humanity, if he persists in giving mercury for this disease. Let those persons who suppose that gonorrhea can be cured by mercury, go round our wards and see whether mercury has any effect on that disease. Look, gentlemen, at 100 patients in our foul wards, many of whom come into the hospital with syphilis and gonorrhea; and many, I am sorry to say, who have only gonorrhea, but who are invariably carried to those wards. What is the miserable treatment of these patients? You are aware, gentlemen, that I scarcely ever enter the foul wards of St. Thomas's Hospital. When a particular case demands my attention, I have the patient removed to the clean ward. I will tell you why I do not enter those wards, gentlemen. I abstain from entering them, because patients under gonorrhea are compelled to undergo so infamous a system of treatment that I cannot bear to witness it. To compel an unfortunate patient to undergo a course of mercury, for a disease which does not require it, is a proceeding which

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reflects disgrace and dishonour on the character of a medical institution. [p 464]

According to *The Lancet* (1836) (26), later discussing Cooper's words, his "denouncement of the odious system was honest, bold, and unflinching."

Another acclaimed mercury medicine is "Merthiolate," the trade name of thiomersal or thimerosal, whose IUPAC name is ethyl(2-mercaptobenzoato-(2–)-O,S) mercurate(1–) sodium ($C_9H_9HgNaO_2S$), Figure 2 (27). A patent (US1672615) (28) was applied for in 1927 by organic chemist Morris Selig Kharasch from College Park, Maryland Later, the pharmaceutical giant Eli Lilly and Company marketed thiomersal under the trade name Merthiolate (29).

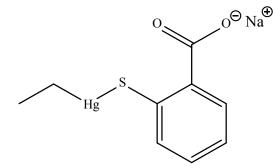


Figure 2. Chemical structure depiction of thiomersal or thimerosal, whose IUPAC name is ethyl(2mercaptobenzoato-(2–)-O,S) mercurate(1–) sodium $(C_0H_0HgNaO_2S)$ (27).

It is possible to find several records in medical literature of the 19th and 20th centuries that advocate the use of mercurial compounds in the treatment of diseases with numerous examples of successful cases, as well as records that abhor it, describing diseases developed by mercury poisoning after treatment with such medicines. This controversy dragged on nearly to the present day, and now the use of medicines containing mercurial compounds is prohibited in several countries. In Brazil, the prohibition was enforced in 2001 by the National Health Surveillance Agency (ANVISA).

Mercury as a Poison: Cases of Acute Poisoning

The use of poisons in murder or suicide is an old and successful practice. As recently as the early 19th century there were few tools to detect toxic substances in corpses. Sometimes investigators deduced the poison's identity based on symptoms that preceded death or built a case by feeding animals with the victim's last meal (30). Of course, few cases were resolved that way. Thus, chem-

istry had a fundamental role in the solution of crimes from the beginning of the 19th century with isolation and identification of chemical elements and the creation of the periodic table. To do so, the knowledge of chemical reactions and methods of separation were essential for developing methods of analyses.

Specifically, for mercury, Mathieu Orfila (1787-1853), professor of chemistry in Paris, published in 1832 a systematic procedure for identification of mercury compounds in *mixtures* (31):

For some years past the various scientific journals have contained instances of poisoning occasioned by mixtures of arsenic and laudanum, proto-nitrate of mercury, and verdigris; but as far as I am aware, no particular attention has been paid to the chemical questions involved in these discussions. I have deemed it my duty to study this subject with the greater care, inasmuch as it offered to my consideration many remarkable and unexpected phenomena. [p 614]

To illustrate this topic, seven cases of poisoning by inorganic mercury compounds, published in the early 19th century will be reported below in their chronological order.

The first case presented here was reported by Alisson (32). In 1829, a girl with suicidal intent, out of jealousy, ingested a quantity of a poison, a "red mercury powder." According to this report, the woman was first given grains of ipecacuanha and zinc sulfate. Afterwards, gastric lavage was performed, and castor oil and laudanum were administered for a few days. The girl gradually recovered her health. Although it was not reported in the account, the powder mentioned is probably mercuric oxide.

The second case, a more serious one, reported by Herapath (33), did not have a happy ending: the evolution of the patient's clinical condition led to her death nine days after poison ingestion. On October 12, 1845, a 27-year-old female patient with epilepsy, who had already suffered various seizures as a result of her disease, swallowed the contents of a bottle containing mercuric chloride dissolved in hydrochloric acid. The following section reports the first steps taken:

Upon our arrival, we learnt that vomiting had occurred within two minutes after the poison was swallowed, and it was encouraged by the frequent administration of copious draughts of warm water by her friends. Purging had also commenced in the first quarter of an hour, and the patient had remained upon the night commode ever since, as it was impossible to remove her. We arrived within an hour after the accident; the patient was cold and clammy, almost pulseless, having an anxious countenance, swollen, and almost livid, vomiting occasionally. Warm water was injected by the stomach pump, and several eggs were beaten up and administered by the same means, which the stomach retained. ... Milk and eggs to be administered frequently at short intervals. [p 699]

The third case, also lethal, involving two brothers, is very impressive. Hall (34) reports the case of two men who rubbed a mixture of mercuric chloride and lard on their bodies in order to cure an itch. One of them, 24, was found after an hour feeling intolerable thirst and excruciating pain. He said he felt as if he was being burned alive. After suffering from vomiting with blood, he died eleven days after intoxication. His brother, 19, used the same amount of the mixture and had the same symptoms, dying four days after his brother.

The fourth case, also involving mercuric chloride poisoning, and also fatal, was reported by Skegg (35). On October 27, 1861, a 54-year-old man ingested about seven grams of mercury chloride solution for suicide. He was treated with egg white and induced vomiting. Milk was given *ad libitum* and, in intervals, brandy and water. However, the patient died three hours after taking the dose. In both cases reported by Herapath (33) and Skegg, the patients presented symptoms of pale skin, covered by cold and sticky perspiration, weak pulse and white tongue.

The fifth case, reported by Meeres and Fox (36), is a tragic instance of a medical treatment gone wrong. In 1871, the physician Edward E. Meeres was accused of poisoning a child after a very concentrated application of mercuric chloride on the head and neck of the victim for local treatment of a mycosis—tinea tonsurans, a cutaneous fungal infection of the scalp caused by the dermatophyte *Trichophyton tonsurans* (37). The practice was common at the time, as supported by physician Tilbury Fox (36):

When I published the first edition of my work on "Parasitic Diseases of the Skin," in 1861, I had already used the remedy a long time, and it was on the strength of my experience that I then approved it ... I contend that my very large acquaintance with the remedy proves that in Dr. Meeres' case there must have been some very exceptional circumstance operating, and that I feel sure was idiosyncrasy; and, as far as I can see, no foresight on his part could have appreciated this. [p 414]

The sixth case is a non-lethal mercuric oxide intoxication reported by Ord (38). In July 1887, a 51-year-old tailor was admitted to St. Thomas's Hospital, unconscious, vomiting, and presenting pupils of average size, equal, and inactive toward light, cold sweaty face and hands, and a weak pulse. There were traces of a reddish powder on the patient that was later identified as mercury oxide. The patient was submitted to gastric lavage and treated with milk, lime water and beaten eggs. He gradually improved and left the hospital well twelve days later.

The seventh case, also reported by Ord (38), is about a non-fatal intoxication by mercuric chloride. In August 1887, a surgical instrument maker aged fortynine, swallowed a small portion of mercuric chloride. The patient vomited a bloodless greenish mucous fluid and complained of burning throat and stomach. He had moist skin, his tongue lightly coated with white material, and congested throat fundus. It was initially treated with zinc sulfate, egg white and milk, in addition to other substances. After a week in the hospital, the patient was released.

Among these seven reported cases, five involved mercuric chloride intoxication and four of them were fatal. The poisoning symptomatology depends on the dose and the exposure rate. Furthermore, biological behavior, pharmacokinetics and clinical significance vary with the chemical species (39).

For example, the lethal dose (oral intake) for mercuric chloride is 0.5 g, while for metallic mercury it is 100 g (7). In the case of the two inorganic compounds, mercuric chloride (HgCl₂) and mercuric oxide (HgO), the difference in toxicity is due to the difference in solubility and their consequent bioavailabilities. Mercuric chloride solubility is 7.31 g/100 g of water (at 25 °C) (8), whereas mercuric oxide is practically insoluble in water (40).

Mercury as a Poison: Cases of Occupational Diseases

In the 17th century, mercury was introduced, first in France, in the process of manufacturing hats. Mercuric nitrate was used in felting for making the outer stiff hairs on the pelt soft, limp, twisted and roughened so that they packed together more easily (41).

In 1902, Porter (42) described in detail this process: through a process called "carroting," hatters produced felt treating the skin of small mammals such as rabbit, hare, beaver and muskrat with mercuric nitrate solution. The hatter removed the skin from this mercury nitrate solution with his hands and subsequently entered the drying chambers to put and remove skins and thus came into contact with mercury vapors. At that time, many hatters developed neurological disorders whose symptomatology gave rise to the popular expression "mad as a hatter." For this reason, it is widely reported that Lewis Carroll drew on this phenomenon to create his character "Mad Hatter" from Alice in Wonderland. However, this does not seem to be the case.

According to Wedeen (43), the first description of mercurialism in hatters was published in 1860 by J.A. Freeman in "Transactions of the Medical Society of New Jersey," only five years before Carroll published his work. Nevertheless, it would be unlikely that Carroll was aware of this report. For Waldron (41), the belief that Carroll's Mad Hatter was the victim of mercurialism is an example of the Bellman's fallacy (44). The author suggests that Carroll was inspired by his acquaintance, Theophilus Carter, an eccentric furniture dealer and inventor, known for wearing a high top hat. Victims of mercurialism exhibit excessive shyness and introspection, qualities that would not be present in Carroll's character (41).

According to Hunter and collaborators (45), organic mercury compounds were first used in chemical research in 1863 by Frankland and Duppa at St. Bartholomew's Hospital. They used dimethylmercury to determine the valence of metals and metallic compounds and two laboratory technicians engaged in this work died after developing symptoms of mercury poisoning. One of them, aged 30 years, had been exposed to dimethylmercury for three months. He manifested hand numbness, deafness, poor vision and gum pain, in addition to slow and dull behavior, unsteadiness in gait and inability to stand. The symptoms quickly worsened, and he died two weeks after the onset of symptoms (45). The second technician, aged 23 years, had worked with dimethylmercury for only two weeks. One month after exposure, he began to show pain in his gums; numbness of feet, hands and tongue; deafness and decreased vision. The speech was confused, and he answered questions slowly. Three weeks after the onset of symptoms, he had difficulty swallowing, inability to speak, urinary and fecal incontinence, and became restless and violent. He remained in a confused state and died of pneumonia twelve months after the first symptoms (45).

Despite these two cases, it was only in the 1940s that contamination by mercury organic compounds was better studied by doctors Donald Hunter and Dorothy S. Russell. Even so, methylmercury poisoning, then known as Hunter-Russell syndrome, gained further attention after the Minamata disaster, which revealed to the world the true toxic potential of mercury. The Minamata disease will be discussed later in this text. In 1940, Hunter and collaborators (45) reported a full account about a clinical and experimental study with a group of four patients, before the Second World War, suffering from profound neurological disturbances as a result of industrial exposure to methylmercury compounds. Years later, in 1954, Hunter and Russell (46) reported a study about the necropsy of one of them. The man, aged 23 when he first came under observation, had been exposed to dust of methyl mercury phosphate and nitrate for four months, beginning five months before admission to hospital. The first symptoms appeared in 1937. The patient's neurological deterioration worsened as years passed by, and he died in 1952, after a pneumonia (46).

Cases of occupational diseases caused by mercury compounds occur worldwide and most commonly among workers in industrial plants and mining. In the early 20th century, mercury was used in numerous industries. Neal (47) presents an extensive listing of mercury applications in industry (chemical, electrical, hat manufacturing, dentistry, pharmaceutical, explosives, pesticides, photography and others) as well as mining cinnabar, gold and silver. In most cases, contamination occurs by exposure to elemental mercury vapors. However, contamination by organic forms is also possible, as in the pesticide manufacturing industry.

Agate and Buckell (48) report a study about mercury poisoning from fingerprint photography, an occupational hazard of policemen. At that time, the powder most commonly used in British and United States police forces was "hydrargyrum cum creta B.P." that is mercury-withchalk or grey powder prepared by triturating one part by weight of metallic mercury with two parts of chalk in a mortar. Out of 32 men engaged regularly on such work, seven were found to have evidence of chronic mercurialism (48).

In the 1970s, two dentists in Utah, USA, experienced mercury poisoning and even after correcting working conditions took almost two years for disappearance of their symptoms (49). Studies have suggested that, at that time, one in seven dentists was contaminated with significant amounts of mercury vapor (50). A study conducted in the same period with 284 dentistry workers showed that dental assistants who prepared dental cavity filling amalgam showed the greatest risk of exposure to mercury vapor (51).

In the 1990s, Italian researchers reported color vision loss in workers exposed to elemental mercury vapor, from factories engaged in the production of precision instruments as thermometers, thermostats and barometers (52, 53). These symptoms were also observed in São Paulo, Brazil, in workers from fluorescent lamp companies (54).

In the scientific community, the most famous case of occupational poisoning by mercury involved the renowned American professor and researcher Karen Wetterhahn in 1997 at Dartmouth College, a victim of dimethylmercury (DMM) contamination. In 1996, professor Wetterhahn spilled a few drops of DMM on her gloved hand while preparing an experiment. The substance passed through the glove and was absorbed by her skin. At that time, it was not known that latex gloves were permeable to DMM. Six months later, she slipped into a coma and died from acute mercury poisoning. Dartmouth has established several memorials in honor of professor Wetterhahn (55).

Mercury as a Poison: the Case of Minamata

From the 1920s to 1960s, the chemical factory Chisso Ltd. (56), located in Kumamoto, Japan, synthesized acetaldehyde and vinyl chloride using mercury(II) sulfate and mercury(II) chloride, respectively, as catalysts. Methylmercury, a by-product of the syntheses, was dumped into Minamata bay by Chisso, contaminating marine biota and water (57, 58).

In the 1950s, a mysterious neurological disease began to affect the population of villages near Minamata Bay. At first, dead fish began to appear in the bay. In addition to the death of fish and crows, some domestic animals, such as dogs and pigs, but mainly cats started to show neurological disorders. As described below by McAlpine and Araki (59), cats had symptoms that led to this disease becoming known as "dancing cat disease."

In the 40 affected families there were 61 cats and 50 died between 1953 and 1956, sometimes in as little as 2 days. Unsteadiness, frequent falls, circling movements, and convulsions were observed; forced running appears to have caused some of them to enter the sea and be drowned. ... The brains of 10 cats were examined; the changes were similar to those observed in the human material, the granular layer of the cerebellum being especially affected. The disease could be readily produced experimentally in cats by feeding them for 2 to 4 weeks with fish from Minamata Bay. [p 630]

In 1956, the mysterious nervous illness had assumed epidemic proportions. Fishermen and their families were mainly affected, and evidence suggests that the illness was caused by eating fish from Minamata Bay (59). In 1959, it was proved that methylmercury was the cause of Minamata disease and in 1960s Chisso was pressured to modify its waste disposal methods. Nevertheless, Chisso and other chemical industries continued to discard inorganic mercury, although not methylmercury, into Minamata Bay until 1968 (60). In the 1960s and 1970s, various health problems were noted in the children of mothers exposed to contaminated fish: neurological disorders (mental retardation, chronic brain damage, developmental disturbances), hypertension, liver disease, and poor metabolism (59, 60).

According to the Minamata Disease Museum (58), by 1997 more than 17,000 people in Kumamoto and Kagoshima prefectures had applied for certification as Minamata disease victims. At the end of May 2013, the number of certified patients was 2,977 (1,784 in Kumamoto Prefecture, 491 in Kagoshima Prefecture, and 702 in Niigata Prefecture), of which 646 (330 in Kumamoto Prefecture, 130 in Kagoshima Prefecture, and 186 in Niigata Prefecture) are still alive (61).

More than a decade passed since the first cases of Minamata disease to government's acknowledgment of Chisso factory's responsibility. Thousands of people were officially recognized as patients with Minamata disease, but how have victims been compensated?

Akio Mishima shows, in the book *Bitter Sea: The Human Cost of Minamata Disease* (60) how nefarious this event is. The preface, written by Lester R. Brown, founder of the Worldwatch Institute, highlights this sentiment:

Bitter Sea is an in-depth case study painfully chronicling the struggle between the victims of Minamata disease (mercury poisoning) and the corporation that discharged the mercury into Minamata Bay. It is gripping account of how the victims and their friends and sympathizers organized to seek justice. It is discouraging to see that the government is sometimes less interested in protecting the victims than those who are responsible for their pain. ... At times, in reading this book, one has the feeling of reading a novel, so dramatic is the account. Unfortunately, it is not fiction. It is a real-life story of how callous corporate greed can cause enormous human suffering. [p 7]

According to Mishima (60), Dr. Hajime Hosokawa, director of the hospital attached to Chisso's Minamata plant, suspected the factory may have been the cause of the mysterious illness. Therefore, he began conducting experiments in which cats were fed with food contaminated with factory effluents. Some time later, one cat had symptoms similar to those exhibited by human victims and its brain tissue was examined. Results revealed degeneration of the cerebellum, characteristic of Minamata disease. When, Hosokawa reported his findings to Chisso executives, they ordered him to stop the experiment and to kill the remaining cats in secrecy (60). Chisso also refused to comply with victims and used to offer despicable financial compensation to victims. Its disregard for dignity of life and human rights was later condemned in court (60).

For further details, the recent work of Yokoyama (62) is a complete study of the Minamata case.

Mercurial Medications: Not Entirely in the Past

There is a popular belief that the difference between a medicine and poison is merely the dose. This statement applies well to mercury.

It has been previously shown that it is possible to find in medical literature from the 19th and 20th centuries authors who advocate(d) the use of mercurial compounds in the treatment of diseases, as well as others that abhor it. This discrepancy in opinion is due to the fact that mercury toxicity, which is responsible for its microbicidal effects, is also responsible for this substance's side effects. In some cases, side effects were minimal; in others, serious and even fatal. Whether they will be serious or fatal depends on the dose administered, the chemical species employed in the treatment, and human physiology. So, the question still remains: should or should we not ban production and marketing of mercury medicines?

The use of mercury compounds in drugs is still defended today, as shown by the work of Mohite and Bhatnagar (63), which demonstrated the efficacy of using Mercurochrome 1% as an antiseptic for burns.

In spite of its effectiveness as a medicine in many situations, in order to respond to this question, we must expand our judgment beyond its usefulness as a medicine and analyze other aspects, especially in regard to environmental issues. Is the utility of mercury medicines so fundamental that it justifies direct and indirect consequences to the environment as a result of its production? Because of this discussion, it is no wonder that the Minamata Convention on Mercury was agreed in 2013.

The Minamata Convention on Mercury (MCM) is an international treaty aimed at protecting human health and the environment from damages caused by mercury. It was agreed on 19 January 2013 in Geneva, at the 50th session of the Intergovernmental Negotiating Committee on mercury and adopted in October 2013, in Kumamoto, Japan, at a Diplomatic Conference (Conference of Plenipotentiaries) (64). The MCM entered into force in August 2017, after the deposit of the 50th instrument of ratification, acceptance, approval or accession. Its aim is to control anthropogenic releases of mercury throughout its lifecycle (mercury emission, storage and disposal) (64).

Before consuming a product, we must evaluate the various stages of its production process, from obtaining raw materials to waste generation. For example, for medicines, one of the ways of generating waste is through excretion with subsequent disposal in sewage networks.

Moreover, when it comes to public health, the use of mercury amalgams in dentistry still generates much controversy among professionals. Amalgam, in addition to being more efficient in many types of procedures, has a much lower cost than resins and other materials. This theme well illustrates the importance of socioeconomic development to be in keeping with scientific development: expensive alternative materials will not be able to replace mercury amalgam in poorer regions of the world, like many cities in Brazil.

Environmental Considerations

Currently, there are numerous reports in the scientific literature about cases of mercury contamination at home and at school. Pediatric cases of elemental mercury poisoning from exposure to mercury by skin contact or inhalation have been reported in schools in different provinces of Turkey (65, ⁶⁶). Several cases are related to the fact that children carry liquid mercury from school to home, and heat it on the stove (67, 68, 69). A case was reported of mercury intoxication of two children (a 9-month boy and a 2.5-year-old girl) who were exposed to mercury from a barometer in a private residence in the Netherlands (70). Sasan and collaborators (71) report a case in Iran about mercury poisoning of two boys who had played with mercury. Also, a case was reported in Iran about two sisters presenting classical mercury contamination symptoms (pain in extremities, itchy rashes, sweating, salivation, weakness, and mood changes) after using a mercury compound for treatment of pediculosis (infestation by lice) (72).

Despite all these tragic events in the past, people keep dying from mercury contamination, as it is the case of a seven-year-old girl who died in August 2015 on an Indonesian island, where small-scale gold mining is an important part of the economy (73). In many developing countries, poor people keep living and working in close proximity to mercury emissions, in artisanal and smallscale gold mining. It is not the purpose of the present work to address pollution caused by artisanal mining, but countless papers in the literature report environmental, socioeconomic and political problems related to this practice. For example, in Antioquia, Colombia, guerrilla and paramilitary activities in rural areas pushed miners to towns so they could process their gold. Because of this, Antioquia developed the world's highest per capita mercury pollution. According to Webster, upon arriving in Antioquia one can feel a metallic taste on the tongue (74).

As previously mentioned, poisoning symptomatology depends on the dose and exposure rate. Moreover, other important factors are nutrition, co-exposures and preexisting conditions, all of which are strongly related to poverty (75).

Within the current pessimistic scenario caused by the environmental impacts generated by irresponsible anthropogenic activities, the Minamata Convention brought light to the end of the tunnel. According to the Minamata Convention, each party shall report on the measures it has taken to carry out the Convention's provisions, the effectiveness of these measures and challenges to achieve the goals of the Convention (64).

Conclusions

Mercury is released by a variety of natural and anthropogenic sources. Its singular physical properties and high toxicity make it a controversial element. Mercury is connected to medical events in history, as the Mad Hatter and Minamata diseases.

Mercury was employed in the past as a medicine because of its bactericidal properties. On the other hand, it also made countless victims through both accidental and intentional actions, in addition to occupational diseases and accidents at work.

Nowadays, there is a global effort represented by the Minamata Convention to minimize the damage caused by mercury to the environment and human health. Nevertheless, poverty places a hard challenge to achieve the goals of this Convention. Therefore, all countries must create public health commitments for combating social and economic inequities that are the greatest environmental threats.

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References and Notes

1. Even today, it is not possible to state without reasonable doubt the exact cause of pathologies suffered by these scientists. There may be other causes or a combination of factors, but mercury poisoning cannot be ruled out since all of them were heavily exposed to this metal's fumes, and the reported symptoms are consistent with the characteristic symptomatology. For more information, see the following studies:

M. Zanello, E. Arnaud and F. Di Rocco, "The Mysteries of Blaise Pascal's Sutures," *Child's Nerv. Syst.* **2015**, *31*(4), 503-506. https://doi.org/10.1007/s00381-015-2622-9.

M. Le Guern, "La maladie de Pascal en 1647 [Pascal's disease in 1647]," *Hist. Sci. Med.*, **2010**, *44*(1), 11-15, http://www.biusante.parisdescartes.fr/sfhm/hsm/ HSMx2010x044x001/HSMx2010x044x001x0011.pdf.

D. Adamson, *Blaise Pascal*, Palgrave Macmillan, London, 1995.

J. F. O'Brien, "Faraday's Health Problems," Bull. Hist. Chem., 1991, 11, 47-50.

J. Lieb and D. Hershman, "Isaac Newton: Mercury Poisoning or Manic Depression?" *Lancet*, **1983**, *322*, 1479-1480.

W. Broad, "Sir Isaac Newton: Mad as a Hatter," *Science*, **1981**, *213*, 1341-1342.

M. Keynes, "M. Sir Isaac Newton and His Madness of 1692-93," *Lancet*, **1980**, *315*, 529-530.

P. E. Spargo and C. A. Pounds, "Newton's 'Derangement of the Intellect:' New Light on an Old Problem," *Notes Rec. R. Soc.*, **1979**, *34*(1), 11-32.

A. Stock, "Die Gefährlichkeit des Quecksilberdampfes und der Amalgame," Z. Angew. Chem., **1926**, *39*(33), 984-989.

- R. Nakagawa, "Estimation of Mercury Emissions from Geothermal Activity in Japan," *Chemosphere*, 1999, 38(8), 1867-1871.
- UNEP Chemicals Branch, *The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport*, Geneva, 2008, https://www.unenvironment.org/resources/report/global-atmospheric-mercury-assessment-sources-emissions-and-transport (accessed Sept. 5, 2020).
- T. W. Clarkson, "Mercury: Major Issues in Environmental Health," *Environ. Health Perspect*, **1993**, *100*, 31-38, https://doi.org/10.1289/ehp.9310031.
- 5. UNEP Chemicals Branch. Global Mercury Assessment

2013: Sources, Emissions, Releases and Environmental Transport; Geneva, 2013, https://wedocs.unep.org/ handle/20.500.11822/7984 (accessed Sept. 5, 2020).

- J. E. Fergusson, *The Heavy Elements: Chemistry, Environmental Impacts and Health Effects*, Pergamon Press, Oxford, New York, 1990.
- N. Langford and R. Ferner, "Toxicity of Mercury," J. Hum. Hypertens., 1999, 13(10), 651-656. https://doi. org/10.1038/sj.jhh.1000896.
- C. R. Hammond, "The Elements," in D. R., Lide, Ed., CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 2005.
- L. J. Norrby, "Why Is Mercury Liquid? Or, Why Do Relativistic Effects Not Get into Chemistry Textbooks?" J. Chem. Educ., 1991, 68(2), 110-113.
- 10. E. R. Caley, "Mercury and its Compounds in Ancient Times," J. Chem. Educ., 1928, 5(4), 419-424.
- F. Calvo, E. Pahl, M. Wormit and P. Schwerdtfeger, "Evidence for Low-Temperature Melting of Mercury Owing to Relativity," *Angew. Chem. Int. Ed.*, 2013, 52(29), 7583-7585.
- 12. W. T. Brande, "On Mercury, and its Compounds," *Lancet*, **1828**, *10*, 168-171.
- 13. L. Dudgeon, "The Treatment of Acute Bacterial Infections," *Lancet*, **1926**, 207, 169-172.
- 14. J. C. Hall, "Leaves from the Case-Book of a Practising Physician," *Lancet*, **1849**, *54*, 85-88.
- M. T. Murray, "Botanical Medicine: A Modern Perspective," in J. E Pizzorno and M. T. Murray, Eds., *Textbook* of Natural Medicine, Churchill Livingstone: St. Louis, 2012, pp 255-260.
- J. G. O'Shea, "Two Minutes with Venus, Two Years with Mercury' Mercury as an Antisyphilitic Chemotherapeutic Agent," J. R. Soc. Med., 1990, 83(6), 392-395.
- J. Abernethy. "Surgical Lectures, Delivered by Mr. Abernethy. Theatre, St. Bartholomew's Hospital," *Lancet*, 1825, *3*, 161-166.
- 18. Normal saline is an aqueous solution of sodium chloride, with a concentration similar to body fluids $(0.9\% \text{ m V}^{-1})$. Therefore, the solution described has a concentration of about 0.405 g L⁻¹ of mercuric perchloride prepared in aqueous solution of 0.9% m V⁻¹ sodium chloride.
- 19. V. G. Vecki, "Some Typical Experiences With Syphilitic Patients," *Cal. State J. Med.*, **1915**, *13*(8), 298-301.
- V. Vecki, "Modern Therapy of Syphilis," Cal. State J. Med., 1913, 11(9), 358-360.
- V. Vecki, "Salvarsan vs. Mercury," Cal. State J. Med., 1912, 10(9), 371-372.
- 22. H. H. Young, E. C. White and E. O. Swartz, "A New Germicide for Use in the Genito-urinary Tract: 'Mer-

curochrome-220,"" J. Am. Med. Assoc., 1919, 73(20), 1483-1491.

- Mercurochrome is a trade name of merbromin, more descriptively known as dibromohydroxymercurifluorescein disodium salt (C₂₀H₈Br₂HgNa₂O₆). ChemSpider, Merbromin, http://www.chemspider.com/Chemical-Structure.10808965.html (accessed Sept. 8, 2020).
- 24. Puerperal fever is an infection that affects the female genital tract in the puerperal period (soon after child-birth). In earlier centuries, it has caused the deaths of thousands of mothers.
- A. Cooper, Lecture LV in Lectures on the Principles and Practice of Surgery, as Delivered in the Theatre of St. Thomas's Hospital, 2nd ed., F.C. Westley, London, 1830, pp 459-469. The lecture was delivered in 1824.
- 26. "The Lancet," Lancet, 1836, 1, 135-143 at 138.
- PubChem, Thimerosal, https://pubchem.ncbi.nlm.nih. gov/compound/Thimerosal (accessed Sept. 1, 2020).
- M. S. Kharasch, "Alkyl Mercuric Sulphur Compound and Process of Producing it," US Patent 1,672,615, issued June 5, 1928.
- J. P. Baker, "Mercury, Vaccines, and Autism," *Am. J. Public Health*, 2008, *98*(2), 244-253, https://doi.org/10.2105/ AJPH.2007.113159.
- 30. D. Blum, *The Poisoner's Handbook: Murder and the Birth of Forensic Medicine in Jazz Age New York*, Penguin Books, New York, 2010.
- M. Orfila, "Forensic Chemistry. On Detection of Mixed Poisons," *Lancet*, 1832, 18, 613-615.
- 32. W. Alisson, "Poisoning with the Red Precipitate of Mercury," *Lancet*, **1836**, *27*, 401-402.
- 33. W. Herapath, "Case of Poisoning with the Bichloride of Mercury," *Lancet*, **1845**, *46*, 650.
- 34. J. C. Hall, "Leaves from the Case-Book of a Practising Physician," *Lancet*, **1849**, *54*, 581-582.
- 35. J. J. Skegg, "Report of a Case of Poisoning with Bichloride of Mercury," *Lancet*, **1862**, *79*, 119.
- 36. E. E. Meeres and T. Fox, "Poisoning by the Local Application of Bichloride of Mercury," *Lancet*, **1871**, *98*, 413-414.
- T. C. White, K. Findley, T. L. Dawson Jr., A. Scheynius, T. Boekhout, C. A. Cuomo, J. Xu, C. W. Saunders, "Fungi on the Skin: Dermatophytes and *Malassezia*," *Cold Spring Harb Perspect Med.*, **2014**, 4(8), a019802. https://doi. org/10.1101/cshperspect.a019802.
- W. M. Ord. "St. Thomas's Hospital: Three Cases of Poisoning (Red Oxide of Mercury, Corrosive Sublimate, and Dinitrotoluene); Recovery; Remarks," *Lancet*, 1888, 132, 570-571.

- R. A. Bernhoft, "Mercury Toxicity and Treatment: A Review of the Literature," J. Environ. Public Health, 2012, 2012, 1-10. https://doi.org/10.1155/2012/460508.
- 40. $K_{sp} = 3.6 \times 10^{-26}$ for Hg(OH)₂ (HgO reacts with water to form Hg(OH)₂). B. M. Ham and A. MaHam, *Analytical Chemistry: A Chemist and Laboratory Technician's Toolkit*, Wiley, Hoboken, NJ, 2015.
- H. A. Waldron, "Did the Mad Hatter Have Mercury Poisoning?," *BMJ*, **1983**, 287, 1961. https://doi.org/10.1136/ bmj.287.6409.1961.
- 42. C. Porter, "Remarks on Felt Hat Making: its Processes and Hygiene," *BMJ*, **1902**, *1*, 377-381. https://doi. org/10.1136/bmj.1.2146.377
- R. P. Wedeen, "Were the Hatters of New Jersey 'Mad?" Am. J. Ind. Med., 1989, 16(2), 225-233. https://doi. org/10.1002/ajim.4700160213
- 44. In Carroll's poem "The Hunting of the Snark," the Bellman repeats "Just the place for a snark!" three times in quick succession, asserting "What I tell you three times is true." By extension the Bellman's fallacy is the belief that repetition of an assertion lends it credibility. L. Carroll, *The Hunting of the Snark: an Agony, in Eight Fits*, Macmillan, London, 1876, p 3.
- D. Hunter, R. R. Bomford and D. S. Russell, "Poisoning by Methyl Mercury Compounds," *QJM*, **1940**, *9*, 193-213.
- D. Hunter and D.S. Russell, "Focal Cerebral and Cerebellar Atrophy in a Human Subject due to Organic Mercury Compounds," *J. Neurol. Neurosurg. Psychiatry*, 1954, 17, 235-241.
- P.A. Neal and R.R. Jones, "Chronic Mercurialism in the Hatters' Fur-Cutting Industry," *JAMA*, **1938**, *110*(5), 337-343.
- J. Agate and M. Buckell, "Mercury Poisoning from Fingerprint Photography: an Occupational Hazard of Policemen," *Lancet*, **1949**, *254*, 451-454.
- D. G. Mantyla and O. D. Wright, "Mercury Toxicity in the Dental Office: a Neglected Problem," J. Am. Dent. Assoc., 1976, 92(6), 1189-1194.
- P. A. Gronka, R. L. Bobkoskie, G. J. Tomchick, F. Bach and A. B. Rakow. "Mercury Vapor Exposures in Dental Offices," J. Am. Dent. Assoc., 1970, 81(4), 923-925.
- M. Schneider, "An Environmental Study of Mercury Contamination in Dental Offices," J. Am. Dent. Assoc., 1974, 89(5), 1092-1098.
- A. Cavalleri, L. Belotti, F. Gobba, G. Luzzana, P. Rosa and P. Seghizzi, "Colour Vision Loss in Workers Exposed to Elemental Mercury Vapour," *Toxicol. Lett.*, 1995, 77, 351-356.
- 53. A. Cavalleri and F. Gobba, "Reversible Color Vision Loss in Occupational Exposure to Metallic Mercury," *Environ. Res.*, **1998**, 77(2), 173-177.

- 54. D. F. Ventura, A. L Simões, S. Tomaz, M. F. Costa, M. Lago, M. T. V. Costa, L. H. M. Canto-Pereira, J. M de Souza, M. A. M. Faria and L. C. L. Silveira, "Colour Vision and Contrast Sensitivity Losses of Mercury Intoxicated Industry Workers in Brazil," *Environ. Toxicol. Pharmacol.*, 2005, 19, 523-529.
- 55. Dartmouth Toxic Metals, A Tribute to Karen Wetterhahn, https://sites.dartmouth.edu/toxmetal/about-us/a-tributeto-karen-wetterhahn/ (accessed Sept. 1, 2020).
- 56. Chisso means "nitrogen" in the Japanese language.
- K. A. Graeme and C. V. Pollack, "Heavy Metal Toxicity, Part I: Arsenic and Mercury," *J. Emerg. Med.* 1998, *16*(1), 45-56. doi:10.1016/s0736-4679(97)00241-2
- Minamata Disease Museum, https://www.minamatadiseasemuseum.net/ (accessed Sept. 1, 2020).
- D. McAlpine and S. Araki, "Minamata Disease: an Unusual Neurological Disorder Caused by Contaminated Fish," *Lancet*, **1958**, *272*, 629-631.
- A. Mishima, (R. L. Gage and S. B. Murata, Trans.) *Bitter* Sea: The Human Cost of Minamata Disease, 1st English ed., Kosei Publishing Company, Tokyo, 1992.
- Ministry of the Environment, Japan, Lessons from Minamata Disease and Mercury Management in Japan, https://www.env.go.jp/chemi/tmms/pr-m/mat01/en_full. pdf (accessed Sept. 1, 2020).
- H. Yokoyama, "Lecture on Methylmercury Poisoning in Minamata (MPM)," in *Mercury Pollution in Minamata*, SpringerBriefs in Environmental Science, Springer, 2018. https://doi.org/10.1007/978-981-10-7392-2_2.
- 63. P. Mohite and A. Bhatnagar, "Mercurochrome 1% as an Antiseptic for Burns: Economical—but Is It Efficacious and Safe?," *Internet J. Surg.*, **2008**, *21*(2). http://ispub. com/IJS/21/2/5354
- UN Environment Programme, Minamata Convention on Mercury, Text and Annexes, http://www.mercuryconvention.org/Convention/Text (accessed Sept. 1, 2020).
- B. N. Akyildiz, M. Kondolot, S. Kurtoğlu and B. Konuşkan, "Case Series of Mercury Toxicity Among Children in a Hot, Closed Environment," *Pediatr: Emerg. Care*, **2012**, *28*(3), 254-258. https://doi.org/10.1097/ PEC.0b013e3182494ed0.
- K. B. Carman, E. Tutkun, H. Yilmaz, C. Dilber, T. Dalkiran, B. Cakir, D. Arslantas, Y. Cesaretli and S. A. Aykanat, "Acute Mercury Poisoning among Children in Two Provinces of Turkey," *Eur. J. Pediatr.*, 2013, *172*(6), 821-827. https://doi.org/10.1007/s00431-013-1970-2.
- L. Aslan, M. Aslankurt, S. Bozkurt, A. Aksoy, M. Ozdemir, H. Gizir and I. Yasar, "Ophthalmic Findings in Acute Mercury Poisoning in Adults," *Toxicol. Ind. Health*, 2015, *31*(8), 691-695. https://doi.org/10.1177/0748233713483189.

- G. Cicek-Senturk, F. A. Altay, A. Ulu-Kilic, Y. Gurbuz, E. Tutuncu and I. Sencan, "Acute Mercury Poisoning Presenting as Fever of Unknown Origin in an Adult Woman: A Case Report," *J. Med. Case Rep.*, 2014, 8(1), 266. https://doi.org/10.1186/1752-1947-8-266.
- S. Sarikaya, O. Karcioglu, D. Ay, A. Cetin, C. Aktas and M. Serinken, "Acute Mercury Poisoning: A Case Report," *BMC Emerg. Med.*, 2010, *10*(1), 7. https://doi. org/10.1186/1471-227X-10-7.
- P. T. J. Scheepers, M. van Ballegooij-Gevers, H. Jans, "Biological Monitoring Involving Children Exposed to Mercury from a Barometer in a Private Residence," *Toxicol. Lett.*, **2014**, *231* (3), 365-373. https://doi. org/10.1016/j.toxlet.2014.03.017.
- M. Sasan, N. Hadavi, R. Afshari, S. Mousavi, A. Alizadeh and M. Balali-Mood, "Metal Mercury Poisoning in Two Boys Initially Treated for Brucellosis in Mashhad, Iran," *Hum. Exp. Toxicol.*, 2012, 31(2), 193-196. https://doi. org/10.1177/0960327111417265.
- E. Khodashenas, M. Aelami and M. Balali-Mood, "Mercury Poisoning in Two 13-Year-Old Twin Sisters," *J. Res. Med. Sci.*, 2015, 20(3), 308-311.

- L. C. Price, Pulitzer Center, Indonesia: Dita's World, July 22, 2015, http://pulitzercenter.org/reporting/indonesiauncommon-disease-ditas-world (accessed Mar 30, 2020).
- 74. P. C. Webster, "Not all that Glitters: Mercury Poisoning in Colombia," *Lancet*, **2012**, *379*, 1379-1380.
- L. R. Goldman, Toxics and Poverty, https://www.who. int/ifcs/documents/forums/forum5/poverty_lynn2.pdf (accessed Sept. 1, 2020).

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Dr. Liliane Catone Soares is professor from the Chemistry Department of the Federal University of Ouro Preto (Brazil). She has experience in Environmental Chemistry, focusing on heavy metals. She is specialist in Adsorption Science, and she worked with mercury speciation in tropical soils. She currently studies the use of biomass to remove contaminants from water and effluents. She is also engaged with safety in chemical laboratories and waste treatment. http://lattes.cnpq. br/2157968516048040.

Notes from Europe

EuChemS Historical Landmarks Award

The call for submissions for the EuChemS Historical Landmarks Award, which aims at celebrating the important link between history, cultural heritage and chemistry, is open for submissions. Deadline is 31 December 2020.

Find out more about the award and enter your submission on the webpage https://www.euchems.eu/awards/ euchems-historical-landmarks/.

The EuChemS Historical Landmarks Award for 2019 have been designated for:

- Mines of Almadén, Spain, for the European Level https://www.euchems.eu/euchems-historical-landmarks-award-2019-european-level/
- Edessa Cannabis Factory Museum, Greece, for the Regional Level https://www.euchems.eu/euchems-historical-landmarks-award-2019-regional-level/

13ICHC Postponed to May 2023

The 13th International Conference on History of Chemistry (13ICHC) organized by the EuChemS Working Party on the History of Chemistry (WPHC), in cooperation with Vilnius University had been announced to be held in Vilnius, Lithuania, from the 18th to the 22nd of May 2021. See: https://www.ichc2021vilnius.chgf.vu.lt/. Due to the evolution of the Covid-19 pandemic, the conference has been postponed to May 2023, still in Vilnius. The new date of May 2023 has been chosen to maintain the biennial schedule of the WPHC.

A one-day online activity will be organized by the WPHC for one of the originally scheduled 2021 conference days.

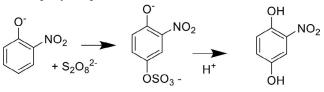
INTRODUCTION TO A TRANSLATION OF "UEBER NITROHYDROCHINON" BY KARL ELBS

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Karl Elbs (1858-1933) was a distinguished chemist at the University of Freiburg (1) specializing in electrochemistry. He was the author of one of the first compendia summarizing methods for the preparation of organic compounds, a very popular book on storage batteries (five editions), and a textbook on laboratory methods for electrolytic preparations which was published in two German editions and also in French and English translations. For details, see ref. 1. He also has two organic reactions named after him, the Elbs Reaction, a method for the synthesis of anthracenes (2) and the Elbs Oxidation, a way of converting phenols to the phenol *p*-sulfate by reaction with peroxydisulfate and so to the *p*-hydroquinone, as in the scheme below.



The translation presented here is Elbs' discovery of the second reaction early in his career at Freiburg. It has been the subject of many reviews (3-5) with hundreds of citations. It is instructive for today's chemists to understand how structural assignments were made in the days before the existence of our current spectroscopic tools. Purity was established by elemental analysis (still a requirement by the better journals) and structure by the method of formation, relationship to known compounds, the formation of predicted derivatives, and cryoscopic determination of the molecular weight. Elbs used the molar freezing point depression of naphthalene. I note that molecular weight determination using a colligative property has certain advantages. Sharp melting points were treasured. In 1893, mononitrohydroquinone was unknown although its monomethyl ether was known. Some dinitrohydroquinones, on the other hand, had been made. Salts of peroxydisulfate had been recently described by Marshall (6). Many ways of oxidizing phenol were known in 1893 (7), but, no doubt, Elbs wanted to try the effect of this new oxidizing agent and his choice of the o-nitrophenol was fortunate as the yields from this phenol are larger than from many others (5). It is interesting that his paper does not show that the product of reaction of o-nitrophenol in alkaline solution was actually the o-nitrophenol-p-sulfate, the diphenol being obtained by subsequent hydrolysis in acid, although acidification was part of his protocol. For references on this discovery see Sethna (3). It is also interesting that although Elbs properly conducted his reaction in alkaline solution as it is the phenolate ion that is the reactive species, he later states, incorrectly, that the reaction proceeds at all pH values. Richter (8) confirmed the identity of Elbs' product by an alternative synthesis via nitration of hydroquinone monobenzoate followed by alkaline hydrolysis. The portions of the translation in brackets [] are interpolations by the translators.

We thank the referee for many excellent emendations.

References and Notes

- 1. E. J. Behrman, "Karl Elbs, 1858-1933," *Bull. Hist. Chem.*, **2005**, *30*, 19-22.
- 2. L. F. Fieser, "The Elbs Reaction," Org. React., **1942**, *1*, 129-154.
- S. M. Sethna, "The Elbs Persulfate Oxidation," *Chem. Rev.*, **1951**, *49*, 91-101.
- Z. Wang, "Elbs Persulfate Oxidation," Comprehensive Organic Name Reactions and Reagents, Vol. 1, Wiley, New York, 2009, pp 977-981.
- E. J. Behrman, "The Persulfate Oxidation of Phenols and Arylamines (The Elbs and the Boyland-Sims Oxidations)," Org. React., 1988, 35, 421-511. E. J. Behrman, "The Elbs and Boyland-Sims Peroxydisulfate Oxidations," Beilstein J. Org. Chem., 2006, 2, https://doi. org/10.1186/1860-5397-2-22. E. J. Behrman, "The Elbs & Boyland-Sims Oxidations: Reactions of Peroxydisulfate-An Updated Literature Survey," Mini-Rev. Org. Chem., 2020, DOI:10.2174/1570193X17999200813153655.

- 6. T. S. Price, *Per-Acids and their Salts*, Longmans, Green, London, 1912.
- 7. *Beilsteins Handbuch*, H6, p. 115-116, 1923. This reference gives about 70 citations up to 1910.
- 8. M. M. Richter, "Über das 2.6-Dinitro-hydrochinon," *Ber. Dtsch. Chem. Ges.*, **1916**, *49*, 1398-1401.

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PRIMARY DOCUMENTS ON NITROHYDROQUINONE

Karl Elbs

"Ueber Nitrohydrochinon," *J. prakt. Chem.* [n.F.], **1893**, *48*, 179-185 Translated by E. J. Behrman, D. M. Behrman, Manuela Davis

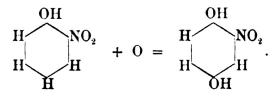
Until now, mononitrohydroquinone has only been known in the form of several of its derivatives. Now it is shown that nitrohydroquinone can be made by direct oxidation of *o*-nitrophenol with ammonium peroxydisulfate (1).

A solution of 35 g [0.25 mol] of *o*-nitrophenol, 50 g [1.25 mol] of sodium hydroxide, and 50 g [0.22 mol] of ammonium peroxydisulfate in 1500 g of water was allowed to stand for 1.5-2 days with occasional shaking. Then the mixture was acidified with sulfuric acid, the unchanged nitrophenol separated by steam distillation, a small amount of resinous material removed by filtration, and then extracted with ether. The ether extract, after evaporation, gave crystals of nitrohydroquinone which after one recrystallization from water or dilute ethanol

is pure. The yield is between 30-40% based on the starting material. Also, about half of the initial nitrophenol was recovered unchanged but increasing the amount of ammonium peroxydisulfate does not increase the yield of nitrohydroquinone but rather diminishes it.

Mononitrohydroquinone crystallizes as rhombohedra or as pyramids which frequently grow together like a cockscomb. The color varies from yellow-red to garnetred. It melts without decomposition between 133-134° and then solidifies within a few degrees of cooling in crystalline form. There is but slight tendency for sublimation in spite of marked volatility already at 100°. It is not subject to steam distillation. It is very soluble in ether and alcohol, less in acetic acid and hot water, moderately in cold water, hardly at all in benzene, and even less soluble in petroleum ether. It is best crystallized from water or dilute ethanol. The crystals are water-free; when strongly heated, they explode weakly and leave behind much carbon. Combustion gives 46.8% C & 3.9% H while theory for $C_6H_3(NO_2)(OH)_2$ is 46.4% C & 3.2% H.

In order to clear up the structure of the oxidation product of *o*-nitrophenol, the molecular weights of the acetate and the benzoate were determined and show that a mononitrodihydroxybenzene is present (2). The attempt to convert the free phenol, the acetate, and the benzoate to the known dinitrohydroquinone or its derivatives was unsuccessful (3). In comparison, methylation yielded without difficulty a monomethyl ether identified as the known nitrohydroquinone monomethylether (4) whereby the position of substitution in the benzene ring for the original oxidation product is established with certainty. The oxidation proceeds according to the equation:



Nitrohydroquinone forms two series of salts which are very soluble except for those with lead, copper, and silver; the solutions of the acid salts are brown while those of the neutral series are violet-blue.

It is difficult to obtain the salts in a pure state for the easily soluble ones are hard to crystallize and they are not very stable in solution. The violet-blue solutions of the neutral salts become dirty brown after a few days and upon acidification give only a little nitrohydroquinone and a brown-black precipitate of variable composition; the acid salts are more stable so that one can easily make the barium salt by heating the nitrohydroqinone with barium carbonate and water.

An oxidation of nitrohydroquinone to the quinone fails just as does that of dinitrohydroquinone. At first, brown, slightly soluble substances with pronounced phenolic character appear, and then decomposition products form.

Diacetylnitrohydroquinone

$$C_{6}H_{3}(NO_{2})(OOC_{(1 \cdot 4)}CH_{3})_{2},$$

forms easily by heating nitrohydroquinone with acetic anhydride and fused sodium acetate; the crude product, precipitated from water and thoroughly washed, is best crystallized from aqueous alcohol. There are commonly persistent traces of impurities which lower the melting point. The diacetate crystallizes in colorless plates or flat prisms or in long, thin , shiny needles by rapid precipitation from 95% ethanol; it is insoluble in water; very soluble in hot ethanol, and moderately soluble in ethanol at room temperature. It melts at 86° and solidifies in a crystalline state upon cooling. A small amount can be distilled almost without decomposition. The molecular weight was determined by freezing point depression in naphthalene and gave 228 whereas 239 is calculated for the formula, $C_6H_3(NO_2)(OOC.CH_3)_2$

The diacetate is slowly saponified with cold dilute sodium hydroxide and it dissolves with a violet-blue color; upon acidification, the color changes to yellow-red and nitrohydroquinone can be recovered upon extraction with ether.

Cold, aqueous ammonia leads to a step-wise saponification; at first a yellow-brown solution which contains the ammonium salt of the monoacetate is formed; later, the second acetyl group is cleaved and the pure violet solution now contains only the neutral ammonium salt of the nitrohydroquinone. The diacetate dissolves easily in cold concentrated sulfuric acid to give a yellow color. By adding water, a red-yellow solution is formed from which pure nitrohydroquinone is obtained by extraction with ether.

The behavior with nitric acid of specific weight 1.5 is peculiar; at 0° the material dissolves easily. If the solution is poured onto ice after standing for a few hours, the unchanged diacetate precipitates as long as the temperature does not rise appreciably above 0°. But if one interrupts the cooling and allows the temperature to rise to 15-20°, a slow release of gas takes place with complete decomposition. Other than a little oxalic acid nothing else was found. The deep yellow color of the liquid is due to a small amount of a phenolic material.

Dibenzoylnitrohydroquinone, $C_6H_3(NO_2)(OOC. C_6H_5)_2$, is easily made by shaking the nitrohydroquinone with benzoyl chloride and sodium hydroxide solution. One may only use dilute solutions of sodium hydroxide which are added in small amounts as the formed compound is easily split and must be worked up quickly. The crude material is easily purified by crystallization from boiling ethanol. It is not soluble in water, slightly in hot benzene, moderately in boiling ethanol. The difference in solubility between the boiling point and room temperature is very large for benzene and ethanol. The compound crystallizes in colorless needles which precipitate from benzene as large half spheres; they melt without decomposition but not very sharply between 140-142°

and char at higher temperatures without distilling. The dibenzoate behaves exactly like the diacetate with concentrated sulfuric acid; by contrast, it is somewhat more resistant to alkalis; with hot ammonia it only gives traces of saponification. The freshly prepared material is gradually decomposed by boiling sodium carbonate solutions. Cold dilute sodium hydroxide gradually decomposes the freshly prepared material but not the material dried at 100°. Saponification takes place rapidly in alcoholic sodium hydroxide solutions.

The freezing point depression in naphthalene gave molecular weights of 391, 349, 381, and 343 for an average of 366; the formula weight of $C_6H_3(NO_2)(OOC. C_6H_5)_2$ is 363.

Dibenzoylnitrohydroquinone is dissolved in nitric acid, sp. g. 1.5, at 0° and allowed to stand for 6 hours while the temperature rises to 26°. The mixture is then poured onto ice. A yellow precipitate forms which is hardly soluble in the usual solvents but which can be crystallized from boiling ether or acetic acid. One obtains a colorless crystalline sandy powder. The substance melts unchanged at 218-220° and remains crystalline upon cooling. It explodes weakly when heated strongly on a platinum plate; it dissolves in cold concentrated sulfuric acid and precipitates unchanged upon the addition of water. Moderately dilute sodium hydroxide solutions give slow saponification and the formation of a violet solution. The addition of sulfuric acid gives a precipitate of not wholly pure m-nitrobenzoic acid while extraction of the vellow-red solution with ether gives nitrohydroquinone. It follows that under these conditions a nitration occurs, but only for the benzoyl groups, not in the desired way of forming an ester of dinitrohydroquinone. The nitration product consists, for the most part, of di(m-nitrobenzoyl) nitrohydroquinone.

A mixture of 6 g nitrohydroquinone, 6 g methyl iodide, 3 g KOH, and 20 g methanol was heated at 100° in a sealed tube for six hours. The contents become dark brown. They are weakly acidified and steam distilled. One obtains 2.1 g of material whose chemical and physical properties agree wholly with those obtained in a different way by Weselsky and Benedikt (4) for nitrohydroquinone monomethyl ether. (The mass consists of large, flat prisms obtained after gradual evaporation of the solution. In the process, due to the weakly acidic character, the ammonia gradually escapes). After the separation by steam distillation, the cooled residue is separated from some resinous material and the filtrate extracted with ether whereby 1.6 g of unchanged nitrohydroquinone was recovered. From the mother liquor of recrystallized monomethylether, a very small amount of yellow needles was identified as the dimethyl ether because of their insolubility in alkali and melting point 71°.

Because of the similarity which mononitrohydroquinone and common dinitrohydroquinone show, it is important to emphasize their differences.

Mononitrohydroquinone crystallizes water-free. Its neutral barium salt is very soluble; its acid methyl ether crystallizes in orange-yellow prisms, melting point 83°, and is very volatile in steam; its diacetate crystallizes in colorless needles, melting point 86°.

Dinitrohydroquinone crystallizes with 1.5 moles of water; its neutral barium salt forms black needles nearly insoluble in water; its acid methyl ether crystallizes in cloudy greenish needles, melting point 102°, which are not volatile in steam; its diacetate crystallizes in sulfur-yellow needles, melting point 96°.

The relatively smooth conversion of nitrophenol to nitrohydroquinone shows that this oxidation by peroxydisulfate is a new method that will prove useful in many cases. It can be used in acid, alkaline, and neutral solution [wrong] and brings oxygen to work in the sense of the equation:

$$2NH_4SO_4 + H_2O = 2NH_4HSO_4 + O$$

Also, the fact that the oxidation agent is colorless and works without giving a precipitate is a factor of importance. This material is not yet commercially available and so in the following paper I describe a good method for its preparation [pp. 185-188].

References and Notes

- 1. For the preparation of ammonium peroxydisulfate see the following communication [not translated here, but see pp. 23-24 of T. S. Price, *Per-Acids and their Salts*, Longmans, Green & Co., London, 1912 which reproduces a translation of Elbs' preparation of ammonium peroxydisulfate taken from R. S. Hutton's translation of Elbs' book *Electrolytic Preparations* (Edward Arnold, London, 1903).]
- 2. Goldstein (Ber. 7, 734) obtained a dinitrodiphenol NO₂. $C_6H_3(OH)$ –(OH) C_6H_3 .NO₂ by oxidation of *o*-nitrophenol with potassium permanganate. [?]
- Strecker, Ann. Chem., 118, 293; Nietzki, Ber. 11, 470; Ann. Chem. 215, 143; Hesse, Ann. Chem., 200, 245. [These papers concern 2,6-dinitrohydroquinone made in connection with the structure of arbutin.]
- Weselsky and Benedikt, Wien. Mon. [Monatshefte für Chemie] 2, 369

EDITH PECHEY AND PROFESSOR CRUM BROWN: A KEY PART OF THE EDINBURGH SEVEN SAGA

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Edith Pechey (1845-1908) was a pioneering woman student who registered at the University of Edinburgh in 1869. Brilliant at chemistry, her cause (discussed below) made the British newspapers and even American magazines. Her nemesis was University of Edinburgh chemistry professor, Alexander Crum Brown. His central role in blocking the academic progress of Pechey and her colleagues has been totally forgotten (or ignored) from accounts of his life. This is the most complete account of the saga to date, constructed largely using contemporary sources and quotes.

Background

On 6 July 2019, seven women collected degree diplomas at the University of Edinburgh (1). An unremarkable event? To the contrary, a *very remarkable* event, as they were collecting the honorary degree diplomas on behalf of seven women students who, 150 years earlier, had tried and failed to graduate with medical degrees from Edinburgh. The seven unsuccessful pioneers have since taken their place in history as the "Edinburgh Seven" but until 2019, justice had not been done. Finally, the prize which they sought was granted in their memory. What has rarely come to the fore is the duplicitous and misogynistic role of Alexander Crum Brown, Professor of Chemistry at the University of Edinburgh, which will be recounted here. The saga began in March 1869 when Sophia Jex-Blake applied for admission to the University of Edinburgh to study medicine (2). Her initial application was accepted by the medical faculty but was overruled by the university court on the grounds that mixed classes were unacceptable and special classes for one woman impracticable. The wording of this ruling, almost certainly unintentionally, left the door open for a *group* of women to apply. Advertising in Scottish newspapers, Jex-Blake asked if any women wished to participate in a joint submission (3).

Edith Pechey

One of the responses was from Edith Pechey (4). (Mary) Edith Pechey had been born in Langham, Essex, to Sarah (*née* Rotton), a lawyer's daughter who, unusual for a woman of her generation, had studied Greek, and William Pechey, a Baptist minister with an M.A. in theology from the University of Edinburgh (5). Homeeducated, she first worked as a governess and teacher.

Interested in a medical career, Pechey had hoped to take the examinations of the Society of Apothecaries. Apothecaries were a recognized Guild with its own Court of Examiners to licence those who wished to dispense the herbal remedies of the time (6). Pechey became indentured to Elizabeth Garrett, later Garrett Anderson (7), who had obtained her Apothecaries' Diploma by the



Figure 1. Edith Pechey (credit: Thomas Fall, Wikimedia Commons https://commons.wikimedia. org/wiki/File:Edith_Pechey.jpg)

indenture route in 1865. Worried that other women might follow Garrett, in 1867, the Court of Examiners of the Apothecaries announced that they would no longer accept privately-tutored applicants. As women were barred from attending formal lectures, Pechey's route to a pharmacyrelated career was firmly blocked.

Reading Jex-Blake's advertisement, Pechey wrote to Jex-Blake (2):

Do you think anything more is requisite to ensure success than moderate abilities and a good share of perseverance? I believe I may lay claim to these, together with a real love of the subjects of study, but as regards any thorough knowledge of these subjects at present, I fear I am deficient in most.

Jex-Blake added Pechey's name to those she put forward to the University Court, the others being: Isabel Thorne, Matilda Chaplin, Helen Evans, Mary Anderson, and Emily Bovell. The Court give its approval, and in November 1869, these seven became the first women admitted to a British university. In the 1869 Calendar of the University, official regulations were inserted—reappearing annually for several years—that: "women shall be admitted to the study of medicine in the University" and that: "their instruction shall be in separate classes confined entirely to women."

In a lecture given by Jex-Blake in 1872, she explained how the system worked for the two courses which they took, one being physiology and the other chemistry (8): Though the lectures were delivered at different hours, the instruction given to us and to the male students was identical, and when the class examinations took place, we received and answered the same papers at the same hour and on identical conditions, having been told that marks would be awarded indifferently to "both sections of the class,"—this latter expression being, by the bye, repeatedly used during the course of the term by both the Professors who instructed us.

Professor Crum Brown

The chemistry course was taught by Alexander Crum Brown (9). An organic chemist, he had attended the University of Edinburgh, graduating in 1858. After working with prestigious chemists in Germany, Crum Brown returned to the University of Edinburgh in 1863 to accept the position of an extra-academical lecturer in chemistry. Then in 1865, he was appointed a Fellow of the Royal College of Physicians. Crum Brown was promoted to the rank of Professor of Chemistry in 1869, holding the Chair until his retirement in 1908.



Figure 2. Alexander Crum Brown (credit: Wikimedia Commons, https://commons.wikimedia.org/ wiki/File:Brown_Alexander_Crum.jpg)

Crum Brown was somewhat eccentric. One of his former students, J. S. Flett, reminisced about Crum Brown's classes (10):

The Professor, Crum Brown, was a charming man and a very bad teacher. ... His lectures were very interesting, but one never knew what subject he would take up and he was fond of parenthetical excursions into all sorts of by-ways of the subject that led nowhere and were a complete waste of time for students who were chiefly concerned in passing examinations. Considerable and important parts of his subject he forgot to mention and from his discursive habits he wandered hither and thither, and was always behind his programme. Towards the end of the year, he made a frantic endeavor to overtake his arrears and this was a ghastly failure.

Crum Brown had no control over his students as Flett recalled (10):

Most of his students very soon gave up all attempt to follow him and the class was exceedingly rowdy. Some days the noise and interruptions were so great that the poor professor had to give up and flee. Then in a few minutes he would return with tears streaming down his cheeks and apologise for his inability to control his class. We all loved him.

F. G. Bell, another of Crum Brown's students, also commented upon the disorder of Crum Brown's classes (11):

... a rowdy, genial disorder prevailed and when the row became intolerable, he would depart to his retiring room. A fervent chorus of "Will ye no' come back again" followed and after a suitable interval, back he came. I think he really enjoyed our bizarre show of affection and teasing.

The students who passed the course were given a Certificate of Attendance, which was required for admission to Medical School. In addition, the four students with the highest marks were entitled to Hope Scholarships. The recipients of the Scholarships received £200 plus free use of the facilities of the University chemistry laboratory for the next term.

The Hope Scholarship

The Hope Scholarships had been instituted by Thomas Charles Hope. Hope had been appointed as the sole Lecturer in Chemistry in 1797 (12). It was in the Spring of 1826, that Hope offered: "a Short Course of Lectures for Ladies and Gentlemen" (13). The presence of women on campus was opposed by many academics, and the gates to the building were closed to the women. Undeterred, Hope converted a ground-floor window on South College Street into a door to enable the women to enter and attend the lectures. In a letter, Lord Cockburn wrote to a T. F. Kennedy (14): "The fashionable place here now is the College; where Dr Thomas Charles Hope lectures to ladies on Chemistry. He receives 300 of them by a back window, ..." The income from these chemistry lectures to women enabled him in 1828 to donate £800 for the founding of a University chemistry prize: The Hope Scholarship.

In Pechey's year, when the marks were announced, she had placed third overall. The two male students above Pechey on the list were repeating the course and were therefore ineligible for the Scholarship. Though the money was welcome, the admission to the University chemistry laboratory was even more important. Women had been excluded from the chemistry laboratories and up to then, Pechey and the other women had to create practical facilities in their lodgings to enable them to perform the experiments.

However, Crum Brown, probably surprised by her outstanding marks, then proclaimed that Pechey was ineligible as she had been taught in a separate class, contradicting his earlier statements (15). It is appropriate to quote Jex-Blake's own observations (8):

It had occurred to us that if any lady won this scholarship she might be debarred from making full use of it as regards the laboratory, in consequence of the prohibition against mixed classes, but it had been distinctly ordained that we were subject to "all the regulations in force in the University as to examinations," it had not occurred to us that the very name of Hope Scholar could be wrested from the successful candidate and given over her head to the fifth student on the list, who had the good fortune to be a man. But this was actually done.

Crum Brown then contradicted himself a second time by awarding Pechey a bronze medal of the University. This was given to the five students with the highest chemistry marks in the class. By this act, Crum Brown acknowledged Pechey was eligible for this as a class member, despite having said that, in the context of the Hope Scholarship, Pechey was not a member of **The** Chemistry Class.

It was never mentioned anywhere as a reason for disbarring Pechey from the Hope Scholarship, but perhaps Jex-Blake was correct in concluding that the possibility of a women in the chemistry laboratory was unacceptable. Ineligibility for the Hope Scholarship was a means of avoiding this unexpected and unwelcome prospect. This explanation was suggested in a lengthy review article on Pechey's case in the *Daily Review* (Edinburgh) (16).

The only excuse that we can with the utmost stretch of charity imagine in this case would be that Dr. Crum Brown thought some difficulty might arise respecting Miss Pechey's use of the scholarship (which gives free admission to the laboratory) ... but we are quite at a loss to see how any legitimate argument can be drawn thence to justify Dr. Brown in laying violent hands on a scholarship which has been fairly earned by one person for the purpose of presenting it to another.

The issue of Pechey's disqualification rapidly escalated, gaining national attention, with articles in support of Pechey's case appearing in *The Manchester Examiner and Times, The Spectator* ("a very odd and gross injustice"), *The Times, The Scotsman, The British Medical Journal*, and *The Lancet*. It even gained international, attention, becoming the subject of a front-page article, "Women's Rights in Scotland" in the American newspaper, *New Era* (17).

Crum Brown's "Strawberry Jam Labels"

The Hope Scholarship denial affected Pechey alone. However, Crum Brown's other slight, one to all the Edinburgh Seven, had more significant implications. To gain admission to Medical School, as mentioned above, a student had to provide the authorities with a University Certificate of Attendance, to show that they had completed the prerequisite courses.

Crum Brown refused to issue the Edinburgh Seven the Certificates of Attendance for the Chemistry Class. Instead, he offered them written certificates of them having attended a: "ladies' class in the University." These, Jex-Blake derisorily referred to as Crum Brown's "strawberry jam labels" (18), as they were totally worthless in the context of admission to Medical School. Lacking the formal Certificates, the women were barred from the School.

The Edinburgh Seven appealed to the Senate of the University of Edinburgh. By a one-vote margin, the University Senate approved the issuing of University Certificates of Attendance to the women. This was only a partial victory, for at the same Senate meeting, by a contrary margin of one vote, the Senate denied the Hope Scholarship to Pechey.

That the Senate supported Crum Brown against Pechey, resulted in a poem titled: "A Cheer for Miss Pechey" being published in the London review magazine, *The Period*. Verses 1 and 8 are provided here (19):

- Shame upon thee, great Edina! shame upon thee, thou hast done
- Deed unjust, that makes our blushes flame as flames the setting sun.
- You have wrong'd an earnest maiden, though you gave her honour's crown,
- And eternal shame must linger round your name, Professor Brown.

- And I blush to-day on hearing how they've treated you, Miss P.,
- How that wretched old Senatus has back'd up Professor B.
- Ah! the "Modern Athens" surely must have grown a scurvy place,
- And the 'Varsity degraded to incur such dire disgrace.

The Surgeon's Hall Riot

Worse was yet to come. In the Fall of 1870, the Edinburgh Seven were members of a mixed class in anatomy which was held at the Surgeons' Hall, outside of the University. All went well until 18 November 1870 when the women arrived to take the anatomy exam.

As the women approached the Surgeons' Hall, they were mobbed by drunken male students. The Hall gates were slammed in their faces as they approached the building. Fortunately, one student, Tom Sanderson, who was already inside, saw their predicament, rushed out of the Hall, and managed to open the gates for them (20).

However, it was the aftermath of the exam which was truly frightening for the women, as Isabel Thorne recounted (21):

By the end of the examination it was dark and a crowd had again gathered around the gates. We were asked if we would leave by a private door; but we felt it would not do to be intimidated, and relying on the support of our class mates, who formed a sort of bodyguard around us, arming themselves, in default of other weapons, with osteological specimens, we passed quietly through the mob, only our clothes being bespattered with the mud and rotten eggs thrown at us.



Figure 3. The Surgeons' Hall, ca. 1890. (credit: Wikimedia Commons, https://commons.wikimedia.org/ wiki/File:Surgeons_Hall.jpg)

The attack on the women was disavowed the next day by many of the medical students, casting the blame on chemistry students and, tracing it back to their chemistry professor, Crum Brown (22):

Are only the hot-headed youths to be blamed who hustle and hoot at ladies in the public streets, and by physical force close the College gates before them? Or are we to trace their outrageous conduct to the influence of the class room, where their respected professor meanly takes advantage of his position as their teacher to elicit their mirth and applause, to arouse their jealousy and opposition, by directing unmanly innuendos at the lady students? ... The truth, however, is that the rioters were called together by a missive, circulated by the students in the *Chemistry Class of the University* [bold italic as in the original letter to the Editor] on Friday morning.

These authors have pointed out elsewhere that, just as some male academics were opposed to the advancement of women, there were others who were highly supportive of the cause of women rights (23). In the context of the continuing attacks on the women, it was not a chemist, but Robert Wilson of the Royal Medical Society of Edinburgh, who came to their support. Following the riot, Wilson sent a letter to Pechey (24):

I wish to warn you that you are to be mobbed again on Monday. A regular conspiracy has been, I fear, set on foot for that purpose. ... I have made what I hope to be efficient arrangements for your protection. ...I had a meeting with Micky O'Halloran who is leader of a formidable band, known in college as "The Irish Brigade" and he has consented to tell off a detachment of his set for duty on Monday. ... May I venture to hint my belief that the real cause of the riots is the way some of the professors [especially Crum Brown] run you down in their lectures. However, as I tell you, you and your friends need not fear, as far as Monday is concerned. You will be taken good care of.

In fact, the "Irish Brigade" continued their escort duties of the women between accommodations and lectures for some time afterwards. Michael O'Halloran, a male medical student at the time, has been overlooked as a hero of the event, having chosen to ally himself and his "Brigade" with the women students, protecting them from what could have been severe assaults. At the time, it was possible for medical students to spend a year at different university medical schools. It seems highly likely that O'Halloran was the Irish student who was noted as having come to Edinburgh from Queen's College, Cork (25). His name is listed in the Queen's College, Cork, Register as having received the degrees of M.D., M.Ch., Dip.Obs., and M.A.O. However, the authors were unable to find any details of O'Halloran's later life.

Several questions arise. Why did the Irish students seem to have such a cohesive identity? Was it that they were socially-excluded, perhaps on the basis of religion? It is curious why the "Irish Brigade" would be particularly supportive of these women. The culture of students in Irish medicals schools was no less masculine than elsewhere (26). Nor was the situation of women's education in Ireland any better than elsewhere in the British Isles. Though Alexandra College, Dublin, opened its doors in 1866 to offer advanced education to young women, it was not until 1879 that women were admitted to university in Ireland (27). However, it is also true that medical schools in Ireland had a more favorable attitude towards the admission of women than was the case in Scotland (28). Perhaps his support of women was more on the personal level. Sadly, we will never know what caused the noble gesture of O'Halloran and his band in defending the women.

The Final Insult

Despite several other attempts to impede their path, the women had passed all the examinations by 1872. However, the University of Edinburgh refused to grant them degrees. The group then took legal action against the University and, on 26 July 1872, initially won their case, the judges being scathing in their condemnation of the University (29). Unfortunately, on appeal in 1873, it was ruled that women should never have been admitted to the University in the first instance, and therefore could not graduate. Moreover, the women were compelled to pay all the legal costs, including the University's appeal, which amounted to the very significant sum at the time of £2,000. The "Committee to Secure a Complete Medical Education for Women in Edinburgh" came to their rescue, asking the public to provide financial aid and moral support, both of which were generously forthcoming.

As the University of Edinburgh had refused to issue them degrees, the British Medical Association refused to register the women as qualified doctors. In fact, it was not until 1889, that the Universities (Scotland) Bill was passed in Westminster which finally required the Scottish universities to admit and graduate women.

London School of Medicine for Women

Though these women had failed in their attempts for higher education in Edinburgh, from this setback was to

come a significant advance. It was the rejection from Edinburgh which caused six of the Edinburgh Seven, including Pechey, to travel south and push for the formation of a medical school exclusively for women. This endeavor resulted in the founding of the London School of Medicine for Women (LSMW), which opened its doors in the Fall of 1874 (30). Thus the founding of the LSMW can be said to be the one fortunate outcome of the rejection. (Previously, these authors have described the pioneering women who taught chemistry at the LSMW (31).)

Pechey's Later Life

And what became of Pechey? In 1877, she obtained a medical diploma from the Irish College of Physicians and, in the same year, an M.D. from the University of Bern, Switzerland. In October of that year, it was as Dr. Pechey that she delivered the inaugural address at the LSMW (5).

For the next 6 years, Pechey practiced medicine in Leeds, specializing in abdominal surgery. Then in 1883, she took up an appointment as Senior Medical Officer at the new Pestonjee Hormusjee Cama Hospital for Women and Children in Bombay (now Mumbai). While there, Pechey married Herbert Musgrave Phipson, taking the name of Pechey-Phipson. She wrote to her maternal aunt (32):

...We have known each other so well, and worked together in so many things these five years, that there is no reason to wait for anything, and we are getting older every day. I am four years older than he is, at which I know you will shake your head, but the real objection to the marriage is that he is so unselfish that there is a great danger of my becoming a mass of selfishness... What seems more certain is that we shall be very happy together.

Accompanied by her husband, and in poor health, Pechey returned to Britain in 1905, becoming active in the Leeds suffrage movement. In 1907, she needed surgery, the surgeon being May Thorne, daughter of Pechey's former classmate of the "Edinburgh Seven," Isabel Thorne. Though the operation was successful, Pechey never fully recovered and she died in 1908 at Folkestone, Kent.

Commentary

Though the Surgeon's Hall Riot has singled out students of the University of Edinburgh for behavior which is beyond our imagination today, it needs to be realized that violent misogynistic—though not as personal—riots occurred at other universities in Britain. In 1913, male students at University College, Bristol, set fire to the "Votes for Women" office in the city and watched it burn to the ground. Their student newspaper of the time expressed its whole-hearted support for the rioters and the subsequent incineration (33). Then in 1921, about 1,000 male Cambridge University students rioted outside the Newnham (women's) College gates, to celebrate the defeat of the proposal to allow women students to receive Cambridge degrees (34).

Did the situation improve for women students at the University of Edinburgh? Apparently not. A writer commented upon the treatment of Edinburgh women students in 1896 (35):

It is unfortunately a matter of not infrequent observance that the treatment of lady students at the hands of their *confrères* has been utterly out of keeping with the cherished canons of gentlemanly conduct. It is a painful fact that ever since the portals of our University were opened to the lady students, as the result between sweet reason and dogmatic rigidity, they have been the victims of gratuitous annoyance. Their entry into the class-rooms opens the floodgates of British chivalry. The tapers and tadpoles of the back benches begin to howl and screech with all the lustiness of rural louts, and seem to be as much amused as if they saw a picked company of the farfamed Dahomeyan Amazons march in all the glory of their military attire.

And what of Crum Brown? The incident did no long-term harm to Crum Brown's reputation. No mention of the events of 1870 could be found in any obituary, including the comprehensive account of his life in the *Journal of the Chemical Society* (36). In fact, a 2018 article in *Chemistry World* on the chemical contributions of Crum Brown, noted that he was "widely cherished by students" (37)—though this comment obviously did not refer to female students.

References and Notes

- "Edinburgh Gives Female Medical Students their Degrees—150 Years Late," *The Guardian* (online), July 6, 2019, https://www.theguardian.com/uk-news/2019/ jul/06/edinburgh-gives-female-medical-students-theirdegrees-150-years-late (accessed Aug. 27, 2020).
- S. Roberts, Sophia Jex-Blake: A Woman Pioneer in Nineteenth Century Medical Reform, Wellcome Institute Series in the History of Medicine, Routledge, London, 1993.

- M. A. Elston, "Edinburgh 7," Oxford Dictionary of National Biography, Oxford University Press, 2015, https:// doi.org/10.1093/ref:odnb/61136 (accessed Jan. 21, 2020).
- P. Anagol, "Phipson, (Mary) Edith Pechey- (1845-1908)," Oxford Dictionary of National Biography, Oxford University Press, 2006, <u>https://doi.org/10.1093/</u> ref:odnb/56460 (accessed Jan. 21, 2020).
- E. Lutzker, Edith Pechey-Phipson, M.D.: The Story of England's Foremost Pioneering Woman Doctor, Exposition Press, New York, 1973.
- 6. P. Hunting, *A History of the Society of Apothecaries*. The Society of Apothecaries, London, 1998.
- J. Manton, *Elizabeth Garrett Anderson*, Methuen, London, 1965.
- S. Jex-Blake, Medical Women: Medical Education of Women, vol. 2, n. pub., London, 1872.
- J. Walker, "Obituary Notices: Alexander Crum Brown, M.D., D.Sc., LL.D., F.R.S.," *Proc. Roy Soc. Edinburgh*, 1922-23, 268-276.
- J. S. Flett, "Memories of an Edinburgh Student 1886-1892," Univ. Edinburgh J., 1949-51, 15, 160-182.
- 11. F. G. Bell, "Period Piece: 1905-1910," Univ. Edinburgh J., 1961-62, 20, 215-230.
- 12. E. L. Hirst and M. Ritchie, "Schools of Chemistry in Great Britain and Ireland-VII The University of Edinburgh," *J. Royal Inst. Chem.*, **1953**, 77, 505-511.
- 13. J. B. Morrell, "Practical Chemistry in the University of Edinburgh, 1799-1843," *Ambix*, **1969**, *16*, 66-80.
- 14. H. Cockburn, *Letters Chiefly Connected with The Affairs* of Scotland, Ridgway, London, 1874, p 137.
- 15. S. Jex-Blake, *Medical Women: A Thesis and a History*. Oliphant, Anderson, & Ferrier, Edinburgh, 1886, p 60.
- Daily Review (Edinburgh), 1 April 1870, reprinted in Ref. 8, p 144.
- 17. "Woman's Rights in Scotland," *New Era* (Washington, DC), June 16, 1870, p 1.
- 18. Ref. 2, p 84.
- "A Cheer for Miss Pechey," *The Period*, May 14, 1870, pp 12-13.
- M. Ross, "The Royal Medical Society and Medical Women," Proc. Royal College Physicians, Edinburgh, 1996, 26, 629-644.
- 21. I. Thorne, "The Time in Edinburgh: 1869-1874," Royal Free Hospital Magazine, **1951**, *13*, 102.
- 22. The Scotsman, Nov. 22, 1870, reprinted in Ref. 8.
- 23. M. Rayner-Canham and G. Rayner-Canham, "Fight for Rights," *Chem. World*, **2009**, *6*(3), 56-59.
- 24. Cited in M. Todd, *The Life of Sophia Jex-Blake*. Macmillan and Co., London, 1918, pp 293-294.

- J. Bradley, A. Crowther and M. Dupree, "Mobility and Selection in Scottish University Medical Education, 1858-1886," *Medical History*, 1966, 40, 1-24.
- 26. L. Kelly, Irish Medical Education and Student Culture, c.1850-1950, Liverpool University Press, 2017.
- 27. E. Breathnach, "Women and Higher Education in Ireland (1879-1914)," *The Crane Bag*, **1980**, *4*(1), 47-54.
- 28. L. Kelly, "'The Turning Point in the Whole Struggle': the Admission of Women to the King and Queen's College of Physicians in Ireland," *Women's History Rev.*, **2013**, *22*, 97-125.
- Case 138. Sophia Louisa Jex-Blake and Others, Pursuers; The Senatus Academicus of the University of Edinburgh, Defenders. *Cases decided in the Court of Session, Teind Court, &c. Third Series*, vol. 11, T. & T. Clark, Law Booksellers, London, (28 June 1873), pp 784-802.
- 30. N. McIntyre, *How British Women became Doctors: The Story of the Royal Free Hospital and its Medical School*, Wenrowave Press, London, 2014.
- 31. M. Rayner-Canham and G. Rayner-Canham, "Women Chemists of the London School of Medicine for Women, 1874-1947," *Bull. Hist. Chem.*, **2017**, *42*, 126-132.
- Letters of Mrs Mary Edith Pechey-Phipson M.D., 1884-1892, Edinburgh University Library (Special Collections).
- 33. "Editorial," The Bristol Nonesuch, 1913, 3(8), 3.
- 34. B. A. Clough, "October 20th," *Newnham Coll. Roll Lett.*, 1922, 48-53.
- 'Sarat Mullick.' "A Plea for the Rational Treatment of Women Students," *The Student: Edinburgh University* 1896 (13 February), *10* (new ser.), 60-61.
- 36. J. Walker, "Obituary Notice for Alexander Crum Brown," J. Chem. Soc., Trans., **1923**, 3422-3431.
- A. Alexander, "Knitting the World," *Chemistry World*, 2018, https://www.chemistryworld.com/opinion/crumbrown-knitting-the-world/3008785.article (accessed Aug. 28, 2020).

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Marelene Rayner-Canham and Geoff Rayner-Canham have undertaken extensive research on the history of women in chemistry. In addition to authoring many publications, their most recent books are: A Chemical Passion: The Forgotten Story of Chemistry at British Independent Girls' Schools, 1820s-1930s (Institute of Education Press) and Pioneering British Women Chemists: Their Lives and Contributions (World Scientific Publishing Co.).

FROM POLYMER TO MACROMOLECULE: ORIGINS AND HISTORICAL EVOLUTION OF POLYMER TERMINOLOGY

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Introduction

For anyone involved with the chemical sciences, the complexities of terminology and nomenclature are an accepted part of the subject, be it students, practicing chemists, or historians of the field. In fact, the mastery of chemical nomenclature and associated terminology has often been compared to the study of a foreign language, complete with separate "dialects," each of which addresses different classes of chemical species and contains its own set of specialized rules and terms (1-4). Of course, nothing is constant and just as regional languages and dialects have changed over time, the meaning of chemical terms and systems of nomenclature have also evolved (5). Sometimes these progressions are gradual and of little real impact, but other times changes can be drastic and surprising, with the same terms adopting completely different meanings and uses over time (6).

As 2020 marks the 100-year anniversary (7-9) of the introduction of the macromolecular concept by Hermann Staudinger (1881-1965) (10), it seems appropriate to review the history behind the origin and evolution of various terms and their usage in polymer science. As much of the discussion here will focus on the terms *polymer* and *macromolecule*, it would be worthwhile to first give the modern definitions as a point of reference. According to IUPAC (11):

Conventionally, the word polymer used as a noun is ambiguous; it is commonly employed to refer to both polymer substances and polymer molecules. Henceforth, macromolecule is used for individual molecules and polymer is used to denote a substance composed of macromolecules. Polymer may also be employed unambiguously as an adjective, according to accepted usage, e.g. polymer blend, polymer molecule.

As such, a polymer would refer to a powder or film comprised of macromolecules, where a macromolecule (or polymer molecule) is defined as (11):

A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

In practice, however, both the terms polymer and macromolecule have continued to be used as interchangeable nouns, as illustrated by the following statement from a recent viewpoint article on the 100th anniversary of macromolecular science (12):

Macromolecules that exhibit both electron transport and ionic mass transport (i.e., mixed conducting polymers)...

The following discussion will attempt to present the origin of these terms, with a particular focus on the evolution of the meaning and use of the term polymer. In the process, the origins and use of other commonly used terms in polymer science (macromolecule, oligomer, copolymer, etc.) will also be discussed, along with the beginnings of formal polymer nomenclature.

Berzelius, from Isomer to Polymer

The first of our terms, *polymer* (from the Greek *polys* "many" and *meros* "part"), finds its origin with Swedish chemist Jacob Berzelius (1779-1848, Figure 1), who introduced the related terms *isomeric* and *polymeric* in 1831 (13) and 1832 (14), respectively. In the 1833 German translation of his original 1832 Swedish paper, Berzelius specified the difference between these two concepts as follows (14b):

But in order not to confuse phenomena of the same kind, it is necessary to determine precisely the concept of the word Isomerism. I mentioned that I understand this to include bodies which are composed of the same absolute and relative number of atoms of the same elements, and have the same atomic weight, as, for example, the two tin oxides, or the two phosphoric acids, which is not to be confused with the case where the relative number of atoms is equal, but the absolute number is unequal. For example, the relative number of carbon and hydrogen atoms in olefiant gas is absolutely the same as in oil of wine (the number of hydrogen atoms being twice as great as that of the carbon atoms). Yet, alone in one atom [i.e., molecule] of the gas there is only 1 atom of carbon and 2 atoms of hydrogen, CH², while on the other hand, oil of wine contains 4 atoms of carbon and 8 atoms of hydrogen, C⁴H⁸. In order to be able to describe this type of equality in composition, but inequality in properties, I would like to propose for these bodies the term *polymeric* (from $\pi o \lambda v \zeta$, multiple).



Figure 1. Jöns Jacob Berzelius (1779-1848) (Stipple engraving by A. Tardieu after F. Krüger, 1828. Courtesy of Wellcome Library, London, under Creative Commons Attribution only license CC BY 4.0).

To put this in context, "olefiant gas" (ölbildendes Gas) is ethylene, for which Berzelius gives what would be considered its modern empirical formula (CH_2) , rather than its molecular formula (C_2H_4) . The second substance, "oil of wine" (Weinöl), refers to the oil by-product obtained during the production of ethylene (olefiant gas) from sulfuric acid-alcohol mixtures. The English chemist and apothecary Henry Hennell (1797-1842) had analyzed this oil in 1826 (15), ultimately determining it to be a mixture of diethyl sulfate and various olefins (Figure 2).

The complex composition of oil of wine has caused some to state that the example given by Berzelius was a poor choice, contained obvious errors, and did not correctly demonstrate the relationship under discussion (16, 17). However, the current author has previously given more detail and clarification on this point (18), explaining that Hennell also showed that diethyl sulfate could be removed by heating the crude oil of wine in water (15). Furthermore, it has been noted by later chemists of the 19th century that this purified olefin fraction was known as "light oil of wine," while the original oil was called "heavy oil of wine," and that these two oils were not always differentiated in the literature (19).

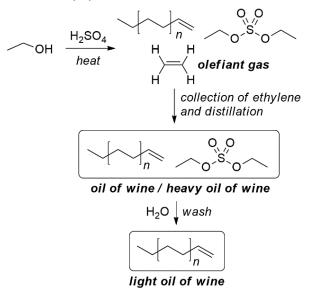
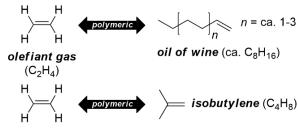
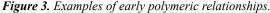


Figure 2. Production of oil of wine.

Although the isolated light oil of wine is still comprised of a mixture of different olefins, Hennel's characterization revealed properties consistent with a mixture with a compositional average of octene (C_8H_{16}) (15). If one assumes that the formula given by Berzelius for oil of wine (C_4H_8) was also halved in the same way as that of ethylene, this would then give a corrected formula of C_8H_{16} , which is in good agreement with that of octene. As such, it appears that Berzelius is referencing light oil of wine here, and the relationship between ethylene (C_2H_4) and this oil (i.e., $4 \times C_2H_4$) is fully consistent with his given definition.

Due to the inherent confusion associated with this example, many authors avoid it altogether when presenting the concept of polymerism as introduced by Berzelius, instead comparing ethylene and isobutylene (16, 20), which had been previously isolated from oil gas by Michael Faraday (1791-1867) in 1825 (21). In his previous paper on isomerism (13), Berzelius had stated that this pair of compounds differed from the isomeric examples discussed, as they exhibited the same relative number of elements, but with different absolute numbers. He did not specifically state, however, that this was a representative example of a polymeric relationship. Nevertheless, both of these sets of examples correctly demonstrate polymeric relationships as originally defined by Berzelius (Figure 3).





The relationship between ethylene and isobutylene illustrates an important distinction of Berzelius' polymer concept, however, as he never specifically stated that a polymer is a molecule formed from the chemical combination of the smaller unit. Thus, while it could be argued that oil of wine can be produced via the chemical reaction of ethylene, this is not the case for isobutylene.

Evolution of the Polymer Definition

Following its initial introduction by Berzelius, the polymer concept was then revisited and modified over time. A notable example of this can be seen in the contributions of the French chemist Marcelin Berthelot (1827-1907, Figure 4). In his *Leçons sur l'isomérie* presented before the Société Chimique de Paris in 1863, he gives polymerism as one of five types of chemical isomerism, presenting his view of polymers as follows (22):

I designate, under the name of polymer bodies, bodies formed of the same elements, in the same proportion, but under a different state of condensation, and capable of being produced from one another.

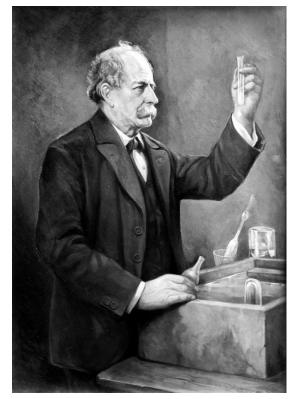


Figure 4. Pierre Eugène Marcelin Berthelot (1827 -1907) (Courtesy of Wellcome Library, London, under Creative Commons Attribution only license CC BY 4.0).

Berthelot then gave several examples to illustrate this relationship. It should be noted that while his definition above could be read to imply reversibility, this was never explicitly stated by Berthelot. Furthermore, both his discussion of polymer bodies and the presented examples dealt solely in the formation of larger bodies from reactant species. Such examples included turpentine (now known to be primarily composed of α - and β -pinene) and di-turpentine (23), as well as amylene (2-methyl-2-butene) and its products diamylene, triamylene, and tetramylene (Figure 5). He then concluded with the following observation (22):

Polymerism is nothing more than a particular case of chemical combination: it is the combination of a molecule of a body with another molecule of the same body.

Thus, as put forth by Berthelot, polymers not only shared the same empirical formula, but now included a direct relationship in which the larger molecule was produced from the smaller, an aspect not present when originally introduced by Berzelius. Berthelot then introduced yet another example in 1866, while detailing the action of heat upon acetylene (24). When heating acetylene over

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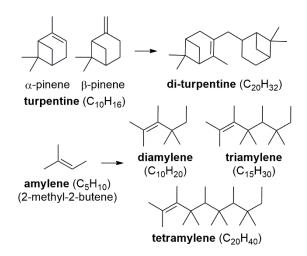
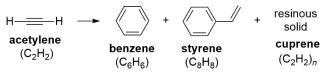
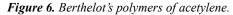


Figure 5. Modern representation of Berthelot's examples of polymer bodies.

mercury in a bell at extreme temperatures, he observed the formation of benzene, styrene, and a resinous solid (Figure 6). The last of these is generally considered to be the acetylene polymer later given the name cuprene (25). Of course, it is important to note that Berthelot's definition of polymer did not include any minimum size requirement, so all three of these products were polymers of acetylene in his view (18, 26).





This definition underwent a bit further modification through the beginnings of the 20th century, as illustrated by the description of the Dutch chemist Arnold Frederick Holleman (1859-1953) (18, 26, 27). In the 3rd edition of his *A Text-Book of Organic Chemistry*, published in 1910, he stated (28):

The union of two or more molecules of a substance to form a body from which the original compound can be regenerated is called polymerization.

Again, this definition made no real specification about size or molecular weight.

This changed somewhat in 1920, when the German chemist Hermann Staudinger gave his own views on polymerization (10). To begin with, he felt Holleman's requirement concerning the ability to regenerate the original species was not essential and did not accurately describe all polymerization products. Instead, Staudinger offered a more general definition as follows (10): Polymerization processes in the broader sense are all processes in which two or more molecules combine to form a product with the same composition, but a higher molecular weight.

Staudinger then went on to show that these polymerization processes could be subdivided into two groups: one in which the bonding of the initial molecule is retained in the polymer product and another in which polymerization results in atomic shifts such that the bonding of the product differs from the initial species. As examples of the first group, he included the production of metastyrene (modern polystyrene) from styrene, rubber from isoprene, and paraformaldehyde from formaldehyde. For the second group, his examples consisted primary of various bimolecular condensation reactions such as aldol condensation or benzoin formation.

Staudinger proposed that the first group should be regarded as real polymerization processes and products, while the second class should be referred to as false polymerizations or condensed polymerization products (10). Thus, in his view, polymers must retain the basic structural nature of the initial molecule polymerized. Staudinger also continued to note that polymerizations often form high molecular weight products, but did not specifically make such high molecular weights a requirement of what defines a polymer.

While Staudinger did much to clarify polymers and polymerization processes, this did not bring an end to the evolving views on the topic. Even as late as 1929, the American chemist Wallace Carothers (1896-1937) pointed out that the polymer definition was unsatisfactory and felt a more useful description of polymers was as follows (29):

They are characterized by a recurring structural unit, so that if this is represented by -R-, the structure of these polymers may be represented in part by the general formula -R-R-R-R-R-R-R-R-R-R-, etc., or $(-R-)_n$ The structural units -R- are bivalent radicals which, in general, are not capable of independent existence.

Staudinger and Macromolecules

By the early 1900's, significant interest had developed in *high molecular compounds* (30), operationally defined as products that cannot be vaporized in high vacuum. Furthermore, it was generally viewed that the molecular weight of these species was essentially too high to determine (31). At the same time, focus was also directed to *colloid phenomena*. As introduced by Thomas Graham (1805-1869) in 1861, colloidal (gluelike) materials were characterized as non-crystalline substances with slow diffusion, whose solutions did not pass through semipermeable membranes (32-34). These collective properties were generally viewed to be due to large particle size. At the time, however, neither large particle size nor high molecular weight was considered evidence for large chemical molecules and many considered both colloids and high molecular compounds as physical aggregations of small molecules (25, 35-38). Thus, these terms generally referred to collections of small molecules.

At odds with this view, Hermann Staudinger (Figure 7) speculated that many of these species instead consisted of covalently-bonded, long-chain molecules (35, 39-41). At the time, however, the established term polymer did not effectively differentiate between the accepted aggregate view and his preferred model of long-chain molecules (26, 30, 42), which led to his introduction of the new term *makromolekül (macromolecule, from the Greek makros "large," i.e., literally "large molecule"*) in 1922 (43):

Caoutchouc [natural rubber] is then a very high molecular weight hydrocarbon with many ethylene bonds, and the chemical behavior fully corresponds to this view. Some or all of the ethylene bonds can be saturated...without the colloidal properties changing, i.e., without the "macromolecule" disintegrating.



Figure 7. Hermann Staudinger (1881-1965).

This was followed two years later with a more formalized definition, stating (44):

For those colloid particles in which the molecule is identical to the primary particles, in which the indi-

vidual atoms of the colloid molecule are bound by normal valences, we propose the term macromolecule for differentiation. Colloidal particles constituted in this way, which occur primarily in organic chemistry and organic nature according to the ability of carbon to bind, form the actual colloidal substances. Here the colloid properties are due to the structure and size of the molecule...

Ultimately, Staudinger preferred to refer to his new model of high molecular weight compounds as makromolekulare Chemie (macromolecular chemis*try*), which is still widely used in Germany (30). The general concept of macromolecules, however, was not well received for some time (26, 36, 38, 40, 45). Still, by 1930, significant evidence had been accumulated in favor of the macromolecular hypothesis. The final part in establishing the concept was due to Wallace Carothers, who had successfully demonstrated the relationship between the structure and properties for a number of such polymers (26, 35, 46). It should be pointed out that the bulk of the characterization efforts up to this point had focused on natural and synthetic polymers comprised of a single repeat unit (cellulose, rubber, polystyrene, etc.), as more complex materials provided too many variables to accurately determine useful relationships between the polymer structure and its properties. It was only later that it was determined that more complex systems such as biological polymers (proteins, etc.) also fit this model. Nevertheless, it eventually became widely accepted that polymeric materials consist of macromolecules, for which Staudinger received the 1953 Nobel Prize in Chemistry.

Meyer, Mark, and High Polymers

During the early years of the macromolecular model, Staudinger became embroiled in arguments with Kurt Heinrich Meyer (1883-1952, Figure 8) and Herman Francis Mark (1895-1992). At the time, both men were working at I. G. Farben, with Mark joining Meyer there at the beginning of 1927 (47-50). Originally trained in organic chemistry, Mark had developed particular expertise in X-ray crystallography, while Meyer was an organic chemist strongly influenced by physical chemistry. With this combined focus, the two collaborated on the study of natural polymers.



Figure 8. Kurt Heinrich Meyer (1883-1952) (Reprinted with permission from Reference 46. Copyright 1950 American Chemical Society).

Mark had come over to Staudinger's view of longchain molecules before his arrival at I. G. Farben (49). Meyer too supported the concept of long-chain, high molecular weight molecules, but the two men disagreed with Staudinger on some details. Based on their work, they ultimately developed a new theory that appeared to be a compromise between Staudinger's macromolecular model and the previous aggregate model. In their view, colloidal particles were not themselves macro-molecules, but rather were aggregates of long-chain molecules held together by "special micellar forces" (35, 48, 49). Thus, they held that the determined weights of colloid particles did not represent molecular weights, but "micellar weights" (49).

In both his published papers and personal correspondence, Staudinger opposed their work, leading to an often bitter debate between Staudinger and Meyer (35, 48, 49). According to Mark, he wrote Staudinger in November of 1928 in an attempt to keep the peace, saying that he was sorry to see that Staudinger was annoyed by Meyer's statements. The growing feud continued, however, until a journal editor finally ended it all by refusing to print their papers on the subject. Mark later recalled (35):

Even the champions of the long chain aspect did not agree with each other, as they easily could have done because instead of concentrating on the essential principle, they disagreed on specific details and, at certain occasion, they argued with each other more vigorously than with the defenders of the association theory.

Throughout their joint work, Meyer and Mark did not use Staudinger's term macromolecule, but instead used the alternate descriptor *high polymer*. It has been proposed that this was in response to the dispute with Staudinger (30), but Meyer had first introduced the terms *hochpolymerer Verbindungen (high polymer compounds)* or *hochpolymerer Stoffe (high polymer materials)* in a paper submitted in the summer of 1928 (51). As this paper preceded both Meyer's joint papers with Mark and the ensuing conflict with Staudinger, this seems unlikely, although the conflict could have influenced their continued use, rather than giving Staudinger the satisfaction of using the term macromolecule.

The term high polymer was then reinforced and popularized through several books published by Meyer and Mark beginning in 1930 (52-54), particularly their critical two-volume Hochpolymere Chemie published between 1937 and 1940 (54). During the buildup to World War II, Mark emigrated first to Canada and then to the United States (50), where he continued to favor the use of high polymer over macromolecule, as illustrated by his multi-volume series High Polymers and Related Substances. As a result, the use of high polymers found acceptance in the United States, with the American Chemical Society organizing a High Polymer Forum in 1946, after which a formal Division of High Polymer Chemistry was founded in 1950 (30, 55). With little time, however, the descriptor "high" was dropped in common usage, thus resulting in the present synonymous usage of the terms polymer and macromolecule. Within this same time period, it should be noted that there was also an internal controversy over the general naming of the discipline (i.e., polymer science vs. macromolecular science) (30). Here, polymer science continues to be the more commonly used term.

Early Polymer Nomenclature

Although the discussion above has focused on the origin and evolution of the two primary terms polymer and macromolecule, it is also worthwhile to highlight some early practices in polymer nomenclature. Thus, while the overall family of materials could be identified as polymers or macromolecules, the names given to specific examples of this family was much less systematic.

The earliest known synthetic polymer, modern polyaniline, was first reported in 1834, but was not given a name until it was first commercialized as a cotton dye in the 1860s. As such, it is perhaps not surprising that it was originally named *aniline black*, according to its source and color (18, 56). However, this name was still retained after its linear chain structure was determined in the early 20th century, with the name polyaniline not introduced until the 1960s (57).

In comparison, the first of the addition polymers, modern polystyrene, was first reported in 1839. As it was originally believed to be an oxidation product, it was originally called *Styroloxyd* (styrene oxide) (18). Further studies in 1845 by John Blyth and August Wilhelm Hofmann (1818-1892) showed that this was not the case, however, after which Hofmann renamed the material *Metastyrol* (metastyrene) (58). The prefix *meta*had been introduced in 1833 by Thomas Graham as a way to denote a modification of an original compound (59). Thus, metastyrene would indicate a modified (i.e., polymerized) styrene.

The first to use the name *Polystyrol* (polystyrene) appears to have been Abraham Kronstein in 1902 (60). Even here, however, Kronstein is not using polystyrene in place of metastyrene, but is using it to differentiate one type of polystyrene from the more common form:

Berthelot's statement that the polymerization of styrene in hydrocarbon solution produces the same metastyrene as the heating of pure styrene is based on a mistake. The very fact that metastyrene is insoluble in hydrocarbons, while the product Berthelot obtained by heating styrene in a hydrocarbon solution is a soluble polystyrene, speaks for the diversity of these products.

Thus, the eventual replacement of metastyrene with the modern polystyrene continued to occur slowly.

While the evolution in naming for polystyrene seems like it should have become a blueprint for the naming of other polymers, this was not immediately the case. Rather, many polymers were still often described rather than given formal names. For example, another early addition polymer, polyvinyl chloride, was still referred to as polymerized vinyl chloride into the 1920s.

Copolymerization and Copolymers

As studies of polymeric materials advanced, so too did the complexity of some polymers being produced. With greater understanding of simple polymerizations and the nature of their products, a next logical step was the polymerization of mixtures of monomeric precursors. In modern practice, such polymerizations are known as *copolymerization*, the products of which are *copolymers*. The first study of such a copolymerization has been credited to Willy Otto Herrmann in 1928 (61), who carried out the copolymerization of vinyl acetate with di- and tri-ethylene. However, as this is based upon his published memoirs in 1963, it is not clear what terms he actually used in 1928. Understanding of copolymerization progressed slowly, however, such that Georg Kränzlein (1881-1943) of I. G. Farben reported the novel observation in 1930 that (61):

copolymers are quite different from blends. Each monomer acts as a regulator on the other and they polymerize into each other.

As such, this may have been the first documented reference to the product of copolymerization as a copolymer.

The first academic study of copolymerization seems to have been reported that same year by Theodor Wagner-Jauregg, who investigated the copolymerization of maleic anhydride with either styrene or stilbene (62). Interestingly, he proposed to call such processes *heteropolymerization*:

For this type of addition reactions, the name additive hetero-polymerization is proposed, in contrast to additive homo-polymerization.

The fact that he proposed this new term, and does not even mention copolymerization, suggests that the term copolymerization was not widely recognized in 1930. By the 1940s, however, both of the terms copolymerization and copolymer were in regular use (63).

Oliogomers and Limits of Size

Of course, a common point of argument is what exactly constitutes a high polymer or macromolecule? In addition, how should one refer to products that are not monomeric, but yet do not meet the criteria of macromolecules? As a solution, the term oligomer (from the Greek *oligo* "few" and *meros* "part") was ultimately introduced to describe low molecular weight products. The introduction of this term has been credited to the American polymer chemist Gaetano Frank D'Alelio (1909-1981, Figure 9) at General Electric Co's plastics laboratory in 1943. According to his coworker L. V. Larsen (64):

In 1943, Frank was preparing a laboratory manual for resins and plastics, which was published late in 1943. One day, several of us who worked with Frank were talking in his office about the proposed book and he remarked that, while there were the words "monomer" and "polymer" for polymerizable monomers, there was no corresponding simple word for "low molecular weight (or number) polymer." I was familiar with the word "oligarchy," and after looking up its etymology to be sure of the meaning of its prefix, I suggested to Frank that the word he wanted should be "oligomer," and I believe he used it in print for the first time in his laboratory manual.



Figure 9. Gaetano Frank D'Alelio (1909-1981) (Courtesy of Smithsonian Institution Archives, Accession 90-105, Science Service Records, Image No. SIA2008-0803).

It has also been pointed out, however, that the German chemist Burckhardt Helferich (1887-1982) had used related, although more specialized, terms prior to 1943 (16). While at the University of Greifswald in 1930, he and his co-authors Eckart Bohn and Siegfried Winkler had used the term *oligosaccharide* to refer to carbohydrates composed of a small number of monosaccharides (i.e., monoses) (65):

For the simpler crystallized sugars that give two or more monoses on hydrolysis, there is so far no name that reflects their position between the monoses and the polysaccharides (so-called for some time now with more general agreement). There is a need for such a name. The name oligo-saccharide is suggested for this.

Later, while at the University of Leipzig in 1940, Helferich and Horst Grunert, had similarly used the term *oligo-peptide* to refer to small sequences of amino acids (66).

Nevertheless, the more general term oligomer is not really seen in the chemical literature until the 1950s. In addition, while the introduction of oligomer has allowed suitable reference to species of limited repeat units, the point of demarcation between an oligomer and a polymer is still an ongoing debate amongst modern polymer chemists.

Conclusions

As can be seen from the above discussion, the word polymer has a long and complicated history, with multiple meanings and connotations over the years. As such, knowledge of its evolution is critical for those attempting to study the history of polymers prior to the mid-20th century. At the same time, it is interesting to see that all of the remaining terms commonly used in polymer science are relatively modern and were all introduced within the last century, all beginning with the introduction of Staudinger's macromolecule.

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References and Notes

- 1. W. P. D. Wightman, "The Language of Chemistry," *Ann. Sci.*, **1961**, *17*(4), 259-267.
- 2. M. P. Crosland. *Historical Studies in the Language of Chemistry*. Dover Publications, New York, 1978.
- S. C. Rasmussen, "The Nomenclature of Fused-ring Arenes and Heterocycles: A Guide to an Increasingly Important Dialect of Organic Chemistry," *ChemTexts*, 2016, 2, 16.1-16.13.
- M. Gordin, "Chemical Linguistics," *Chemistry World*, 2015, https://www.chemistryworld.com/opinion/chemical-linguistics/8685.article (accessed April 15, 2020).
- P. E. Verkade, A History of the Nomenclature of Organic Chemistry, D. Reidel Publishing Company: Dordrecht, 1985.
- S. C. Rasmussen. The Quest for Aqua Vitae: The History and Chemistry of Alcohol from Antiquity to the Middle Ages, Springer Briefs in Molecular Science: History of Chemistry, Springer, Heidelberg, 2014, pp 2-7.
- U. S. Schubert and S. Zechel, "The Year of Polymers—100 Years of Macromolecular Chemistry," *Macromol. Chem. Phys.*, **2020**, *221*, 1900530.
- 8. M. Hillmyer, "Editorial," *Macromolecules*, **2020**, *53*, 1.
- 9. S. J. Rowan, "Happy 100th Anniversary to Polymer Science and Engineering," ACS Macro Lett., 2020, 9, 122.
- 10. H. Staudinger, "Über Polymerisation," *Ber. Dtsch. Chem. Ges.*, **1920**, *53*, 1073-1085.

- A. D. Jenkins, P. Kratochvíl, R. F. T. Stepto and U. W. Suter, "Glossary of Basic Terms in Polymer Science (IUPAC Recommendations 1996)," *Pure & Appl. Chem.*, 1996, 68, 2287-2311.
- J. Chung, A. Khot, B. M. Savoie and B. W. Boudouris, "100th Anniversary of Macromolecular Science Viewpoint: Recent Advances and Opportunities for Mixed Ion and Charge Conducting Polymers," *ACS Macro Lett.*, 2020, 9, 646-655.
- J. Berzelius, "Körper von gleicher Zusammensetzung und verschiedenen Eigenschaften," *Jahres-Bericht über die Fortschritte der physischen Wissenschaften* 1832, *11*, 44-48 (translation of the original 1831 Swedish publication).
- (a) J. J. Berzelius, "Unterscheidung der Isomerie von analogen Zuständen," Ann. Phys. 1832, 102, 320-322. (b) J. Berzelius, "Isomerie, Unterscheidung von damit analogen Verhältnissen," Jahres-Bericht über die Fortschritte der physischen Wissenschaften 1833, 12, 63-67 (translation of the original 1832 Swedish publication).
- H. Hennell, "On the Mutual Action of Sulphuric Acid and Alcohol, with Observations on the Composition and Properties of the resulting Compound," *Philos. Mag.*, 1826, 68, 354-359.
- H. Morawetz, *Polymers: The Origins and Growth of a* Science, Wiley, New York, 1985, pp 5-6.
- P. J. T. Morris, *Polymer Pioneers: A Popular History of* the Science and Technology of Large Molecules, Center for the History of Chemistry, Philadelphia, 1986, p 27.
- S. C. Rasmussen, "Revisiting the Early History of Synthetic Polymers: Critiques and New Insights," *Ambix*, 2018, 65, 356-372.
- P. Claesson, "Ueber die neutralen und sauren Sulfate des Methyl- und Aethylalkohols," *J. prakt. Chem.*, 1879, *19*, 231-265.
- 20. Ref. 2, p. 328.
- (a) M. Faraday, "On New Compounds of Carbon and Hydrogen, and on Certain Other Products Obtained during the Decomposition of Oil by Heat," *Philos. Trans. R. Soc. London*, **1825**, *115*, 440-466. (b) M. Faraday, "Sur de nouveaux Composés de carbone et d'hydrogène, et sur d'autres produits obtenus pendant la décomposition de l'huile par la chaleur," *Ann. Chim.*, **1825**, *30*, 269-291.
- M. Berthelot, *Leçons sur l'isomérie*, Société Chimique de Paris Leçons de Chimie, L. Hachette et Compagnie, Paris 1866, pp 18-19.
- 23. The dimerization of α- and β-pinenes can produce a number of various homo- and hetero-dimers, of which a representative example is given in Figure 5. For example, see J.-J. Zou, N. Chang, X. Zhang and L. Wang, "Isomerization and Dimerization of Pinene using Al-Incorporated MCM-41 Mesoporous Materials," *ChemCatChem*, **2012**, *4*, 1289-1297.

- (a) M. Berthelot, "Action de la chaleur sur quelques carbures d'hydrogène (Première partie)," *C. R. Acad. Sci. Paris*, **1866**, *62*, 905-910. (b) M. Berthelot, "Les polymères de l'acétylène. Première partie: synthèse de la benzine," *C. R. Acad. Sci. Paris*, **1866**, *63*, 479-484.
- (a) S. C. Rasmussen, "Cuprene: A Historical Curiosity Along the Path to Polyacetylene," *Bull. Hist. Chem.*, 2017, 42, 63-78. (b) S. C. Rasmussen, *Acetylene and Its Polymers. 150+ Years of History*, Springer Briefs in Molecular Science: History of Chemistry, Springer, Heidelberg, 2018, pp 37-65.
- 26. J. W. Nicholson, "Etymology of 'Polymers," *Educ. Chem.*, **1991**, *28*, 70-71.
- Y. Furukawa, Inventing Polymer Science. Staudinger, Carothers, and the Emergence of Macromolecular Chemistry, University of Pennsylvania Press, Philadelphia, 1998, pp 18.
- A. F. Holleman, A Text-Book of Organic Chemistry, 3rd ed.; John Wiley & Sons: New York, 1910, p. 136.
- W. H. Carothers, "Studies on Polymerization and Ring Formation. I. An Introduction to the General Theory of Condensation Polymers," J. Am. Chem. Soc., 1929, 51, 2548-2559.
- 30. Ref. 27, pp. 4-6.
- 31. Ref. 16, pp. 90-91.
- 32. Ref. 27, pp. 12-14.
- 33. Ref. 16, pp. 47-52.
- M. Kaufman, Giant Molecules: The Technology of Plastics, Fibers, and Rubber, Doubleday Science Series, Doubleday & Company, Inc., New York, 1968, pp 15-17.
- G. A. Stahl, "Development of Modern Polymer Theory," in R. B. Seymour, Ed., *Pioneers in Polymer Science*, Kluwer Academic Publishers, Dordrecht, Netherlands, 1989, pp 13-28.
- 36. Ref. 17, pp 45-47.
- 37. Ref. 27, pp 34-35.
- 38. Ref. 16, pp 86-89.
- 39. Ref. 17, pp 48-50.
- 40. Ref. 34, pp 18-23.
- 41. Ref. 27, pp 64-67.
- 42. W. B. Jensen, "The Origin of the Polymer Concept," *J. Chem. Educ.*, **2008**, *88*, 624-625.
- 43. H. Staudinger and J. Fritschi, "Über die Hydrierung des Kautschuks und über seine Konstitution," *Helv. Chim. Acta*, **1922**, *5*, 785-806.
- H. Staudinger, "Über die Konstitution des Kautschuks (6. Mitteilung)," Ber. Dtsch. Chem. Ges., 1924, 57, 1203-1208.
- 45. Ref. 27, pp. 69-76.

- 46. Ref. 27, pp. 124-135.
- R. E. Oesper, "Kurt H. Meyer," J. Chem. Educ., 1950, 27, 665.
- 48. Ref. 16, pp 79-85.
- 49. Ref. 27, pp 76-82.
- 50. H. Mark, "Polymer Chemistry in Europe and America– How it all Began," J. Chem. Educ., **1981**, 58, 527-534.
- K. H. Meyer, "Neue Wege in der organischen Strukturlehre und in der Erforschung hochpolymerer Verbindungen," *Angew. Chem.*, **1928**, *41*, 935-946. A modified version was then republished later in 1928: *Die Naturwissenschaften*, **1928**, *16*, 781-793.
- K. H. Meyer and H. Mark, Der Aufbau der hoch-polymeren organischen Naturstoffe: auf Grand molekularmorphologischer Betrachtungen, Akademische Verlagsgesellschaft, Leipzig, 1930.
- 53. K. H. Meyer and H. Mark, *Aufbau der hochpolymeren Substanzen*, Hirschwaldsthe Buchhandlung, Berlin, 1930.
- (a) K. H. Meyer and H. Mark, Hochpolymere Chemie, Bd. I: Allgemeine Grundlagen der hochpolymeren Chemie, Akademische Verlagsgesellschaft, Leipzig, 1937. (b) K. H. Meyer, Hochpolymere Chemie, Bd. II: Die hochpolymeren Verbindungen. Leipzig, 1940.
- J. C. H. Hwa, "History of the POLY division of ACS 1951-1990," https://polyacs.org/wp-content/uploads/ 2018/05/POLY-history-1951-1990-by-Hwa.pdf (accessed April 20, 2020).
- 56. S. C. Rasmussen, "The Early History of Polyaniline: Discovery and Origins," *Substantia*, **2017**, *1*, 99-109.
- P. Constantini, G. Belorgey, M. Jozefowicz and R. Buvet, "Préparation, propriétés acides et formation de complexes anioniques de polyanilines oligonzères," *C. R. Seances Acad. Sci.*, **1964**, *258*, 6421-6424.
- J. Blyth and A. W. Hoffman, "Ueber das Styrol und einige seiner Zersetzungsproducte," *Ann. Chem. Pharm.*, 1845, 53, 289-329.
- 59. Ref. 2, pp 328-329.
- 60. A. Kronstein, "Zur Kenntniss der Polymerisation," *Ber. Dtsch. Chem. Ges.*, **1902**, *35*, 4153-4157.
- 61. Ref. 16, pp 133-135.
- T. Wagner-Jauregg "Über addierende Heteropolymerisation," . Dtsch. Chem. Ges., 1930, 63, 3213-3224.
- 63. See for example (a) F. T. Walt, "The Structure of Vinyl Copolymers," *J. Am. Chem. Soc.*, 1941, 63, 1862-1866.
 (b) R. Simha and H. Branson, "Theory of Chain Copolymerization Reactions," *J. Chem. Phys.*, 1944, *12*, 253-267. (c) F. R. Mayo and F. M. Lewis, "Copolymerization, I: A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene

and Methyl Methacrylate," J. Am. Chem. Soc., 1944, 66, 1594-1601.

- 64. L. V. Larsen, "Origin of the Term 'Oligomer," *Chem. Eng. News*, **1984**, *62*(4), 58.
- 65. B. Helferich, E. Bohn and S. Winkler, "Ungesättigte Derivate von Gentiobiose und Cellobiose," *Ber. Dtsch. Chem. Ges.*, **1930**, *63*, 989-998.
- 66. B. Helferich and H. Grünert, "N-Methansulfonyl-derivate von Aminosäuren und Oligopeptiden," *Liebigs Ann. Chem.*, **1940**, *545*, 178-196.

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DR. FRITZ J. HANSGIRG AND HEAVY WATER PRODUCTION: THE UNTOLD STORY

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Hansgirg deserves the credit for being first to file a patent that exploits the [catalytic exchange] reaction. He was clearly a knowledgeable, inventive and energetic man, and could have led a team to design a heavy water plant if given the opportunity (1).

> Dr. Anthony Busigin, Ph.D., P.Eng. nuclear chemical engineer

Abstract

During World War II, both the Germans and the Americans produced heavy water in large quantities by combining two well-known chemical processes: catalytic exchange and electrolysis. Several years earlier, before scientists understood the value of heavy water as a moderator in a nuclear reactor, an Austrian-born electrochemist by the name of Dr. Fritz J. Hansgirg had patented the catalytic exchange and electrolysis heavy water process in a number of countries throughout the world, including the U.S. Patent Office in Washington, DC, and the patent offices of Nazi Germany and Imperial Japan. And yet, despite his international fame as a wartime expert in magnesium production, Hansgirg's accomplishments vis-à-vis heavy water production have yet to be fully recognized by scientists or historians.

Introduction

Dr. Fritz J. Hansgirg of Yonkers, New York, the Austrian-born chemical engineer who invented the

internationally-known "Hansgirg method" of metallic magnesium production, an important strategic material during WWII (2), died at Columbia-Presbyterian Medical Center's Harkness Pavilion in upper Manhattan on Saturday evening, July 23, 1949. He was 58. He also held patents in countries throughout the world for a heavy water production process known as catalytic exchange and electrolysis. While Hansgirg's obituary in the *New York Times* (below) emphasized his brilliant career as an electrochemist and his world-renowned magnesium process, it failed to mention his heavy water patents (3):

At the age of 28, in a Viennese laboratory, Dr. Hansgirg devised a new and quicker process for extracting pure magnesium from the ore. After several years of unsuccessful efforts to reap financial rewards for his improvement, he left Austria in 1934 and tried his fortune in various other countries.

During his six-year stay in Japan before the war, Hansgirg supervised the construction of a magnesium plant for the Japanese at the industrial port city of Konan in northern Korea; and later, he served as technical advisor to the South Manchurian Railway Company. The Japanese magnesium plant at Konan was built for Nippon Magnesium Metals Company, Ltd., an industrial firm formed by American Magnesium Metals Corp. of Pittsburgh, Pa., for which Hansgirg served as its vicepresident.

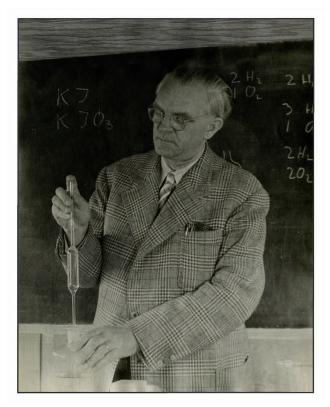


Figure 1. Fritz Hansgirg at Black Mountain College. Photo courtesy of Western Regional Archives, Department of Natural & Cultural Resources, Asheville, NC.

As noted in his obituary, Hansgirg arrived in California at a time when aircraft manufacturers throughout the world were "intensely interested" in magnesium due to the high strength-to-weight ratio of magnesium alloys. There, Hansgirg secured the attention of Henry J. Kaiser, an internationally-known industrialist, who engaged Hansgirg's talents and inventions for the new Permanente Corporation plant located near San José, California. Kaiser had secured a \$3 million loan to start the enterprise, to which another \$20 million was later added. Before his arrival in California, prior to the U.S. entry into World War II, Hansgirg had already erected a pilot magnesium plant in Austria and a large, full-scale magnesium plant for the Japanese in northern Korea (3).

Then on December 17, 1941, ten days after the Japanese attack on Pearl Harbor, and nine months after Hansgirg had begun working for Kaiser in California, he was arrested by FBI agents and deputy sheriffs as a "dangerous enemy alien." Despite being incarcerated in the San José jail, Hansgirg continued to advise Kaiser on the magnesium plant in California under construction. Two months after his arrest, Hansgirg was reportedly directing chemical operations at Permanente by telephone from jail, using the Sheriff's private telephone. The Sheriff declared his prisoner a "charming man" (3).

According to Natasha Goldowski (Renner), an expert metallurgist and former Manhattan Project scientist, Hansgirg had developed a new process for the production of heavy water "in his spare time"—this was several years before President Roosevelt signed an order creating a secret project to develop a nuclear weapon, later dubbed the "Manhattan Project." In addition to his U.S. heavy water patents, Hansgirg also obtained patents for that same invention in Austria, Nazi Germany, and Imperial Japan.

Before WWII began, and shortly afterward, Hansgirg's patents came to the attention of a Japanese industrialist in what is now North Korea and to top German and American experts on heavy water production and. And yet, Hansgirg's important achievements vis-à-vis heavy water production seem to have slipped through the cracks of history, barely mentioned, if at all, in books on heavy water production and the wartime race to develop an atomic bomb. After providing some background on deuterium and heavy water and filling in more detail on Hansgirg's life, this paper will focus on his patents for heavy water production and on wartime programs for large-scale production of heavy water.

The Discovery of Deuterium and Heavy Water

The discovery of deuterium (heavy hydrogen) in 1931 was hailed by scientists the world over as "one of the most significant discoveries of modern science" (4). Since its discovery, it was known that hydrogen occurs naturally in the form of two stable isotopes; protium (H) and deuterium (D), both of which are present in combination with oxygen (O) in natural water. "Heavy water," a combination of deuterium oxide (D₂O) and HDO, however, is extremely rare in nature; only a few drops are present in a liter of water (5). Likewise, the ratio of deuterium to hydrogen (D/H) in water is only 155.76 ppm (6).

Dr. Harold C. Urey, a Columbia University professor of chemistry, was the 1934 recipient of the Nobel Prize in Chemistry for his discovery of deuterium—an isotope of hydrogen but with about twice the atomic weight (7). The newly-discovered substance was coined "deuterium," from the Greek word meaning "second."

Earlier that same year, Urey was also awarded the Willard Gibbs Medal for his discovery of "heavy wa-

ter." Awarded annually by the Chicago Section of the American Chemical Society, the Willard Gibbs Medal is considered one of the highest scientific honors. At the time of the announcement, the *New York Times* suggested two potential uses for the 'deuteron,' the nucleus of the newly-discovered deuterium atom, originally called 'deuton' (8). For one, the deuteron was useful for bombarding the nucleus of atoms—even if erroneously hyped as the heaviest "atom-gun" so far discovered. Another potential use involved yeast cells, which biologists had found grow much more rapidly in ordinary water than in heavy water. Since yeast cells possess the quality of multiplying very rapidly, a quality also of cancer cells, biologists were hopeful that heavy water would prove valuable in the study of cancer (4).

Columbia University's announcement of the Willard Gibbs Medal said Urey's discovery promised to rank among the great achievements of science. "No scientific accomplishment of the present day," the statement read, "has had so immediate and so widespread an influence on research programs, or has given rise to a more highlycompetitive race among men of science" (4). Indeed, following Urey's discovery, scientists from around the world began experimenting with various methods of production—the extraction of deuterium from hydrogen and heavy water from ordinary water.

During the early months of 1931, Urey conceived and worked out a method for the concentration of a possible heavy hydrogen isotope (deuterium). Later, a sample of deuterium was extracted for the first time by the fractional distillation of liquid hydrogen; the feat was accomplished in collaboration with George M. Murphy and Ferdinand G. Brickwedde at the National Bureau of Standards (NBS) in Washington, DC. Gilbert N. Lewis, *Urey's* mentor at Berkeley, later isolated the first *sample* of pure heavy water by electrolysis (9). The first two patents relating to heavy water production, however, were obtained by others.

Albert Edgar Knowles of London, a chemical engineer, filed in Great Britain for a patent for heavy water production by electrolysis at the British Patent Office on February 21, 1934, and later at the U.S. Patent Office (10). Another heavy water process, the catalytic exchange between water and hydrogen—later utilized by the Germans at Norsk Hydro and in Canada by the Americans at Trail, BC—was first patented in Austria by Fritz Hansgirg, also from a 1934 filing. Catalytic exchange is represented by the following chemical equation:

$$HDO + H_2 \rightleftharpoons HD + H_2O$$

Hansgirg filed for a pair of patents related to heavy water production by catalytic exchange at the U.S. Patent Office, each before the discovery of nuclear fission by the Germans in 1938. His first application, "Production of Water Enriched with Heavy Water" (11), was filed in December 1935, and his second, "Production of Heavy Water" (12) was filed about a year later. Hansgirg also filed for patents (for that same pair of inventions) in a number of other countries including Germany (13), Japan (14), and Great Britain. When Hansgirg was issued his second Japanese heavy water patent, he was employed by the Japanese in Kantō-shū Dalian (Manchuria) (15).

Before the decade would come to a close, both Nazi and American atomic scientists began engineering the catalytic exchange process as part of their countries' respective wartime heavy water projects. Some of the latter would later join the Manhattan Project. By this time, heavy water was known to be an effective moderator in nuclear fission, and fission reactors would eventually be used to produce material for nuclear weapons. In fact, nearly pure D_2O could moderate fission even from natural uranium, in principle eliminating the need for isotopically enriched uranium. After the war, heavy water remained in demand for nuclear programs.

At first, heavy water cost about \$60,000 per pound. In 1934, following the discovery of a new process developed at Columbia University, the price fell to about \$6,000 per pound.4 During the war, however, the average production cost per pound fell to only \$186 (16). What had caused this precipitous drop? According to an article from the 1950s on the preparation of heavy water by catalytic exchange, "With the development of nuclear engineering, heavy water has advanced from an academic curiosity to a vital chemical product" (17). We will return to methods of production in some detail, in particular to their implementation during the war.

"In his Spare Time"

Born on June 20, 1891 in Graz, Austria's second largest city, Fritz Hansgirg received his Ph.D. in Chemistry in 1914 from the University of Graz. And in the fall of 1928, he invented a method of using carbon to extract nearly pure magnesium from its ore at his private laboratory in Vienna. Hansgirg would later describe his patented carbothermic magnesium reduction process as "simple and immediately successful" (18). With the financial assistance of Emil Winter (1857-1941), an American industrialist and one of the original founders of Pittsburgh Steel, Hansgirg built the world's first magnesium plant to utilize the "Hansgirg Process" at Radenthein, Austria, the home of Winter's \$10 million magnesite mine (19).

Since Winter felt he was too old to build a plant on his own, he offered Hansgirg's patents to other countries. When Hansgirg felt he was no longer able to work amidst the growing Nazi menace in Europe, he was commissioned to design and erect a large magnesium plant for Japan, and his Japanese magnesium patents were disposed to a newly founded company, Nippon Magnesium Metals Company, Ltd. (20). Hansgirg also managed to help his Jewish patent attorney, Richard Reik, like so many other Jewish refugees, flee Austria and certain death at the hands of Adolf Hitler and the Nazis (21).

Dr. Hansgirg and his wife, Josephine "Maria," left Radenthein "for good" in the fall of 1934 for the U.S., and from there, they sailed to Japan in December of that year (22). And from there, they traveled to the industrial port city of Konan, Korea, where the Japanese wanted their magnesium plant built. From 1910 until the end of WWII, all of the Korean peninsula was a colony of Japan.

At Konan, Hansgirg erected for Jun Noguchi (1873-1944), the Japanese engineer-turned-entrepreneur industrialist, large plants for the production of magnesium and other strategic materials. In 1927, Noguchi had established *Chosen Chisso Hiryo K.K.* (Korea Nitrogenous Fertilizer Co., Ltd.), the largest and most heavily capitalized enterprise in colonial Korea, with over twenty subsidiary companies in diverse industries (23).

At one point during the Japanese industrial buildup of Konan, Hansgirg traveled to the United States where he discussed the Korean project with Winter in Pittsburgh. In New York, Hansgirg and his wife were introduced to Miss Frances Grant, the vice president of the Roerich Museum in Manhattan. When Grant later received a Christmas card from the Hansgirgs in Korea, she noted on the back: "Exceedingly interesting couple met at RM [Roerich Museum]—they went on to Japan and Korea" (24). By the time the Hansgirgs arrived at Konan, Nicholas Roerich, a world-famous artist, explorer, author, scientist, philosopher, and the Museum's founder, had already passed through Korea en route to Manchukuo (25), Japanese-controlled Manchuria.

About seven months after arriving at Konan, Hansgirg wrote a 12-page handwritten letter to Grant dated September 23, 1935 (26). (See Figure 2.) In it, he addressed the situation in Europe. Calling it "rather alarming," Hansgirg said it made him think "every day" of the "basic idea of the foundation of the Roerich Museum, to preserve all [of] the real science and beauty of the world." And by way of his work at Konan, Hansgirg confessed he was "always thinking of the [Roerich] Urusvati Research Station"—located high in the Himalayan Mountains. "To retire to this place for more work is also a dream of mine," Hansgirg wrote (27).

Koiran, Sept 23rd. 1935. DE FRITZ HANSGIRG Dear Hiss grant, it is now nearly a year, that we said good by to you on the corner of fight An fifty first street, and you leard nothing But all the new impressions us. some broubles with the congre mes a tension 1... in mulcole time, that I never format the equanimity for a letter for yo 140 plula We i ved with close syche. the wes mentality of the East gives the wer to lelittle things, which seemyou noner

Figure 2. The first page of Hansgirg's letter to Frances Grant and a photo of Hansgirg feeding tame deer in Japan. MC 671: Papers of Frances R. Grant, Special Collections and University Archives, Rutgers University Libraries.

Before returning to a discussion of Roerich's ideas and philosophy, Hansgirg's letter turned briefly to Noguchi, who he said was "very trusting" in him, closing a number of contracts based on Hansgirg's Japanese patents. By 1938, the magnesium plant—two units of 1,000 ton yearly capacity each—was operating successfully. Hansgirg also erected for Noguchi a cracking plant, an electro-iron process, and a plant for the production of synthetic precious stones (28). He also suggested to Noguchi that a heavy-water production facility be built at Konan, which Hansgirg described in his letter as a "quite unique opportunity to produce this substance in large scale" (27).

Hansgirg was later hired as a chemical consultant to the Japanese-controlled South Manchurian Railway in Dairen, Manchukuo (now Dalian, China), where he

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remained in contact with his Japanese industrial projects in Korea until 1940. However, when Japan became completely pro-Axis and hostile to foreigners, he and his wife decided to depart Japan for the U.S. in the hope of helping to develop the magnesium industry there. And in December of that year, Hansgirg was approached by the American industrialist Henry Kaiser who hired him to set up the enormous Permanente magnesium plant in California using his patented carbothermic magnesium reduction process (29).

Following the Japanese attack on Pearl Harbor and

the German declaration of war on the U.S., Hansgirg, who by then was considered a German national following Anschluss, the German annexation of Austria in March 1938, was arrested by the FBI as a "dangerous enemy alien" (30). Following his arrest, Hansgirg was interned at various enemy alien camps in the U.S. High on a list of enemy aliens, he was transferred first to Sharp Park Detention Station near San Francisco; then onto the Fort Sam Houston Internment Camp in San Antonio, Texas; and finally, to a camp in Stringtown, Oklahoma (31). Eventually, he was paroled into the custody of Black Mountain



Figure 3. "SAN JOSE, CALIF — Permanente's magnesium expert is Dr. Fritz J. Hansgirg (above), 52-year-old Austrian, who helps direct the plant from the San Jose jail where, as 'enemy alien,' he has been given comfortable quarters with his wife." [World Wide Photos, San Francisco Bureau, Feb. 6, 1942; from Hansgirg's FBI file]

College in North Carolina where he taught chemistry and physics until 1947 (29).

While interned at Fort Sam Houston, Hansgirg authored a memorandum entitled "The Permanente Magnesium Plant" in which he described his role in the development of magnesium, but his heavy water invention is also mentioned. In it, he wrote (20):

In 1934, I was also granted the patents for the manufacture of heavy water and heavy hydrogen [deuterium] in connection with my hydrogen process, using several catalysts for the adjustment of equilibrias to concentrate the heavy hydrogen isotope. This process is at present only theoretically developed and no plant has been built yet. When Hansgirg died suddenly on July 23, 1949, at the age of 58, he was living in New York where he was serving as chief engineer for the American Electro Metal Corporation and the Bach Corporation, and consultant for the Standard Oil Company of New Jersey. The following year, Natasha Goldowski (Renner) presented a glowing tribute to her friend and colleague, Fritz Hansgirg, at a Conference of State Academies of Science, which included this comment (32)

In the midst of his work on the production of magnesium, he became interested in the chemistry of iso-

> topes and in his spare time devised a method for the production of heavy water.

Catalytic Exchange and Electrolysis

Since deuterium is, chemically speaking, a form of hydrogen, it would have been natural for Hansgirg and other top chemists to have taken an interest in the newly-discovered hydrogen isotope (deuterium), and would have begun by reviewing everything known about hydrogen production, reactions, catalysts, etc. (33). During the 18th and 19th centuries, hydrogen as a gas, fuel, and chemical

reactant was already known to be useful and valuable. Hydrogen can be produced by a well-known water-gas shift reaction.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

That reaction was discovered in 1780 by Italian physicist Felice Fontana (34). As more applications for hydrogen were being invented during the early 20th century (e.g., the Haber process), there was a need for more efficient methods of hydrogen production. Research on hydrogen production using a nickel catalyst and coke's interaction with steam was conducted at BASF in 1913. Another patent by I.G. Farben in 1927 elaborated on the idea of coke reacting with steam by means of a high temperature steel tube and catalyst (35).

Hansgirg was likely aware of these early patents. Nevertheless, his contribution was to apply this alreadyknown "steam reforming process for hydrogen" as a more efficient means of separating the hydrogen isotopes (that is, hydrogen from deuterium) using catalytic exchange. Though Hansgirg was the first to patent a process to enrich the deuterium content in water by catalytic exchange, he may not have been the first to experiment with the process. In 1933, the British scientific journal Nature published the results of an experiment concerning the catalytic exchange between hydrogen and water (36). Hansgirg, who began with the well-known chemical techniques for extracting, manipulating, distilling, and separating hydrogen from water (steam), tweaked some of these well-known techniques a bit to separate the heavier deuterium from the lighter hydrogen.

As the name suggests, catalytic exchange reactions require the use of a catalyst. At room temperature, the equilibrium reaction is so slow that for practical purposes it doesn't occur. Even at 200°C, a catalyst is required for the reaction to be fast enough to be practical (1). As Hansgirg explained in his May 1939 "Production of Heavy Water" U.S. patent (12):

As catalyzers for establishing the distribution equilibrium of deuterium between hydrogen and water there may be employed for example the metals of the nickel and platinum group, platinum preferably in the form of platinum-black.

These are the same catalysts, nickel and platinum, that were later used by the Germans at the Norsk Hydro heavy water facility in Norway and by Manhattan Project scientists at the heavy water plant operated by Consolidated Mining and Smelting Company of Canada, Ltd., or COMINCO, at Trail, British Columbia. Worthy of note is that both nickel and platinum were already well known as catalysts in hydrogenation reactions.

By carefully choosing the optimal temperature, pressure, catalysts, etc., Hansgirg was able to shift the reaction equilibrium, to favor the separation of deuterium at the product side of the process. Only by utilizing his expert knowledge of chemistry and equilibrium reactions, could a significant and useful amount of deuterium fractionation occur.

In all likelihood, Hansgirg was the first to detail in writing (in the form of an Austrian patent application) how catalytic exchange between hydrogen and steam could efficiently fractionate the deuterium isotope. The first was filed at the Austrian Patent Office on December 6, 1934 (37) and the second on December 23, 1935.

Incidentally, both patents carried the same title: "Verfahren zur Darstellung von schwerem Wasser [Process for the Production of Heavy Water]." These Austrian applications provide the priority dates for Hansgirg's U.S. patents related to heavy water production. This was Hansgirg's contribution to the field. Other chemists of similar caliber may have arrived at the same conclusion, or would have done so shortly thereafter, but it appears Hansgirg's patent is the earliest written record we have of that idea (33).

In January 1935-that is, after Hansgirg had filed for a patent for his heavy water process in Austria-Urey published a 61-page monograph on deuterium and heavy water titled "The Hydrogen Isotope of Atomic Weight Two" (38). Quoting Adalbert and Ladislas Farkas (39), Urey suggested that the $H_2O + DH = HDO + H_2$ exchange reaction "might easily be adapted to a countercurrent process by use of an apparatus similar to fractionation columns," for the purpose of separating deuterium from hydrogen. This is similar to the apparatus described in Hansgirg's catalytic exchange heavy water patent. But Urey's prediction came with an important caveat: "Even without the electrolytic method of separation, pure deuterium could be prepared at the present time without prohibitive effort," Urey said. "The electrolytic method, however, is so simple that as yet no chemical method gives great promise of displacing it" (38).

Hansgirg, Heavy Water, and Japan

Hansgirg had offered to erect a heavy water plant for the Japanese in northern Korea and in Manchukuo, but neither took him up on his offer. The details of negotiations between Hansgirg and the Japanese at Konan came to light after the war, when the Economic and Science Section of the OSS (the predecessor of the CIA) interviewed Saburo Tashiro, the Director of the Noguchi Institute in Japan. As Tashiro explained, Hansgirg was at Konan to erect a magnesium plant based on his patented carbothermic reduction process. At the time, Tashiro was Chief of the Research Department at the Konan plant. Tashiro said Hansgirg had encouraged him to conduct test production of heavy water by catalytic exchange and electrolysis, Hansgirg's patented heavy water process; he had even seen articles on the subject and was interested. However, "because of problems concerning equipment, etc., the plan was dropped" (40).

Others believe Hansgirg may have gone so far as to draw up plans for a heavy water plant at Konan, and that the construction of a pilot plant may have actually begun. According to an article on Japanese wartime nuclear weapons research in *Historia Scientiarum*, a peer-reviewed journal of the History of Science Society of Japan, "Although preliminary plans were drafted for the construction of a heavy water pilot plant...Nitchitsu apparently terminated the project due to problems encountered with the prototype equipment" (41). Although Hansgirg's Japanese heavy water patent (Figure 4) (42) contains no drawings, his 1938 U.S. patent contains an illustration of the apparatus. (See Figure 5.)

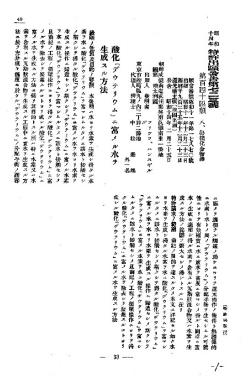


Figure 4. Hansgirg's Japanese heavy water patent.

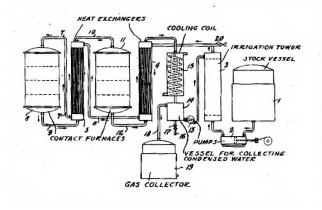


Figure 5. Hansgirg's heavy water apparatus from U.S. Patent #2,134,249.

Later, Tashiro offered another (but frankly less credible) explanation for abandoning the idea of constructing a heavy water plant at Konan: "There was talk from Hansgirg about doing it [conducting heavy water research] in Konan, but he gave up the idea thinking it was better not to do it just for fun." He also said the project was dropped due to "circumstances" (43). Perhaps Tashiro was being intentionally vague.

Did the Japanese later engage in heavy water production at Konan? An article in Tokyo Shimbun titled "Atom Bomb Experiment Undertaken by Former Japanese Armed Forces in Korean Peninsula Just Prior to the End of the War — According to Secret Investigation by GHQ [U.S. Army, General Headquarters]," discovered at a U.S. archive by the Washington, DC, Bureau of *JiJi Press*, the Japanese news agency, may shed light on this topic. According to *Tokyo Shimbun*, the secret, 300-page GHQ/SCAP report shows the U.S. ordered a thorough investigation in nuclear activities at Konan. Their investigation concluded that the Chosen Nitrogen Fertilizer Plant at Konan "produced heavy water jointly with the Japanese Navy" since "pre-war times" (44).

The demand for heavy water from Japanese university scientists began around 1940, around the time Hansgirg and his wife departed Korea for California. During the war, Japan had two, largely independent nuclear programs. One was led by Dr. Yoshio Nishina at Tokyo Imperial University who intended on using it for experiments utilizing the large cyclotron at Riken (41). Though it is known that Nishina's program never advanced very far, he was quoted in Hankyoreh 21, a weekly Korean journal, having made the following bold assertion: "If I succeeded before America, we would have been the ones who dropped the bomb" (45).

Japan's other nuclear weapons program was led by Dr. Bunsaku Arakatsu, a professor at Kyoto Imperial University. After the war, Arakatsu told post-war Atomic Bomb Mission investigators that heavy water was "obtainable in Japan from electrolytic plants in Kyushu and Korea" since Japan Nitrogenous Fertilizer Corporation (Nitchitsu) had heavy water plants at both locations (46). Nevertheless, without the addition of catalytic exchange, Japan's wartime heavy water production remained pitifully small when compared to the German and American programs.

By September 1941, the Nobeoka laboratory of Noguchi Enterprises, the parent company of Nitchitsu, was producing heavy water for commercial sale, but it could hardly be considered large-scale mass-production. The processing equipment consisted of five 100-liter and five 32-liter electrolytic cells utilizing 0.01 percent deuterium as the base material to produce 40 liters at concentration of approximately 0.4 percent heavy water per production cycle (41).

Despite plans to increase production to 100 milliliters per month of 100% pure heavy water, even after the laboratory at Nobeoka had gradually increased production, only about 10 milliliters of 90% pure heavy water per month, or somewhat more, was produced by the end of 1942. Even after further improvements were made, the Nobeoka plant could still only produce some 50 milliliters of 90-100% pure heavy water by April 1944 (41). By comparison, the plant at Trail, BC—which produced heavy water by the patented catalytic exchange and electrolysis process—had a capacity of 6 Mg/y (or 6 metric *tons* per year); and by the end of 1945, production had averaged more than 1,100 pounds of 99.8% pure heavy water per month (47).

"No Invention over [Fritz] Hansgirg"

As part of the Manhattan Project, heavy water production was referred to as the "P-9 Project." A good percentage of the heavy water produced during the war was by water distillation (48). DuPont built heavy water production facilities in three cities: Morgantown Ordnance Works, near Morgantown, West Virginia; Wabash River Ordnance Works, near Dana and Newport, Indiana; and Alabama Ordnance Works, near Childersburg and Sylacauga, Alabama. The water distillation systems, the largest ever built, were designed and constructed at record speed. For example, Morgantown's decision to build was made in December 1942. Design, construction, commission, and startup took less than two years (49).

Heavy water was also produced in Trail, British Columbia. The heavy water plant at Trail was built as an addition to the COMINCO plant to take advantage of the existence of the electrolytic units which provide hydrogen for ammonia synthesis for use in the production of fertilizer. So in that respect heavy water must be regarded as a by-product, since the major portion of the plant was in existence and operating for many years prior to the commencement of heavy water production.

Prof. Hugh S. Taylor of Princeton, a British subject, knew that COMINCO was the largest producer of electrolytic hydrogen in North America. Before the end of 1941, Taylor had visited Trail and convinced Consolidated management that it would be practical to operate heavy water equipment as a loop in the Trail ammonia plant. And thus, the deuterium would be extracted from the hydrogen supply. Experiments showed that by early 1942 it would work well, but entirely too slow. So Taylor suggested using steam at atmospheric pressure in place of water in the exchange process (50)—the same process Hansgirg had patented years earlier.

The plant at Trail comprised three parts. The first was known as the "primary plant" of four stages including the original electrolytic hydrogen plant, plus certain modifications, and the catalytic exchange towers, in which the catalytic exchange between hydrogen and water vapor was accomplished. A secondary plant, a three-stage, batch electrolysis operation, was built especially for heavy water production (51). Heavy water production at Trail began in January 1944 (52).

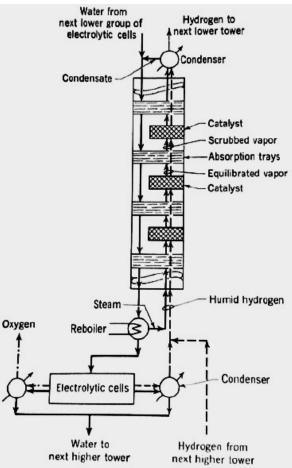


Figure 6. The heavy water plant configuration at Trail, BC (Canada).

In the catalytic exchange of hydrogen atoms between hydrogen gas and [liquid] water, the water contains between three and four times as great a concentration of deuterium as the hydrogen gas in equilibrium with it.. With hydrogen and water vapor, the effect is of the same general type but equilibrium is more rapidly established. The above is from *Atomic Energy for Military Purposes*, the official post-war report on the development of the atomic bomb by Henry De Wolf Smyth, a nuclear physicist with the Manhattan Project, written under the auspices of the U.S. Government (53). The "Smyth Report" was released to the public on August 12, 1945, just days after the atomic bombings of Hiroshima and Nagasaki.

Just as Hansgirg had suggested nearly a decade earlier in his "Production of Heavy Water" patent, the most effective catalyst for the above exchange reaction (used in the first three exchange towers) was found to be platinum-on-charcoal. A nickel-chromium catalyst was used in the fourth. Trail adapted the above to a continuous countercurrent flow arrangement (53), with the catalytic exchange units arranged in the form of a tower—with liquid water flowing from the top and steam rising from the bottom. Why hadn't Hansgirg thought of that—or had he?

Hansgirg undoubtedly understood that a tapered countercurrent cascade (vertical or otherwise) was required. The cascade would have had large "stripping" stages in the front end recovering (stripping) a small amount of deuterium from a large volume of feed material, and progressively smaller "enrichment" stages concentrating deuterium into a small heavy-water product stream. This type of arrangement is standard chemical engineering know-how (54).

The designer of such a plant would have had to consider many more factors than the cost of materials and a simple drawing, like the one that appeared in Hansgirg's patent application. The economic viability of the process, for example, would depend on equipment and operating costs. Technical viability would need to be demonstrated in successful pilot plant operation. Constructability would depend on availability of materials for plant construction, skilled workers, suitable location for the plant, inexpensive energy, etc. Finally, in any capital project, one always evaluates risk of failure, and sometimes a conservative and proven technology is preferred because it is the lowest risk option, even if there might be advantages in a new technology (54).

Like the plant at Trail, Hansgirg's patent suggested his heavy water process be repeated any number of times, up to a certain level of enrichment. Then the process was finished off with electrolysis. "In this manner," Hansgirg wrote, "it is possible to obtain not only water very rich in deuterium compounds, but also, given a sufficiently large number of repetitions of the process, even pure deuterium oxide $[D_2O]$ " (12).

Urey, who led the Manhattan Project's heavy water project, understood that to achieve a heavy water concentration of 100%, the catalytic exchange scheme be repeated or be finished by fractional distillation, or "the well-known electrolytic method" (55).

According to a 1969 status report titled *Production* of *Heavy Water* from Battelle Northwest Laboratories, once the primary plant raised the concentration of deuterium in the water to 2.37%, a secondary plant, consisting entirely of electrolytic cells, increased the purity of heavy water to 99.8% (56). Only heavy water enriched to this level, or higher, is suitable for use as a moderator in a nuclear reactor that uses natural uranium—for the purpose of generating electric power or to produce plutonium for use in a nuclear weapon. When energy is produced in a reactor that uses ordinary water, known as a light-water reactor, the uranium needs to be highly enriched.

Unaware that Hansgirg had patented the same heavy water process nearly a decade earlier, Manhattan Project scientists attempted to patent the catalytic exchange process at the U.S. Patent Office. In November 1942, Urey, who by then had assumed responsibility for formulating and coordinating all federally-funded academic and industrial work in isotope separation and heavy water production (57), along with Aristid V. Grosse, a German nuclear chemist, filed a patent for heavy water production on behalf of the Manhattan Project (55). Later, however, P. W. Shepard, Urey's patent examiner at the U.S. Patent Office, returned with bad news.

In a letter to the applicant on October 5, 1943, the patent examiner initially rejected all of Urey's patent claims. Some were rejected for technical reasons; but others, including Claim Nos. 1-6, 13, and 14, were "rejected as involving no invention over [Fritz] Hansgirg" and "Eley and Eley et al." Daniel Douglas Eley, a British chemist and Professor of Physical Chemistry at the University of Nottingham, had previously suggested nickel, tungsten, or platinum catalysts. Shepard also said, "to support the catalyst on a material which is unreactive [just as Hansgirg's heavy water patent had mentioned] appears to be the obvious thing to do" (58). In the end, the patent examiner required Urey's heavy water patent, "Process for Production of Deuterium Oxide as a Source of Deuterium," to cite one and only one patent: Hansgirg's "Production of Heavy Water" (12).

Another patent that cites Hansgirg's heavy water patent is Raymond N. Fleck's 1957 "Isotope Separation Process." In it, Fleck laid out some of the current methods of isotope separation. "The advent of atomic energy processes on a commercial scale" had created, and in the future would continue to create, large demands for relatively pure single isotopes. Many methods have been proposed and employed for isotope separation, he said, such as fractional distillation, gaseous diffusion, electromagnetic methods, mass spectrographic methods, chemical isotopic exchange reactions, selective electrolysis, etc. (59).

Hansgirg's U.S. heavy water patent was not without problems, however. According to the patent, hydrogen can be produced by a well-known water-gas shift reaction $(CO + H_2O \rightleftharpoons CO_2 + H_2)$. Although the above process converts "essentially" all of the carbon monoxide (CO) to harmless carbon dioxide (CO₂), some CO remains; and CO would poison a platinum catalyst, thereby reducing its effectiveness. Hansgirg should have known this, and likely did know this, but for some reason neglected to mention the need for a separate process to strip the residual CO from the hydrogen before proceeding to the next step in his heavy water process (60).

Alistair Miller, Researcher Emeritus at Atomic Energy of Canada Ltd. (AECL), was surprised to learn that Hansgirg's patent failed to mention a follow-up step, a process "known to those skilled in the art," needed to remove the remaining traces of carbon monoxide. Perhaps there was no need to explain how this was to be accomplished, Dr. Miller said, but the patent would have been strengthened if Hansgirg had been exhaustively explicit (60).

During the war, the U.S., and to a lesser extent Germany, exerted a very large effort to evaluate and develop the various methods of heavy water production; among these were two promising chemical exchange processes: the water-hydrogen process examined above in detail, and dual-temperature water-hydrogen sulfide exchange. The former was the basis of the first heavy water production at a reasonable cost from industrial-scale plants. The latter, known as the GS (Girdler-Sulfide or Geib-Spevack) process, though superior to the Hansgirg process in a number of ways, only became popular post-war.

Norsk Hydro and the German Heavy Water Project

The hitherto secret details of the grisly race between Germany and the Allies to find a weapon so destructive that it would insure absolute victory—a race not only between scientists but also between under-cover agents—were recounted in London tonight after it had been disclosed that the atomic bomb had been dropped on Japan (61).

> "Report by Britain" New York Times, August 6, 1945

As noted, the Japanese at Konan became aware of Hansgirg's Japanese heavy water patent when he traveled to Korea to set up a large magnesium plant there. Likewise, Manhattan Project scientists became aware of Hansgirg's U.S. heavy water patent when two of them attempted to obtain a patent for that same process. One question remains: Did the Germans, who famously produced heavy water during the war at Norsk Hydro, also become aware of Hansgirg's heavy water patents?

A few short years after Urey discovered heavy water, Norsk Hydro, a Norwegian chemical company, began construction of the world's first commercial plant designed specifically to produce heavy water, a byproduct of hydrogen electrolysis at the company's ammonia plant. In fact, for nearly a decade, all worldwide commercialscale production of heavy water was by electrolysis (62). At the time. Norsk Hydro was the only company in the world producing heavy water on an industrial scale (63).

Much of the history of the German heavy water program that follows is from a book titled *The Virus House* by David Irving, an English writer and historian. When war broke out in Europe, the only firm capable of producing heavy water was the Norsk Hydro hydrogenelectrolysis plant at Vemork, just outside of Rjukan, Norway. In a friendly letter to Prof. Werner Heisenberg, a German theoretical physicist, on January 15, 1940, Paul Harteck said he thought heavy water production was "every bit as vital as that of uranium," adding (64)

From my own experience of our War Office, the production of large quantities of heavy water will certainly take several years if we leave it to them; but I can well imagine that if I personally take this up with the right gentlemen in our heavy industry the time could be cut to a mere fraction of that.

When "it seemed unlikely that the Norwegian plant would meet all the requirements of the German [heavy water] project," Irving wrote, Harteck and his assistant, Dr. Hans Suess, were preoccupied with the development of catalytic exchange, the "new heavy-water process" that Irving said was developed several years earlier (64). In a book review of *Virus House* in the June 1968 issue of *Bulletin of the Atomic Scientists*, Suess called the catalytic exchange process "common knowledge" (65). Had Harteck and Suess learned of Hansgirg's heavy water patents at some point, and if so when? They may have seen one in the 1939 U.S. Patent Office's "Official Gazette" or perhaps in the Austrian or German equivalent.

On January 24, 1940, Harteck wrote to the War Office suggesting that the catalytic exchange between hydrogen and water, which proved to be far cheaper than electrolysis alone, be examined because, as Irving said, "Heisenberg's calculations suggested that the reactor would probably need about equal quantities of uranium and heavy water; in other words many *tons* would be needed." But if Norway refused to supply Germany with her need for heavy water, Irving said their only alternative would have been to use steam-generated electrolysis; but this would have required 100,000 tons of coal to produce just one ton of heavy water (64).

"The War Office was suitably shaken by this estimate," Irving said, "but sternly rebuked Harteck for his temerity in communicating directly with Heisenberg." The project, they said, was "covered by security regulations...the transmission of such reports direct from one institute to another is in [the] future forbidden. In each case they will be forwarded through the Army Ordinance Department" (64).

According to *Heavy Water And Nonproliferation*— *Topical Report*, by Marvin M. Miller, by May 1940, with the German occupation of Norway, "the efficacy of heavy water as a moderator—particularly in a heterogeneous arrangement with natural uranium—was well appreciated; the idea having occurred to several German scientists; Paul Harteck and Werner Heisenberg in particular, during the fall of 1939" (66).

Harteck, one of the key players in the German atomic bomb project during the war, "had gained first-hand knowledge of heavy water production via electrolysis while working under Lord Rutherford at the Cavendish Laboratory in England in 1934" (66).

From its founding in Germany in 1925 until its dissolution by the Allies after WWII, I.G. Farben was the world's largest chemical concern, or cartel (67). One of I.G. Farben's numerous plants was Leuna Ammonia Works in Merseburg, an industrial city in eastern Germany, near Leipzig. When Harteck first proposed the construction of a pilot heavy water plant at Leuna Ammonia Works, he was advised to discuss the idea with Prof. Dr. Karl-Friedrich Bonhoeffer, a German chemist and a professor of Physical Chemistry at the University of Leipzig. The German War Office agreed, so Harteck took up his idea of appending a catalytic exchange plant to an

existing hydrogeneration plant there—hydrogen being key to the catalytic exchange process. The construction of a hydrogen plant at Leuna, capable of generating six million cubic feet of hydrogen per hour, had begun over a decade earlier (68).

Around six months after the outbreak of war in Europe, initiated by the German invasion of Poland on September 1, 1939, and the declaration of war by Britain and France in retaliation, Bonhoeffer sent an inquiry to the Leuna Ammonia Works. In his letter, Bonhoeffer requested information concerning the speed at which their heavy water equipment operated. (By "speed," I presume Bonhoeffer meant "level of production" or "capacity.") The inquiry was addressed to Dr. Heinrich Bütefisch, an industrial physical chemist and head of Leuna Works. A major in the SS, Bütefisch was also one of the youngest members of I.G. Farben's managing board (69).

In their March 5, 1940 response to Bonhoeffer's letter, Leuna Works Merseburg said they recently became aware of some "interesting patents" by Dr. Fritz Hansgirg of Dairen, Manchukuo. One (Figure 7) was Hansgirg's German patent #674,965 ("Method of Producing Heavy Water") (70). The other (Figure 8) was German patent application #H148186 IVb/12i ("Process for the Production of Heavy Water") (71), submitted on July 8, 1936 (72). The letter concluded with these words (73):

This patent describes working methods for the production of heavy water, as they were also discussed when you visited us in Leuna. In this context, we would like to draw your attention to these patent specifications.

In a letter marked "Destroy after reading," Bonhoeffer reported to Harteck having discussed the idea with



Figure 7. Hansgirg's German heavy water patent (13).

I.G. Farben's ammonia plant at Merseburg who were "all in favor of the idea." Leuna Works had no objections in principle. As Bonhoeffer noted, "the whole idea stands or falls by the catalyst." Meanwhile, the German government approached Norsk Hydro directly (74).

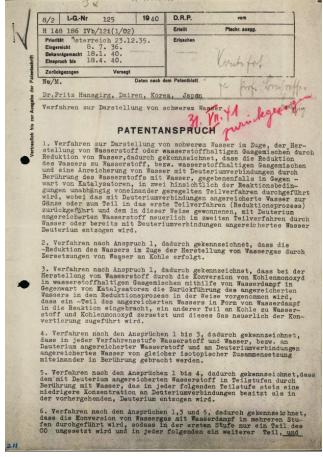


Figure 8. Hansgirg's German heavy water patent application.

In a follow-up letter to Bonhoeffer (75) dated March 12, Leuna Works Merseburg again referenced Hansgirg's two patents: "In our reply of 5 March, we referred to two patent specifications, which concern the extraction of heavy water." The letter went on to say that they had since learned—through a phone call from Bonhoeffer to Dr. Paul Herold—that Bonhoeffer was able to obtain Hansgirg's patent, but not the patent application mentioned above. "You asked on the telephone [for us] to help you get this document, since you see no way to get it into [Herold's] possession." So they enclosed a photo of the account. "...but we would like to point out that the application has been filed, and that we are obliged to treat it confidentially and therefore ask you to handle the matter accordingly" (75).

Both letters closed with the obligatory "Heil Hitler!" Meanwhile, copies of that follow-up letter were distributed to various key I.G. Farben scientists including Bütefisch, Herold, and Director Dr. Hans Adolf von Staden. Who was Dr. Staden?

During the Nuremberg Trials after the war, Curtis G. Shake, Presiding Judge in the I.G. Farben trial, asked Bütefisch who Dr. Staden was, when he spotted his name on the distribution list of another document. "Now, who is Dr. Staden?" the judge asked. In response, Bütefisch said, "Dr. von Staden was the head of planning matters for Auschwitz, in detail... He was also a plant leader at Leuna" (76). Auschwitz was the notorious Nazi concentration camp and extermination center where over 1.1 million men, women, and children were gassed to death.

Apparently, the heavy water process discussed by the Germans at Leuna, and later implemented at Norsk Hydro, was similar to the one patented in Germany by Hansgirg in April 1939. According to Rainer Karlsch, the author of *Hitlers Bombe*, "I agree the Harteck-Suess process (which [was] based more or less on Hansgirg's work) was the key element to increase the heavy water production in Norway" (77). Nevertheless, despite their success in producing heavy water during the war, Norsk Hydro never achieved full capacity due to British sabotage and a subsequent U.S. bombing raid.

The request for confidentiality over the patent application by Hansgirg still in process is somewhat ironic,



Figure 9. Fritz Hansgirg's 1938 Austrian (Österreich) heavy water patent (78).

for the invention had already been published by a patent office of the German Reich (78). By the time Hansgirg's second Austrian heavy water patent (Figure 9) was issued in November 1938, Nazi Germany had annexed Austria (on March 12, 1938) in a process known as *Anschluss*. The application filed with the Austrian patent office in December 1935 was granted by the Austrian branch of the

German Reich's patent office (Reichspatentamt, Zweigstelle Österreich). Thus the Third Reich was the issuing authority of the Austrian patent, which had a swastika at the top. The application under discussion by Herold and Bonhoeffer was a version of the same invention filed in Germany before the Anschluss and not yet granted.

Atop Hansgirg's post-Anschluss Austrian heavy water patent (#155029, issued Nov. 25, 1938) are the following words, handwritten: "Account closed for Prof. Bonhoeffer." Why was Hansgirg's patent account closed when it was? As the result of extensive research (in German) by Alfred Lang, in cooperation with

Christian Laufer of the

Austrian Patent Office,

there is no need to specu-

late.

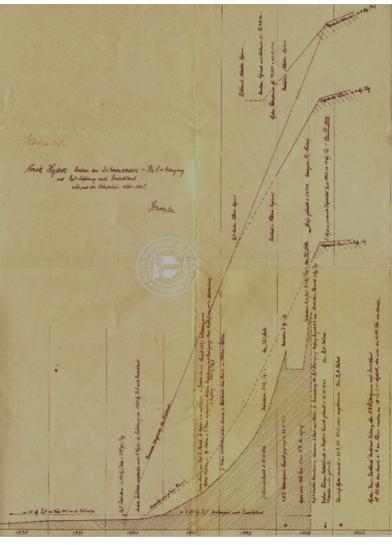


Figure 10. Paul Harteck's Norsk Hydro heavy water production chart. Institute Archives and Special Collections at Rensselaer Polytechnic Institute.

We now know that annual payment requirements start when the patent application is published in the Austrian *Patent Gazette* (*Österreichisches Patentblatt*). Since Hansgirg's patent application was made in December 1935, and based on the publication cycle of the *Gazette*, the payment liability for the first annual payment began in months at Farm Hall near Cambridge, England, as part of Operation Epsilon, the investigation of German efforts to manufacture an atomic bomb. Three years following his release, in 1948, Harteck was appointed Rector of the University of Hamburg. Then in 1951, he emigrated to the United States, later to become the Distinguished Research Professor of Physical Chemistry at RPI, where

January 1936. From that time on, annual payments were required. Evidently, payments were made by Hansgirg through 1941, which was the sixth annual fee for this patent. According to a note in the Austrian Patent Registry dated July 24, 1942, however, Hansgirg's patent "expired due to non-payment of the seventh annual fee" (79). Having been arrested by the FBI on December 17, 1941,

> following the Japanese attack on Pearl Harbor, Hansgirg was in no position to make a payment to the Austrian Patent Office. But even if Hansgirg had managed to write out a check, it would have been confiscated by the FBI.

> Figure 10 is Harteck's Norsk Hydro heavy water production chart. It is published here with permission from the Institute Archives and Special Collections at Rensselaer Polytechnic Institute (RPI) where Harteck taught between 1953 and 1982, when he retired (80). How RPI obtained Harteck's heavy water production chart is a long story, which began in 1945 shortly after the German surrender.

Following his arrest, Harteck was detained by the Allied Armed Forces for six he "provided leadership in chemical kinetics, and especially in atom and radiation chemistry." He retired from RPI in 1982 and died three years later (81).

Harteck's chart graphically represents many of the key events concerning heavy water production at Norsk Hydro. As seen on the chart, relatively small quantities of heavy water were produced by electrolysis through 1940. A handwritten note (in German) says Harteck and others paid their first visit to Norsk Hydro in 1941, where they suggested improvements (*"schlägt Verbesserungen vor"*) to increase the level of heavy water production at Norsk Hydro. That same note registered the fact that the Germans had recently increased their demand for heavy water to 5,000 kg (up from their previous order of 1,500 kg (82)).

Then around 1942, when, in an effort to increase heavy water production, the Germans began the installation of a catalytic exchange unit at Norsk Hydro, the conversion was interrupted by a commando raid (62). Upon the installation of a catalytic exchange unit, the chart shows how production levels increased substantially through early 1943; that is, until the early-morning hours of February 28 when twelve British saboteurs conducted a daring raid on the facility. The men climbed down a gorge, across a frozen river, and up the rock face on the other side, where they emerged by the railway track to the hydrogen plant. Upon entering the plant, two members of the explosive team mounted the explosive charges, and lit 30-second fuses (83).

The chart shows how the explosion resulted in a sharp, albeit temporary, reduction in the level of heavy water produced. Once the plant was repaired, however, production resumed; that is, until the night of November 16, 1943 when 140 U.S. bombers swooped in and totally demolished the Vemork power station and electrolysis plant. At that point, German heavy water production at Norsk Hydro ceased (83).

Another handwritten note at the bottom of Harteck's heavy water chart ("*ca. 185 kg D*₂O *im März 1940 an die Allierten*") makes reference to a lesser-known episode in Norsk Hydro history, how the Allies acquired the total stock of heavy water at Norsk Hydro (as of March 1940): 185 kg (about 410 pounds). The Norwegians had previously refused to sell their entire stock of heavy water to the Germans, when the Germans refused to say why they wanted it (84).

In 1940, as the commercial and military potential of heavy water sank in, French military intelligence (the

Deuxième Bureau) learned that there was considerable German interest in not only obtaining existing Norwegian stocks, but in a contract for large and regular supplies. Prior to the German invasion of Norway (April 9, 1940), *Deuxième Bureau* removed the 185 kg of heavy water in 26 canisters from then-neutral Norway.



Figure 11. One of the containers used for shipping Trail heavy water, now in the museum at Rossland, BC. Photo courtesy of Chris Waltham (52).

The 26 canisters were transported first to Oslo, and then on to Perth, Scotland. When the heavy water landed safely in Scotland, it was transported to the French Military Mission in London, and across the English Channel, where it was installed in a special air raid shelter in the Collège de France. Eventually the heavy water returned to London, where it was deposited in Wormwood Scrubs prison. It was later moved to the Cavendish Laboratory in Cambridge, where the Collège de France team were setting up to continue their experiments (52).

Back in March 1940, Lieutenant Allier of the *Deuxième Bureau* departed Paris for Oslo to negotiate with Norsk Hydro. The resulting agreement ensured that France was to acquire not only Norsk Hydro's entire stock of heavy water at the time, but also a priority claim to the plant's entire output (52).

Postscript: Postwar Heavy Water Production

By 1949, the U.S. Atomic Energy Commission required larger quantities of heavy water for construc-

tion of reactors that might prove more economical than the light-water, graphite-moderated reactors then used exclusively in the U.S. for the manufacture of plutonium. Over the years, hundreds of methods have been proposed for the production of heavy water, many of which were tried at least on a small scale, but only a few had shown any real promise. A 1953 survey carried out by a group at the Esso Research and Engineering Company (on behalf of the U.S. Atomic Energy Commission) examined 98 potential processes for the production of heavy water.85

The factors which dictate the choice of a process for use in the laboratory or a small-scale plant, where flexibility and low capital cost are important, however, are very different from the factors governing industrial scale plants, in which low energy and materials use, ease of operation, and high reliability tend to be more important.

By 1978, heavy water was only being produced on an industrial scale by a limited number of chemical processes. At a symposium on the separation of hydrogen isotopes, H. K. Rae of Chalk River Nuclear Laboratories, Atomic Energy of Canada Ltd., said, "so far plant operating experience has been obtained with [only] five processes" (86) some of which remain in use today.

According to John Augustus Ayres, the author of Production of Heavy Water, a 1969 status report by Battelle Northwest Laboratories (now Pacific Northwest National Laboratory) in Benton County, Washington, "The GS process appeared to be a very attractive candidate for producing large amounts (hundreds of tons per year) of heavy water because of low energy requirements and rapid exchange rate" (87). The GS process (the dual-temperature chemical exchange between hydrogen sulfide (H₂S) and water) had several advantages over the Hansgirg process. For one, the feed (liquid water) is cheap, universally available, and unlimited. Another advantage is the GS reaction is "ionic," and therefore proceeds rapidly without a catalyst; and the temperatures and pressures required are moderate (88). And yet, despite the advantages of the GS process over Hansgirg's, plus the fact that the GS process was one of the candidate processes considered by the Manhattan Project in 1942, the GS process was not utilized during the war. Why is that? It was thought that some difficult corrosion problem might arise when the hydrogen sulfide came into contact with the materials of construction, especially since there was a shortage of stainless steel at the time (87).

After the war the world-wide use of catalytic exchange (plus electrolysis) fell to just 6%, having been replaced by more efficient heavy water methods such as the GS process (89). By 1968, the fraction of world-wide heavy water production by water-hydrogen catalytic exchange, the process Hansgirg had patented decades earlier, had fallen to only 4.4%.85 The GS process dominated because it had the cost advantage of not requiring an expensive precious metal catalyst for the exchange reaction.

In Conclusion

Had the Japanese at Konan missed an opportunity to erect the world's first plant capable of producing heavy water on a large scale by means of catalytic exchange, or had they secretly done so after Dr. Hansgirg departed Korea? The electrolytic hydrogen plants at Trail and Norsk Hydro only began gearing up heavy water production after the German discovery of nuclear fission on December 17, 1938, and Lise Meitner's subsequent analysis. Hansgirg, however, had offered to erect a pilot heavy water plant in Korea in the mid-1930s; it is likely that this plant would have been the first.

By late 1945, the American effort had yielded 55 tons of heavy water; 23 tons by water distillation and another 32 tons by the "Trail process" (48). The German heavy water project, utilizing a 24-hour production schedule at Vemork, had only managed to produce, in round numbers, some 3 tons of heavy water (48)—at first by electrolysis and later by the combination of catalytic exchange and electrolysis.

In any event, both the American and German wartime programs made use of Hansgirg's process for producing heavy water. Furthermore, it is clear that important figures in those programs became aware of Hansgirg's patents on the subject, whether or not they conceived the same ideas independently.

Just as Dr. Fritz J. Hansgirg's obituary in the *New York Times* failed to mention his heavy water patents, and their connection to the wartime heavy water projects in Germany, Japan, and the United States, the obituary of Dr. Paul Harteck, who died at his home in Santa Barbara, California at the age of 82, also neglected to mention his role in the German heavy water project at Norsk Hydro (80).

The obituary of Harteck, the co-discoverer in 1934 of tritium and later the co-designer of the world's largest atmospheric simulation chamber, said he was "known for his research on radiation, upper-atmosphere chemistry, isotope exchange reactions including those involving nitrogen, nitrogen reactions with hydrocarbons, and the application of kinetics to nuclear chemistry" (80).

Harteck received his doctorate from the University of Berlin in 1926 under Prof. Max Bodenstein, his doctoral advisor. He later worked at the Kaiser Wilhelm Institute in Berlin with Karl Friedrich Bonhoeffer, providing experimental support for the emerging quantum theory (80). Incidentally, Bonhoeffer, who had urged I.G. Farben to implement catalytic exchange at Norsk Hydro, was also the one who became aware of Fritz Hansgirg's "interesting" heavy water patents.

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References and Notes

- 1. A. Busigin, e-mail to author, Mar. 29, 2020.
- U.S. Senate Special Committee Investigating the National Defense Program, *Additional Report: Third Annual Report*, 78th Cong., 2d sess., 1944, S. Rep. 10, pt. 16. Available online at https://catalog.hathitrust.org/ Record/010362200 (accessed Aug. 10, 2020).
- 3. "F. J. Hansgirg Dies: Chemical Expert," *New York Times*, July 25, 1949, p 15.

- "Scientific Medal Awarded To Urey," New York Times, Feb. 10, 1934, p 17.
- 5. This calculation assumes there are 20,000 drops of liquid in a liter of water.
- Vienna Standard Mean Ocean Water provided by the International Atomic Energy Agency (IAEA); B. Riffenburgh, Ed., *Encyclopedia of the Antarctic*, Routledge, New York, Vol. 1, p 554.
- The Nobel Prize, Harold C. Urey, Facts, https://www.nobelprize.org/prizes/chemistry/1934/urey/facts/ (accessed June 9, 2020).
- 8. The origin of the word deuton/deuteron is from Jaemoon. Yang, *Deuterium: Discovery and Applications in Organic Chemistry*, Elsevier, Amsterdam, 2016, p 9:

Deuteron was adopted as the name for the nucleus of deuterium by the Committee on Nomenclature, Spelling, and Pronunciations. The name "deuton" was objected by certain scientists in England, who believed it was too easily confused with the name neutron when used orally. Another candidate was diplon suggested by Lord Rutherford. At a symposium on heavy hydrogen, Dr. Ladenburg [Rudolf W. Ladenburg, a professor of physics at Princeton University] proposed during discussion the use of deuteron instead of deuton or diplon. He reported that this suggestion came from Professor [Niels] Bohr, and that he had brought it back to American via England where he secured Lord Rutherford's willingness to adopt it. Finally, Dr. Urey himself agreed that a vote be taken and this vote resulted in approval for deuteron.

- F. G. Brickwedde, "Harold Urey and the Discovery of Deuterium," *Phys. Today*, **1982**, *35*, 34-39; https://physicstoday.scitation.org/doi/10.1063/1.2915259.
- 10. A. E. Knowles, "Electrolysis of Water," US Patent 2,044,704, issued Jun. 16, 1936 (filed Mar. 29, 1935).
- F. Hansgirg, "Production of Water Enriched with Heavy Water," US Patent 2,134,249, issued Oct. 25, 1938 (filed Dec. 3, 1935). Hansgirg filed for this patent while he was a resident in Konan, Korea (now Hungnam, North Korea).
- F. Hansgirg, "Production of Heavy Water," US Patent 2,156,851, issued May. 2, 1939. Filed while residing in Konan, Korea, on Nov. 10, 1936. Priority filing in Austria on Dec. 23, 1935.
- 13. F. Hansgirg, "Verfahren zur Darstellung von schwerem Wasser," German Patent 674,965, issued Apr. 26, 1939.
- 14. F. Hansgirg, "Method of Producing Water Enriched in Deuterium Oxide," Japanese Patent 130,346, (issued Feb. 25, 1939 (filed: Dec. 23, 1936). "酸化 'デウテリウム' 二 富メル水を生成する方法" (酸化 = oxide, デウテリウム = deuterium, 富める = rich, 水 = water, 生成する = generate, 方法 = how to)

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- 15. National Archives of Japan, Tokyo, e-mail to author, June 29, 2020.
- 16. *Manhattan District History*, Book III, the P-9 [heavy water] Project, pp S18-S19. Also, See Ref. 4.
- 17. M. G. Hawes, "Preparation of Heavy Water by Catalytic Exchange," *Platinum Metals Review*, **1959**, *3*(4), 118-124 at 118.
- F. J. Hansgirg, "Thermal Reduction of Magnesium Compounds," *The Iron Age*, **1943**, *152*(21, Nov. 18), 56-63 and *152*(22, Nov. 25), 52-58 at (21) 52.
- Österreichische Magnesit AG (OEMAG) and its subsidiaries had a net value in excess of \$10 million. Reparations, Deliveries & Restitutions Department, Property Division, SCAEF (Supreme Commander, Allied Expeditionary Forces) to Col. Charles S. Reid, July 6, 1945.
- 20. F. J. Hansgirg, "Memorandum Concerning the Permanente Magnesium Plant," May 9, 1942, p 1; Enemy Alien Internment Camp at Ft. Sam Houston, Texas. This document was part of Hansgirg's FBI file (200+ pages), obtained through a Freedom of Information Act (FOIA) request from the US National Archive and Records Administration (NARA).
- 21. While in Washington, DC, Hansgirg was introduced to the Chief of the Bureau of Immigration and, with his assistance, was able to obtain an American visa for his former patent attorney; Richard Reik: Copy of Affidavit, State of California, June 24, 1942.
- 22. Hansgirg's CV is part of his FBI file obtained through FOIA (NARA); Hansgirg prepared his CV while interned at the Stringtown (Okla.) enemy alien internment camp on July 21, 1942.
- C. H. Kim, "North Korea's Vinalon City: Industrialism as Socialist Everyday Life," *Positions: Asia Critique* 2014, 22(4), 809-836 at 812-813.
- 24. Hansgirg to Frances Grant, undated; MC 671, Papers of Frances R. Grant, Special Collections and University Archives, Rutgers University Libraries.
- 25. In 1932, Manchukuo was founded following the Japanese invasion of Manchuria. Manchukuo later became a constitutional monarchy under Japanese control. Hansgirg later worked as a chemical consultant for Japanese-controlled South Manchurian Railway in Dairen.
- 26. Hansgirg to Frances Grant, Sept. 23, 1935; MC 671, Papers of Frances R. Grant, Special Collections and University Archives, Rutgers University Libraries.
- 27. "Fritz Hansgirg," Faculty's Who's Who Dossier, Black Mountain College 1933-1956 Faculty Files, Box 1, Western Regional Archives, State Archives of North Carolina.
- At his laboratory in Graz nearly a decade earlier, Hansgirg developed an electrolytic process for the production of zinc. "Verfahren zur elektrolytischen Herstellung von

Zink," Glückauf: Berg- und Hüttenmännische Monatshefte, No. 17, April 25, 1925.

- 29. B. Streifer, "1945: When Korea Faced Its Post-Colonial Future," *Transactions, Royal Asiatic Society* (Korea Branch), **2013**, *88*.
- 30. L. E. Davies, "Shelters Picked at San Francisco," *New York Times*, Dec. 18, 1941, p 25.
- Hansgirg was held at Sharp Alien Camp: Apr. 13 Oct. 24, 1942. He was INT-4AU-208, the 208th Austrian among 911. US Office of Strategic Services, *Foreign Nationalities Branch Files*, 1942-1945, Vol. 2, p 154.
- 32. N. Goldowski, "Fritz John Hansgirg," *Journal of the Elisha Mitchell Scientific Society*, **1950**, *66*(2), 105-106.
- 33. Ken Ricci, e-mail to author, Jan. 6, 2020.
- 34. Zhen Ma and Sheng Dai, Eds., *Heterogeneous Gold Catalysts and Catalysis*, Royal Society of Chemistry, 2014, p 111.
- 35. C. Murkin and J. Brightling, "Eighty Years of Steam Reforming," *Johnson Matthey Technical Review*, **2016**, *60*(4), 263-269 at 263.
- J. Horiuti and M. Polanyi, "A Catalysed Reaction of Hydrogen with Water," *Nature* (London), **1933**, *132*, 819.
- F. Hansgirg. "Verfahren zur Darstellung von schwerem Wasser," Austrian Patent 462,191, issued Nov. 15, 1936 (filed Dec. 6, 1934).
- H. C. Urey and G. K. Teal, "The Hydrogen Isotope of Atomic Weight Two," *Rev. Mod. Phys.*, **1935**, *7*, 34-94 at 49.
- A. Farkas and L. Farkas, "Experiments on Heavy Hydrogen—Part I," Proc. R. Soc. London A, 1934, 144, 467-480.
- 40. "Abstract of Attached Report Submitted by Mr. Saburo Tashiro, Director of Noguchi Kenkyujo," 29 June 1949; Masao Kubota to Director Tashiro (translation), Noguchi Research Lab, 13 July 1949, National Archives and Records Administration, College Park, MD, RG 331, Entry 224, Box 2, Folder #14: "Heavy Water."
- 41. K. Nagase-Reimer, W. E. Grunden and M. Yamazaki, "Nuclear Weapons Research in Japan During the Second World War," *Historia Scientiarum*, **2005**, *14*(3) at 15-16.
- 42. Hansgirg's Japanese heavy water patent was obtained at the Japanese Patent Office in Tokyo; Also, See Ref. 14.
- 43. T. Saburo, *"Konan kenkyujo no koto* [About the Hungnam research labs]," in K. Shoji, Ed., *Nippon Chisso shi e no shogen*, Vol. III. Tokyo, 1978, p 24.
- 44. B. Streifer, "Hungnam, North Korea: Delving into Pyongyang's Long Nuclear Past," National Security News Service: DC Bureau, June 25, 2013.
- 45. Hankyoreh 21, No. 268, July 7, 1999.
- 46. R. K. Wilcox, *Japan's Secret War*, 3rd ed., Permuted Press, 2019.

- J. A. Ayres, Production of Heavy Water Status Report, BNWL-884 (UC-80, Reactor Technology), AEC Research & Development Report, Battelle Memorial Institute, March 1969, p 124. Various pages in Ref. 16 mention 1,100 pounds per month.
- P. F. Dahl, *Heavy Water and the Wartime Race for Nuclear Energy*, Institute of Physics Publishing, Bristol, UK, 1999, p 286.
- A. Busigin, "Comparison of Water-Hydrogen Catalytic Exchange Processes Versus Water Distillation For Water Detritiation," Apr. 22, 2014. (Presented at Tritium Focus Group Meeting, April 22-24, 2014, Aiken, SC).
- R. G. Hewlett and O. E. Anderson Jr., A History of the United States Atomic Energy Commission, Vol. 1, The New World, 1939-1946, Pennsylvania State University Press, University Park, 1962, p 67.
- E. A. Barlow, *The Production of Heavy Water at Trail,* B.C., CRE-374, AECL (Atomic Energy of Canada, Ltd.), Mar. 8, 1948, pp 1, 5.
- C. Waltham, "An Early History of Heavy Water," August 1998; revised June 2002; minor corrections October 2011; https://arxiv.org/abs/physics/0206076 (accessed Aug. 20, 2020).
- H. D. Smyth, Atomic Energy for Military Purposes, Princeton University Press, Princeton, NJ, 1945 Section 9.24.
- 54. A. Busigin, e-mail to author, Apr. 4, 2020.
- H. C. Urey and A. V. Grosse, "Process for Production of Deuterium Oxide as a Source of Deuterium," US Patent 2,690,379, issued Sept. 28, 1954 (filed: Nov. 2, 1942).
- 56. Ref. 47 (Ayres), p 124.
- 57. Columbia University Department of Chemistry, Harold Clayton Urey (1893-1981),

http://www.columbia.edu/cu/chemistry/fac-bios/brus/ group/pages/urey.html (accessed Aug. 11, 2020).

- 58. The examination of Urey's heavy water patent by P. W. Shepard (Edwards, Bower, and Pool, Wall Street, New York City).
- 59. R. N. Fleck, "Isotope Separation Process," US Patent 2,780,526, issued Feb. 5, 1957.
- 60. A. Miller, e-mail to author, Apr 16, 2020.
- 61. C. Daniel, "Report by Britain," *New York Times*, Aug. 7, 1945, p 1.
- C. M. Lederer, *Isotopes*, Lawrence Berkeley National Laboratory, LBL-10124, Oct. 1980, pp 19-20.
- 63. "Norsk Hydro Increased Production and Sales Last Year," *News of Norway*, Apr. 4, 1963, p 51; *Atomic Scientists News*, **1952**, *2*, 225.

- 64. D. Irving, *Virus House*, Parforce UK Ltd., 2002 (first published 1967), pp 61-63.
- 65. H. E. Suess, "Virus House: Comments and Reminiscences," *Bulletin of the Atomic Scientists*, June 1968, 36-39. In Suess' book review, he stressed that his views were his alone and were written "independently of Heisenberg's." Werner Heisenberg was the scientific head of the German nuclear program during WWII.
- M. M. Miller, *Heavy Water and Nonproliferation—Topical Report*, MIT Energy Laboratory Report No. MIT-EL 80-009, May 1980, pp 21-22; available online at https:// studylib.net/doc/10521223/heavy-water-and-nonproliferation-topical-report-by-marvin (accessed Aug. 11, 2020).
- 67. IG Farben, German Cartel,

https://www.britannica.com/topic/IG-Farben (accessed Aug. 11, 2020).

- 68. Namely in 1926. *International Petroleum Trade*, U.S. Bureau of Mines, Dept. of the Interior, **1939**, *8*(12), 313.
- M. Walker, German National Socialism and the Quest for Nuclear Power, 1939-49, Cambridge University Press, Cambridge, UK, 1989, p 82.
- 70. The Swastika at the top of the German patent was blackened out after the war.
- 71. Verfahren zur Darstellung von schwerem Wasser.
- 72. "In diesen Tagen sind uns einige Patents über die Darstellung von schwerem Wasser bekannt geworden, und zwar das deutsche Patent 674,965 sowie die deutsche Patentanmeldung H 148,186 IVb/12i (1/02) von Dr. Fritz Hansgirg."
- 73. "In diesem Patentschriften sind Arbeitsweisen zur Darstellung von schwerem Wasser beschrieben, wie sie auch bei Ihrem Besuch bei uns in Leuna erörtert wurden. Wie möchten in diesem Zusammenhang Ihre Aufmerksamkeit auf diese Patentschriften lenken." Leuna Works to Mar. 5, 1940; Deutsches Museum von Meisterwerken der Naturwissenschaft und Technik (Munich, Germany). Translation by John English.
- 74. Ref. 64, pp 63-64
- 75. Leuna Works Merseburg to Bonhoeffer, March 12, 1940; signed by Grob and Koppe; obtained from The Deutsches Museum in Munich.
- 76. Trials of War Criminals Before the Nuremberg Military Tribunals Under Control Council Law No. 10, Nuernberg, October 1946-April 1949, Vol. VIII, p 785, https://phdn. org/archives/www.mazal.org/archive/nmt/08/NMT08-T0785.htm
- 77. R. Karlsch, e-mail to author, Dec. 28, 2013.
- F. Hansgirg. "Verfahren zur Darstellung von schwerem Wasser," Austrian Patent 155,029, issued (German Patent office, Austrian Branch) Nov. 25, 1938, (filed (Austrian Patent office) Dec. 23, 1935).

- 79. Austrian Patent Register (155001-156000); Alfred Lang and Christian Laufer.
- "Paul Harteck, Research Scientist" New York Times, Jan. 24, 1985, p B5.
- 81. Paul Harteck (1902-1985), Biographical Note, Guides to Institute Records and Manuscript Collections, RPI.
- 82. Ref. 48, p 153.
- Hydro, 1943: The Heroes of Telemark, https://www. hydro.com/en-US/about-hydro/company-history/1929---1945/1943-the-heroes-of-telemark/ (accessed Aug. 11, 2020).
- B. C. Reed, *The History and Science of the Manhat*tan Project (Undergraduate Lecture Notes in Physics), Springer, 2019, p 447.
- 85. Ref. 62, p 9.
- H. K. Rae, "Selecting Heavy Water Processes," in H. K. Rae, Ed., *Separation of Hydrogen Isotopes*, ACS Symposium Series 68, American Chemical Society, Washington, DC, 1978, pp 1-26.
- 87. Ref. 47 (Ayres), p 18.
- 88. Ref. 47 (Ayres), p 44.
- M. M. Miller, "Uranium Enrichment And Heavy Water Production," *Energy*, **1984**, *9*, 829-846 at 841.

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Bill Streifer, MBA (Beta Gamma Sigma), is the only American on the Editorial Board of Vostok (Journal of Asian Studies) published by the Russian Academy of Sciences, Moscow. He is currently writing Fritz Hansgirg's biography titled Dr. Fritz J. Hansgirg: The Father of Heavy Water Production (co-authored by Dr. Kenneth N. Ricci, PhD Physics, Stanford). Some of Streifer's previous publications include "Vindicating the USS Swordfish" (co-authored by Irek Sabitov) in Acta Asiatica Varsoviensia (2020), Institute of Mediterranean and Oriental Cultures, Polish Academy of Sciences; "Improbable Allies': The North Korean Downing of a U.S. Navy Reconnaissance Plane and U.S.-Soviet Cooperation" (co-authored by Irek Sabitov) in U.S. Navy War College Review (2020); and "Anything Could Happen: Newly Declassified CIA Documents Tell an Entirely Different North Korea 'Pueblo Incident' Story," North Korean Review (2016), McFarland & Co.

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IN REMEMBRANCE OF I. BERNARD COHEN

Dudley Herschbach, Department of Chemistry, Harvard University, dherschbach@gmail.com

I. Bernard Cohen (1914-2003) was one of the towering figures in history of science in the 20th century by any measure. His best-known scholarship was on 17thand 18th-century physics, especially on Isaac Newton and Benjamin Franklin. He held such prominent posts in the field as editor of *Isis*, president of the History of Science Society, and first chairman of the History of Science Department at Harvard. Cohen's life and work are described in detail in a lengthy article in *Isis* published a few years after his death (1).

Given the opportunity to publish recollections of such a prominent historian of science by such a prominent chemist as Dudley Herschbach, I gladly took it. What follows are Herschbach's remarks from a memorial service for Cohen at Memorial Church, Harvard University, Nov. 19, 2003 (with bibliographic references added by the editor).

-Carmen Giunta, Editor

To my regret, I came to know Bernard Cohen only during the last ten years of his life. But that opportunity proved to be a joy and privilege that I count among my most valued experiences at Harvard.

It came about when I was asked to give a talk to the American Academy of Arts and Sciences, to be delivered in January 1994. In choosing a topic, I had to consider that January was a dreary time of year, and that the President of the Academy said recent talks had been exceedingly dull. Accordingly, I proposed a topic intended to signal that even a talk by a scientist might be fun: "Ben Franklin's Scientific Amusements."

Most of what I'd learned on that topic I'd found in two of Bernard's books: *Benjamin Franklin's Science* (2) and *Franklin and Newton* (3). I had also read and admired two other books of his, *Birth of a New Physics* (4), and *Revolution in Science* (5). But I had not met Bernard, so a few weeks before my talk I called and he agreed to have lunch. At our lunch, I was delighted to learn that Bernard's first talk to the American Academy, given in 1950 soon after his election, was also on Ben Franklin. Then and later, I was enchanted by Bernard's courtly dignity and his earnest lucidity. He had a cornucopia of apt stories, artfully recounted in his lovely baritone voice. His vivid depictions of episodes and people often had the character of biblical parables.

After my talk, at another lunch, Bernard gave me a present I greatly cherish: a copy of his first book, published in 1941, in which he had edited, with a 150 page introduction, a reprint of the final edition of Ben Franklin's famous book, titled *Experiments and Observations on Electricity, Made at Philadelphia in America* (6). The original text, published in 1774, is a collection of letters sent by Franklin to a friend in England. In his introduction and editorial annotations, Bernard elucidates wonderfully the historical context and scientific significance of the experiments and interpretations developed by Franklin and traces the evolution and impact of the book, which went through ten editions, including five in English and three in French, during twenty years.

In 1995, Bernard published a book I have enjoyed giving to many friends: Science and the Founding Fathers (7). It has a subtitle in 18th-century style: Science in the Political Thought of Thomas Jefferson, Benjamin Franklin, John Adams & James Madison. In marked contrast to our day, Bernard demonstrates that for these founders in the Age of Reason, science was an integral part of intellectual life. He examines their scientific education and how they used their knowledge of science, which was "esteemed as the highest expression of human reason...as a means of transferring to the realms of political discourse some reflections of the value system of the sciences." The book offers a host of compelling stories and analyzes the scientific perspectives, metaphors, and analogies incorporated in the Declaration of Independence, the Constitution, the Federalist Papers. and other canonical political scriptures.

Other cherished memories of Bernard came from gatherings held at his home in Belmont, early each year. There I first met his wife Susan and many of their friends, and also had the chance to admire superb photographs Bernard had taken on journeys all over the world.

A special joy was another afternoon in his Widener study with him and his delightful friend, Claude-Anne Lopez. She had come up from Yale, where she had worked on the Franklin Papers project (8) for over two decades, to discuss with Bernard and me her ideas for a TV series on Franklin. Eventually this led to the fourhour PBS program produced by Middlemarch Films. The program, shown nationwide in November 2002 and several times since, received the Emmy award for the best documentary series (9). Bernard appears in several portions, drawn from a two-hour interview filmed in his study in May 2001. Middlemarch Films has donated the original master film to the Harvard Archives. Using excerpts from this interview, Professor Sara Schechner and I are preparing a twenty-minute DVD edition, to be sent as a gift to friends and colleagues of Bernard.

From Professor George Smith at Tufts University, a long-time collaborator of Bernard's, I learned of his charming autobiographical essay titled "A Harvard Education" (10). In that essay, Bernard begins by describing the two courses in history of science offered when he was an undergraduate in the mid-1930s: "One began with the Greeks and ended with Galileo; the other began with Newton and went up to fairly recent times." Ironically, the course on early science was given by L. J. Henderson, a biochemist, whereas the modern science course was given by George Sarton, a historian whose major research dealt with early science.

Bernard had come to Harvard hoping to become a "theoretical or mathematical physical chemist" (a rare breed in those days). As a sophomore, he took a course in "rational mechanics," then "still traditionally given in the mathematics department." It was taught by George Birkhoff, "America's first great mathematician...a true genius who radiated enthusiasm for mathematics from every pore." Bernard became a concentrator in mathematics, and a tutee of Birkhoff, a special honor as Birkhoff was then serving as Dean of the Faculty so only took on one or two undergraduate tutees (in addition to teaching regular courses). Birkhoff emphasized the historical and philosophical bases of rational mechanics. Bernard comments that "This must have had a strong influence on my subsequent interest in writing about Isaac Newton and my eventual career in the history of science."

After graduating in 1937 with honors in mathematics, Bernard entered Harvard Graduate School, in a new program in the History of Science and Learning, launched only the year before by President J. B. Conant At that time, Bernard notes, graduate school was "merely a way of postponing the inevitable." As the grip of the great depression remained strong, academic jobs of any kind were scarce; there were none at all in the history of science. Fortunately, Bernard was appointed Librarian of Eliot House, which provided him room and board. As a graduate student, Bernard undertook a remarkably broad range of studies. In science, this included work in astronomy with Fred Whipple, in optics with Theodore Lyman, with Edwin Kemble in electromagnetic theory, and with Otto Oldenburg in spectroscopy and quantum theory. In history, Bernard did work in the history of religions with Arthur Darby Nock, intellectual history with Crane Brinton, and American history with Samuel Eliot Morison and Perry Miller.

During the war years and until the end of 1946, Bernard was also much engaged in teaching physics, in the absence of most of the regular faculty. After nine years as a graduate student, he knew that "my academic future was in considerable jeopardy, since I had not fulfilled any formal requirement for the Ph.D. degree except residence." He finally took his general examination late in 1946, and then presented a long outline of a book he proposed for his thesis. (Much later this became his *Franklin and Newton.*) He was astonished when Crane Brinton urged Bernard to complete his degree immediately, by submitting his annotated edition of Franklin's book on electricity, published in 1941. Bernard objected that he "did not want to get out of fulfilling requirements." However, Brinton pointed out that the graduate school rules said nothing about *when* the thesis had to be written; he felt Bernard had already "fulfilled the thesis requirement fully and honorably." Brinton also offered to persuade Bernard's nominal thesis advisor, George Sarton, who told Bernard that it was his choice, if he wanted to take such an "easy way out." That was how, in 1947, Bernard became "the first American to receive a formal Ph.D. in the history of science."

In the final years of his life, when a cruel disease was robbing him of oxygen and energy, Bernard did not choose an easy way out. With the great help of Susan and others, he endured frequent blood transfusions and persevered to finish his last book, *The Triumph of Numbers* (11). After his manuscript was sent to press, Bernard decided to end the transfusions, which had become less and less effective.

Susan kindly invited me to visit him, about a week before his death. Bernard was serene while recalling favorite people and events of his life. I reminded him of a story I'd heard him tell a group of freshmen at an orientation program a few years before. It had to do with a visiting minister who came to preach at Harvard, having never before been to New England. It was in the fall, and his host took the visitor up to see the foliage in Vermont. Walking along a country road, they admired a splendid farm. Just then the farmer himself appeared, behind his horse and plow, and politely paused by the pair of preachers. The visiting minister exclaimed: "It's marvelous to see what a beautiful farm you and the Lord have made!" The farmer, after some reflection, replied: "Yes, it is a beautiful farm. But you should have seen it when the Lord was taking care of it by himself." This story had come to mind, as I said to Bernard, because he had done so well the Lord's work.

About the Author

Dudley Herschbach is Frank B. Baird, Jr. Professor of Science, Emeritus, at Harvard University.

References and Notes

- J. W. Dauben, M. L. Gleason and G. E. Smith, "Seven Decades of History of Science: I. Bernard Cohen (1914-2003), Second Editor of *Isis*," *Isis*, **2009**, *100*, 4-35.
- I. B. Cohen, *Benjamin Franklin's Science*, Harvard University Press, Cambridge, MA, 1990.
- 3. I. B. Cohen, Franklin and Newton: An Inquiry Into Speculative Newtonian Experimental Science and Franklin's Work in Electricity as an Example Thereof, American Philosophical Society, Philadelphia, 1956.
- I. B. Cohen, *Birth of a New Physics*, Doubleday, New York, 1960; revised and updated, Norton, New York, 1985.
- I. B. Cohen, *Revolution in Science*, Belknap Press of Harvard University Press, Cambridge, MA, 1985.
- B. Franklin, I. B. Cohen, Ed., Benjamin Franklin's Experiments; a New Edition of Franklin's Experiments and Observations on Electricity, Harvard University Press, Cambridge, MA, 1941. Cohen's edition showed a facsimile of the title page of the 1774 fifth edition, published in London. The first edition was B. Franklin, Experiments and Observations on Electricity Made at Philadelphia in America, E. Cave, London, 1751.
- I. B. Cohen, Science and the Founding Fathers, Norton, New York, 1995.
- To date, Yale University Press has published 43 of an anticipated 47 volumes of Franklin's papers over the period 1959 through 2018. For more information, see The Papers of Benjamin Franklin, https://franklinpapers.yale. edu (accessed Nov. 10, 2020).
- 9. Middlemarch Films, *Benjamin Franklin*, 2002; for more information see

https://middlemarch.com/film/benjamin-franklin/ (accessed Nov. 10, 2020).

- I. B. Cohen, "A Harvard Education," *Isis*, **1984**, Vol. 75, 13-21.
- 11. I. B. Cohen, *The Triumph of Numbers : How Counting Shaped Modern Life*, Norton, New York, 2005.

BOOK REVIEW

A Field on Fire: The Future of Environmental History, Mark D. Hersey and Ted Steinberg, Eds., University of Alabama Press, 2019, 316 pp, ISBN 978-0-8173-2001-0 (cloth) or 978-0-8173-9208-6 (ebook), \$49.95.

This collection of essays describes a set of visions and directions for the field of environmental history influenced by one of its formative figures, Donald Worster. Many of the contributors are former colleagues or students of Worster, Professor Emeritus of history at the University of Kansas.

Before describing the book in some detail, I feel compelled to disclose that it contains fairly little overlap with the subject matter in history of chemistry-considerably less than I expected when I requested a copy of the book to review. That mismatch says more about me than about the book, though. As a chemist interested in the history of environmental topics such as atmospheric chemistry and leaded gasoline, my exposure to environmental history was to a part of that discipline's literature that does overlap history of chemistry substantially. After reading the volume, I compare myself to one of the proverbial blind men trying to form a picture of an elephant from feeling just its trunk. The book suggested to me many possibilities for combining disciplinary lenses and categories of analysis in constructing narratives of human activities over time.

The book's 17 essays are organized under three broader sections, each alluding to a title of an essay or talk of Worster's: "Facing Limits," "World without Borders," and "Doing Environmental History." The introduction to the entire volume is also an introduction to Worster and his vision of environmental history. In that introduction, Mark Hersey notes that even as historians broadened their focus from ruling elites and political history over the course of the 20th century, they still neglected nature "as an agent and presence" in human affairs. Of course, not only does nature affect people, people affect nature and are indeed a part of nature. Worster's methodology for environmental history called for analysis on a material level that accounts for relevant ecosystems, a political and economic level that describes political and economic forces that motivate human interactions with the ecosystems under study, and an intellectual level that explores how the relevant human cultures thought about those ecosystems. Worster was influential, but toward the end of the 20th century, many environmental historians took an approach that was less materialist than his and that emphasized the cultural construction of nature more.

Two essays in the first section caught my attention as particularly relevant to history of chemistry. Kevin Armitage discusses the unintended environmental consequences of the inventions of Thomas Midgley Jr., in particular of leaded gasoline and chlorofluorocarbon refrigerants. He argues that technological "lock-in" was at least a contributing factor in the development of these modifications to the existing technologies of automobiles powered by internal combustion engines and refrigerators based on the evaporation and condensation of working fluids. This essay left me interested in the role that lock-in (the tendency to attempt to improve existing technologies rather than invent completely new ones) plays in all sorts of systems, from the siting of cities to the dimensions of vehicles. But it left me skeptical that lock-in was a significant contributor to the unexpected environmental harm of these particular inventions. To be sure, the plan of the book for relatively brief essays ensures that none could be comprehensive, their arguments no more than suggestive.

Brian Black's essay "Energizing Environmental History" points to the production and distribution of energy as a fruitful area for environmental history. He notes that studies of energy have been undertaken by economic historians and historians of science and technology. Highly visible current and recent incidents of environmental impacts from energy production, such as the 2010 BP-Macondo oil spill in the Gulf of Mexico, with its dramatic video images of spewing petroleum, will ensure the continued relevance of environmental histories of energy to contemporary readers.

Readers interested in science and technology will also find some in the third essay, "Seeing Like a God." Here Frank Zelko worries that recent ideas in earth and environmental sciences could unintentionally promote a Promethean attitude in environmental management. Ecologists have moved away from "balance of nature" as a paradigm toward non-equilibrium views of ecosystems, and earth scientists have labeled the current geological epoch the Anthropocene. Zelko wonders, might the recognition that nature is always out of balance and that humans have already profoundly affected the planet promote excessive technological optimism and hubris?

The limits explored in the first set of essays, including the three already mentioned, are limits to economic growth that nature imposes. Ted Steinberg argues in the first essay that environmental history as practiced by Worster is a kind of radical history, underpinned by moral and political commitments. His moral commitments are to nature and against a capitalism that attempts to dominate nature and refuses to respect its limits. In the next essay, Adam Rome poses the question, "Can capitalism ever be green?" His conclusion, pace Worster, is "maybe," and he is keen to see businesses try. In the section's last essay, Christof Mauch uses Malibu, California, as a touchstone for reflections on human conceptions, perceptions, and illusions regarding nature. For example, to inhabit that particular landscape requires considerable effort to defend dwellings from natural disasters.

The second section, "World without Borders," has as a common theme transcending borders, whether national or disciplinary. The essay in this section that abuts science most closely is Robert Wellman Campbell's essay, "Down in the Sky: The Promise of Aerial Environmental History." It is largely an exercise in description from an unusual perspective, namely that human beings are "creatures of the sky." However much we might think of the sky as extending above us, perhaps bordering the ground at a distant "skyline" on the horizon, the interface between the sky and the ground extends to the surface at our feet. Human beings live at the interface of the sky and the ground; although we live on the latter, we live in the former. After physically locating humans in the air, Campbell asks the reader to consider "human aeriality on the biological level"-which is actually at least partially a chemical level. We require oxygen to survive. We are made mainly from elements that come from the sky, hydrogen, oxygen, and carbon. Our bodies are largely water, and since we require fresh water, that is water from the sky rather than water from the oceans; and the carbon in our bodies came from atmospheric carbon dioxide via photosynthesis-although Campbell concedes that humans do not do the photosynthesizing. Having established humans as aerial creatures, Campbell invites historians to explore the many cultural connections of human beings to the sky, such as winged cultural symbols, aviation in warfare, and a migration of Americans over time to higher-altitude settlements.

In the section's first essay, Sterling Evans uses the abaca trade to connect the Philippines to Spanish America in an example of a transnational environmental history. Abaca is a plant cultivated in the Philippines whose fibers make excellent sails and rope. These properties made it highly valuable to maritime empires such as that of Spain in the 16th and subsequent centuries. Environmental history that transcends the nation-state was a direction Worster had predicted and encouraged for the field. The section's second essay, by Mikko Saikku, sketches a comparative study of ideas of hunting and wilderness in North America (particularly the United States) and Nordic Europe (particularly Finland). Next Shen Hou argues that studies comparing experiences of different nations can be particularly insightful if scholars select wisely the places and periods to be compared. They need not be close to each other either spatially or temporally: for example, she finds much worth comparing between ancient China and the modern United States. Marco Armiero takes crossing borders literally in his essay, focused on migrants in environmental history. The biota that Europeans brought with them to the Americas wrought havoc on those lands' previous inhabitants, as is now well understood. Less dramatic are some of the cultural practices around domestic animals and plants brought by later migrants, sometimes to the disapproval of their longer-established neighbors. Armiero also points out that environmental and occupational hazards often disproportionately affect vulnerable migrant communities. In the section's last essay, Karl Boyd Brooks points to the intersection of environment and the law, chiefly in environmental regulation, as an area ripe for exploration by environmental and legal historians.

Edmund Russell's essay is the one from the book's final section that is most related to science and its history. Indeed, its title, "Low-Hanging Fruit: Science and Environmental History," suggests that environmental historians would do well to develop familiarity with a scientific discipline much as historians value facility with another language as a scholarly asset. Ecology is the scientific field with which environmental history is most closely associated, but viewing the interactions of humans and nature from the perspectives of astronomy, chemistry, geology, meteorology, microbiology, neuroscience, physics, or statistics could provide interesting insights.

The title of the first essay of the final section, "Whole Earth without Borders," could well have placed it in the previous section. Neil Maher's emphasis, though, is not so much on the iconic photograph known as Whole Earth (Figure 1) as on using photos and other elements of visual culture in environmental history. He demonstrates rather convincingly that Whole Earth did not play a pivotal role in the launching of the environmental movement in the United States, as has sometimes been claimed. He argues (less convincingly, in my opinion, but at least plausibly within the length constraints of the essay), that displays of data plotted over a significant fraction of the earth led to the environmental movement's embrace of Whole Earth as an icon around 1990.



Figure 1. Whole Earth image taken during Apollo 17 mission, 1972.

Sara Gregg explores possibilities of using Geographical Information Systems (GIS) and other tools from the "spatial humanities" in history. Such systems can be used for analysis as well as visualization of conclusions.

The book's last two essays explore suggestions on combining environmental history with military history-beyond the obvious effects of terrain and weather on individual battles and campaigns and the ravages of war on natural and built environments. Brian Allen Drake takes the American Civil War as an example. Some recent studies have asked about the role of weather in the food shortages suffered by the Confederacy and the Union's superiority in food production during the conflict; about the role of disease in the execution of some campaigns and possible delay or prevention of others; about the effect of sectional differences in land use policies on sectionally divergent attitudes and policies around slavery in the decades before the war. Lisa Brady notes that an attempt to "understand war in its totality" will sometimes find surprising environmental effects in war and its aftermath. The trench warfare of the first World War provided opportunities for lice and disease microorganisms to reduce the fighting fitness of the humans who made the trenches in the first place. Less odious organisms, such as field poppies, also colonized areas whose soils were disrupted by the fighting. Half a world away, the Korean War has given rise to a long, narrow nature preserve in the peninsula's demilitarized zone.

Daniel Rodgers has the final say in an afterword, "The Distinctiveness of Environmental History." He identifies four aspects for emphasis, particularly in the brand of environmental history practiced and advocated by Worster. It comes to grips with ideas: those of science, myth, and various cultures about the natural world. It describes how power—in the form of social, economic, and political forces—affects the natural world. It reaches across vast scales of time and space. And it is a moral endeavor, infused by ethical seriousness.

I greatly enjoyed reading this collection of essays, and I appreciated how it broadened my horizons. The volume is in many ways like a meal of tapas—a great variety of small servings. Each essay provides many references to examples of the kinds of studies treated in the essay, giving the reader interested in a larger portion some clues on how to go about finding one. The variety of the book's essays leaves me impressed with the interdisciplinary possibilities of the field. I remain interested in the history of environmental science, but I now realize that that comprises only a small part of environmental history.

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The Back Story

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Carl Djerassi (1923-2015) The Man of Multiple Lives

Much has been written about Carl Djerassi. By me. By others. And by Carl, himself.

Carl was indefatigable. He lived many lives, each so full of achievements and adventures that to live just one of them would be sufficient for most of us. He was an industrial chemist-co-inventor of the first commercial antihistamine and the first commercial birth control pill. An academic-professor at Stanford University and author of well over 1000 scientific publications and many scientific books. A writer-poet, playwright and author of fiction. A memoirist, author of three or four or even more autobiographies, depending on how one counts. An art connoisseur at the highest level. A major philanthropist. A highly decorated individual. In a room, he was a presence, especially with his Bulgarian-Austrian accent and stock of glorious hair, a physical attribute of which he was quite proud. A ladies' man, also an attribute of which he was quite proud.

Once he graduated from poverty and refugee status, Carl was to be "linked" with the in-crowd, the royalty. He was always the center of attention, at the head table, wearing the costumes of the upper crust. Even when it came to the most unanticipated connections.

Which brings us to this edition of *The Back Story*. In 1957, to resolve a tubercular knee, Djerassi chose a surgeon who was practicing in Mexico City. Yes, that does seem like an odd decision.

As Carl wrote in his first autobiography,

In 1957 I took a 2-year leave of absence from Wayne State University to return to Mexico City as a research vice president and board member of Syntex—a company for which I had served as a consultant in the intervening 5 years. Syntex had just been sold by its Mexican owners to an American investment banking firm and was about to go public, a move that would permit a substantial growth in its research expansion. Even more important was the great physical pain in my knee from which I suffered during Detroit winters. In 1957, I was living on 24 aspirins per day and had to use crutches. I decided to go to Mexico City for a major operation: a permanent knee fusion to be performed by an internationally known Mexican surgeon, who himself had undergone such an operation. Somehow, I felt more comfortable with a surgeon who knew from personal experience what it meant to live with a fused knee joint. The operation was so successful that I have since resumed skiing, even though this involved developing a new "fusedknee" technique.

That surgeon was Dr. Juan Farill. Dr. Farill can be seen in his portrait painted by the famous Mexican artist Frida Kahlo (1907-1954) in what is also a Kahlo selfportrait. Why Kahlo and Farill?



Self-portrait with the portrait of Doctor Farill. © 2019 Banco de México Diego Rivera Frida Kahlo Museums Trust, Mexico, D.F. / Artists Rights Society (ARS), New York

In 1925, Kahlo, returning home from school, was severely injured when the wooden bus in which she was riding was in a major collision. The bus's iron handrail impaled her pelvis, among other injuries. Kahlo was in pain for the rest of her life. Dr. Farrill performed seven surgeries on Kahlo's spine in the early 1950s. In her diary, Kahlo wrote, "Dr. Farill saved me." One interpretation of this painting is as follows: Kahlo is the suffering ill person who was saved by the saint, Dr. Farill. Kahlo, in her wheelchair, uses a pallet that resembles her bloody heart.

As for Djerassi, he drew some measure of pride to have shared Dr. Farill with Frida Kahlo. And the fused left knee did not seem to hinder his life. As Carl wrote, "I have learned to cope well with a stiff knee ... I also enjoy the fringe benefits ... first-class plane travel and excellent opera and theatre seats ... [when skiing] I have even been known to show off in public."



Djerassi in his Vienna apartment, ca. 2012. Photograph courtesy Carl Djerassi.

Even in Carl's choice of a surgeon, there was a uniqueness to his story. This is a matter worthy of savoring. How does one compactly yet fully describe a person of singularity? Unanalyzable, no. Irreducible, yes.

Carl had an immediate impact on all who interacted with him. Indeed, those effects were quite idiosyncratic. And Djerassi was himself idiosyncratic. His perception of others was acute as was his perception of himself. He could be and often was brutally honest. Nonetheless, he refused to alter his own behaviors to achieve some of the very personal necessaries he so deeply desired—perhaps to be liked and welcomed, certainly to be considered and was so poignantly wounded in their absence.

On January 15, 2015, just 15 days before Carl's death, Roald Hoffmann wrote me, "He is going from us, I can feel it." Upon Carl's death, I wrote to Hoffmann, "The only way that he could be stopped was in death." Roald responded, "Yes, Jeff, he's gone. A true force of nature is what he was."

American Chemical Society Spring 2021 Meeting

The Spring 2021 national meeting of ACS will be entirely online. It will consist of 10 days of live sessions during the weekdays between April 5 and April 16, 2021. The meeting's theme will be Macromolecular Chemistry: the Second Century, the theme that had been in place for the cancelled Spring 2020 national meeting.

HIST is planning programming for the Spring 2021 meeting including a symposium on the history of polymer science, one on a decade of SpringerBriefs in History of Chemistry, and general papers. Submission of abstracts will be open December 16, 2020, through January 19, 2021. Please note that if you submitted an abstract for the cancelled HIST programs for either 2020 meeting and if you would like to present it at the spring 2021 meeting, you will have to submit the abstract anew: previous submissions will not carry over.

While the division looks forward to in-person symposia in the future, we recognize the opportunity that the virtual format presents for members for whom travel to national meetings is difficult. Presenting and/or attending could be easier under the virtual format.

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