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Models of Cyclohexane.



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The Cover... Models of Cyclohexane Conformations Designed by Sachse (Top) and Derx (Bottom) (p 198)

THE COMPOUNDING OF CINNABAR (RED MERCURY(II) SULFIDE) IN THE PERSIAN POETRY OF THE ELEVENTH CENTURY

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Abstract

A study of Persian poetry in the tenth and eleventh centuries, when it had just been revived after three centuries of neglect under Arab rule, reveals a frequent repetition of the word "cinnabar" [Persian (Farsi) shangarf], now known as HgS (mercury(II) sulfide). It is especially noteworthy that certain poems in the eleventh century described cinnabar from a synthetic perspective, including one poem (by Naser-e Khusraw) that qualitatively described the compounding of cinnabar accurately, including naming mercury and sulfur in a way nearly identical to the standard wording used today. The origin of the chemical idea reflected in the poem is investigated and attributed to an account of the preparation of cinnabar, by heating elemental mercury and elemental sulfur together, given by the Persian Muhammad al-Razi, also known in Europe as Rhazes.

Dedication

Dedicated to the memory of my father, Seyed Masoud Mousavi, who introduced me to *Shahnameh* ("Book of Kings"), the Iranian national epic, when I was a young child.

In the autumn of 633, about one year after the death of the Prophet Muhammad and at the conclusion of the wars during which the Muslim Arabs conquered Arabia, they marched northward and began operations in Syria. This was the beginning of an approximately

twenty-year period during which not only the Byzantine lands of Syria and Egypt, as well as North Africa, but also the Sasanid Persian empire fell to Arab hands (1). It was in June 637 when the Arab commander Sa'd ibnabi-Waqqas entered the Persian capital, Ctesiphon, and the death of the Sasanid Yazdagird III in 651 was the end of the last ruler of an empire that had flourished, with only one interruption (caused by Alexander the Great), for approximately twelve centuries (1).

In the following three centuries of Arab rule, Arabic became not only the official language but also the speech of the cultured society of Persia (1). A natural consequence of the Persian (Farsi) (2) language being neither an official language nor a speech of the cultured society of Persia was the decline of Persian literature; however, in the words of Philip Hitti (1), "the old spirit of the subject nation was to rise again and restore its neglected tongue." The first highly noteworthy poet in Muslim Persia who composed poems in Persian was Rudaki, who lived in the second half of the ninth century and first half of the tenth century; optimism, charm, and later melancholy are words that have been applied to his poetry (3). Still, poetry in Muslim Persia was not to rise fully until the second half of the tenth century, when the Persian poet Ferdowsi composed the Shahnameh ("Book of Kings"), the epic of the kings of pre-Islamic Persia (4).

In the stories of the Shahnameh, Ferdowsi repeatedly mentions a certain ore that was widely used as the red pigment vermilion in the ancient world: cinnabar [Persian *shangarf*], which we know as HgS (mercury(II) sulfide) (5). In general, Ferdowsi does that in metaphorical references to the blood shed in battles by the warriors in his stories. An example follows ("cinnabar water" metaphorically meaning "blood") (6):

پر از ناله کوس تند مهر و میغ پر از آب شنگرف شد جان تیغ

The Sun and the clouds became full of drum sounds; The sword bodies became full of cinnabar water.

The presence of the word "cinnabar" in Persian poetry becomes especially attractive to historians of chemistry when the Persian poems of the eleventh century are searched for it. Interestingly enough, a relatively unknown Persian poet of the eleventh century, named Azraqi Heravi, at whose father's house Ferdowsi had lived for six months (7), gives the following direct reference to how cinnabar and elemental mercury (Hg), also called quicksilver, are related to each other (8):

شگفت نیست گر از برف لاله ساخت زمین که هست لاله جو شنگرف و برف جون سیماب

No wonder if the earth makes tulips from snow, For tulips are like cinnabar, and snow is like quicksilver.

The Persian word for quicksilver in this poem is *simab*, which literally means "silvery water" (somehow similar to the Latin word for mercury, *hydrargyrum*, which literally means "liquid silver" (5)).

The main use of quicksilver in the eleventh century, as well as many centuries before and after that, was the extraction of gold and, especially, silver by amalgamation. The process of extracting quicksilver from cinnabar (the only important ore of mercury) has been basically the same since ancient times (9): roasting cinnabar in a current of air (Equation 1) and condensing the produced vapor (5).

(1)
$$HgS + O_2 \rightarrow Hg + SO_2$$

The poet, however, does not say that quicksilver can be made from cinnabar. He rather says that cinnabar can be made from quicksilver. Why would he think so? A reasonable answer would be that his knowledge that quicksilver was extracted from cinnabar led him to believe that quicksilver could be used to make cinnabar. Still, further poetic evidence from the same century shows that this answer might be too simplistic to be the whole truth or even true.

One of the most noteworthy writers in Persian literature, who is nearly as famous as Ferdowsi and certainly not less known than Rudaki is Naser-e Khusraw, not only another poet, but also a theologian and religious propagandist of the eleventh century (10). In the writings of Naser-e Khusraw, the following poetic question, apparently referring to God (arguing for the existence of God by trying to show that the universe is a work of a powerful intelligent designer), would be intriguing to historians of chemistry (8):

که بود آنکه او ساخت شنگرف رومی ز گوگرد سرخ و ز سیماب لرزان

Who was the one who made Byzantine cinnabar, From red sulfur and from shaking quicksilver?

Burke et al. (11) note the existence of the numerous mercury mines, which contain cinnabar, in present-day western Turkey and show how present-day Turkey is made of what used to be the Byzantine mainland. Therefore, the term "Byzantine cinnabar" is explained. Also, when elemental sulfur at room temperature (α -S₈, which is yellow (5)) melts, the molten sulfur is a yellow to *red* liquid (12). Further, Greenwood and Earnshaw (5) acknowledge that cinnabar (red HgS) "can be prepared from the elements." The reaction may be shown by Equation 2: (2) Hg + S \rightarrow HgS

Still, the main question is how Naser-e Khusraw, who lived about one thousand years ago, was able to qualitatively describe the compounding of cinnabar accurately, including naming mercury and sulfur in a way nearly identical to the standard wording used today. If there are reasons to believe that the reaction shown by Equation 2 had ever been carried out sometime before Naser-e Khusraw indirectly stated (in his poem) that cinnabar is a mercury-sulfur combination and that he was aware of that synthesis, then it is entirely predictable that he would think as his poem says. Are there such reasons?

In the second half of the ninth century and first half of the tenth century, around when Rudaki was reviving poetry in Persian in Muslim Persia, another Persian was making his name, in the words of Philip Hitti, "the greatest in the field of medieval chemical science:" Muhammad al-Razi, known in Europe as Rhazes (1). A thirteenth-century Latin translation of a part of Rhazes's work entitled *Razis de aluminibus et salibus* contains "a fairly clear account" of the preparation of cinnabar, by heating the two elements together (9). Parts of the account in English are addressed by Farrar and Williams as follows (9):

Another coagulation of mercury with the vapour of sulphur. There is another method, and it is the coagulation of [mercury] with the odour [vapour] of sulphur. ... Then you will find a red salt *uzifur* [Arabic *zanjufur* = cinnabar].

Naser-e Khusraw's intellectual dimensions are several. In fact, as capable as he was as a poet, he may also be viewed as a learned ideological activist. He was not only a convert by joining the Isma'ili sect, headed by the Fatimid dynasty, but also a missionary sent by the Fatimids to propagate their beliefs throughout the Islamic world. Further, among his many writings is a treatise entitled Jami'al-hikmatayn ("Union of the Two Wisdoms"), an attempt to harmonize Isma'ili theology and Greek philosophy (10). A person of such a high intellectual caliber in the eleventh century most probably encountered Arabic alchemical ideas, including alchemical accounts given by Rhazes. Philosophy was the central science at that time, and intellectual pursuits were not as specialized or compartmentalized as they are today. In fact, additional evidence for Naser-e Khusraw's awareness of the details of Rhazes's alchemical writings is that Jami' al-hikmatayn (13) includes Naser-e Khusraw's critical review of Rhazes's philosophical ideas, with Rhazes named in the purely Persian form "Muhammade Zakariva Razi" several times. Naser-e Khusraw even mentions in Jami'al-hikmatayn (13) that in order to refute a certain philosophical belief of Rhazes, he has spoken against him in a book entitled Bustan al-'uqul ("Garden of the Reasons").

If Naser-e Khusraw's complete qualitative description of the compounding of cinnabar is due to his familiarity with Arabic alchemical writings, then it is possible that Azraqi Heravi's poem saying that cinnabar is from quicksilver is also due to his exposure to Arabic alchemical ideas. This conclusion is all the more plausible because Azraqi Heravi's father was a bookseller (7) and, according to the retired teacher of Persian literature Gholamreza Kashani (14), who started teaching in 1963, Persian booksellers, even until about the end of the twentieth century, often followed the tradition of reading the books that they sold. This means that Azraqi Heravi might have been exposed to Arabic alchemical ideas through his father. To what extent has poetry in Muslim Persia during its history been influenced by Arabic alchemy? The answer requires comprehensive research. However, considering that both Naser-e Khusraw and Azraqi Heravi lived in the eleventh century, a focused study on the other Persian poets of the eleventh century would be a reasonable first step in the future.

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HIST to Celebrate 100th Birthday

The American Chemical Society (ACS) Division of the History of Chemistry (HIST) will celebrate its hundredth birthday as an ACS Division in 2022. Today, HIST has about 1,000 members from every sector of the ACS, mounts symposia regularly at ACS National Meetings and at many regional meetings, publishes two Newsletters per year, and since 1988 has published this journal, the *Bulletin for the History of Chemistry*. HIST's publishing record also includes 37 history-related volumes published over the course of the past 60 years that include topics in archaeological chemistry, biography, anniversaries of important chemical events, and history of chemical sub-disciplines.

Two major projects to celebrate its Centennial Year are currently in development:

1) The Centennial History of the Division of the History of Chemistry: A thorough treatment of what happened before, during the foundation, during its evolution and up to the present. The project will be open access and published online. Gary Patterson, Historian of HIST, is organizing the project. Further information, including a projected table of contents, can be found on the HIST website at acshist.scs.illinois.edu/centennial/index.php Gary welcomes contributions: please send him written material, photographs, ephemera, etc. at gp9a@andrew. cmu.edu. You too can author a full or partial chapter!

2) The *Bulletin for the History of Chemistry* is preparing a special issue in honor of the centennial. Guest editor Jeffrey I. Seeman and Editor in Chief Carmen Giunta have obtained essays from several recipients of HIST's major awards and current leaders in the history of chemistry to write on the theme "Novel Insights in the History of Chemistry: Looking Back Yet Mostly Looking Forward." The issue will be open access to all online; HIST members will receive hard copies.

THE HISTORY OF THE CHEMICALS FROM SEAWEED INDUSTRY IN IRELAND

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Introduction

The collection and burning of seaweed for turning into kelp, used first as a source of alkali for bleaching and other industries and then as a source of iodine, was a major industry on the West and Northern Coast of Ireland in the 18th. and 19th. centuries and up until the mid-20th century. Kelp was the name given to the burnt ash of seaweed, rather than of the giant seaweeds as today. The Scottish Highlands and Islands were also heavily involved in kelp production, and it seems that the industry was imported from Ireland. Warren (1980) in his history of the alkali industry states "the industry seems to have begun in Ireland, but soon became important in Scotland" (1). Robert Jameson, writing in 1800, confirms this (2):

It will not then surprise us, when we learn, that its first introduction was about the year 1730, into the island of Uist, by a Highland gentleman, of the name of McLeod, who brought the art from Ireland, where it had been carried on many years before.

The Channel Islands, the Scillies, France (particularly Brittany), Spain and Norway have also had long-established industries based on seaweed gathering and kelp production. This article will focus mainly on Ireland.

The word *kelp* (or *kilp*) referring to seaweed ash derives from an Old English word *culp(e)*, in Irish and Scots Gaelic *ceilp*, and probably meant ashes, and is referred to in French as *varec(h)* and in the Channel Islands as *vraic*. These came from Old French *wrach*,

which became in English *wreck* or *wrack*, an alternative name for seaweed. Seaweed is called *ware* in Scotland, which comes from an Old English word, probably from the Dutch for seaweed. Seaweed is sometimes referred to as ore. Kelp is now used to refer to a large type of seaweed, known as giant kelp. In this article it will be used in its 19th-century meaning of burnt seaweed slag.

The history of the utilization of seaweed in Ireland is an interesting and unfinished story, going back three centuries. It has been celebrated by various writers including J. M. Synge, Tomás O'Flaherty, Pat Mullen, Seamus Mac an Iomaire and Tim Robinson amongst others, and by artists such as Aloysius O'Kelly, Sean Keating, Samuel Lover, Jack Yeats and others. However, it is today largely a forgotten industry, whose fortunes have waxed and waned over the years, although seaweed is still collected in Connemara and Donegal for the production of seaweed meal. This is used mostly for export to produce alginates in Scotland, though there is a growing use in small indigenous industries.

In this introduction I will give an overview of the industry before looking in more detail at each of its three temporal phases, each of around 140+ years:

1) kelp as a source of alkali—from ~1700 to ~1840;

2) kelp as a source of iodine-from 1811 to ~1950;

3) seaweed as a source of alginates—from ~ 1880 to the present.

The dates are approximate and production of alkali and iodine from kelp declined slowly rather than coming to an abrupt stop when alternative sources of these chemicals were found, e.g. iodine in Chile and potash in Germany.

Kelp burning goes back at least three centuries in Ireland and survived until just after World War II, so that there are still living memories of what was once a familiar sight in the summer along Ireland's west coast: rolling white clouds of smoke by day and the twinkle of the kelp fires at night.

At the end of summer and the beginning of Autumn the coast of Connemara is alight. There are hundreds of kilns to be seen. Aren't they a lovely sight, their smoke rising slowly skywards in the quiet of the evening ... The smell from the same smoke is healthy fragrance. (3)

Unlike the parallel Scottish industry, very little has been written about the Irish kelp industry, the exception being the chapters in Robinson's book Stones of Aran: Pilgrimage (4) and chapters in a recently republished book The Shores of Connemara (5), written in the mid-1920s by a native of Connemara. A new archaeological survey of Strangford Lough (6) has a chapter on the kelp industry, as many of the remains around the Lough are due to kelp burning. A survey of the early Irish chemical industry by Childs (1998) mentioned the iodine from kelp industry (7). The best older sources for the use of kelp as a source of chemicals are the series of articles by Booth (1977-1979) (8), the book on Seaweeds and their Uses by Chapman (1970) (9), the chapter on kelp in Scotland in Archibald and Nan Clow's book on The Chemical Revolution (1952) (10) and their earlier article on kelp (11), and articles written in the 19th century such as those by Glassford (12) and Stanford (13), among others.

In one sense kelp production was a cottage industry, as it was mostly done by whole families near their homes, along some of the most desolate shores in the country. The cash income obtained by selling kelp was a significant part of their annual income, anything from 25 -50% according to the sample family incomes produced by the Baseline Studies of the Congested Districts Board (14). The situation in Scotland was very similar to that in Ireland, and here the industry was concentrated in the islands.

Kelp produced from seaweed is also part of the history of the chemical industry, as kelp was an important raw material that was traded internationally. Kelp provided an early, indigenous source of alkali, for soap, glass, textiles, alum and paper, competing mainly with wood and plant ashes, which were often imported-wood ash (potashes) from North America and barilla (plant ashes) from Spain. Later kelp was the first source of iodine, together with potash salts, and finally it is still the only source of alginates and seaweed-derived organic chemicals. As well as these chemical uses of seaweed, it has also been used since time immemorial in coastal areas as a green manure (as it is rich in trace elements including potassium and iodine), and certain species have been and still are used as animal and human food. You can still buy edible seaweeds on the streets of Limerick and Galway today, and this year I saw a farmer collecting seaweed on a beach in Mayo. Seaweed baths are back in fashion and the green, natural image of seaweed as a sustainable resource has brought it back into fashion as a health supplement, as a liquid fertilizer, in cosmetics, etc.

Kelp-making was not a small industry, although it was located mainly in isolated coastal regions. These regions were in fact over-populated relative to their resources and were known as the Congested Districts. A recent book has republished some of the reports of the Congested Districts Board, many of which refer to kelp-making. The reports were written between 1892 and 1898 (15) and give a picture of an industry in decline. At its height at the end of the 18th and beginning of the 19th centuries, seaweed-gathering and kelp production employed tens of thousands of people in Ireland, and possibly up to 100,000 people in the Highlands and Islands of Scotland. In fact, almost every able-bodied person, young and old, in the coastal areas was involved in collecting, drying and burning seaweed to kelp, often at the expense of agriculture. Figure 1 shows the location of the jodine works in Ireland. In the Aran Islands off the coast of Galway and on the coast of Donegal, this lasted until after World War II, although it had died out in most other places before then. Major quantities were traded and transported, seashore leases (kelp shores) were actively traded, and the industry brought a measure of wealth and cash income to areas where subsistence was the norm. Some landowners in Scotland made a fortune at the end of the 18th. century and into the 19th century from kelp, although at the expense of their tenants.

The price of kelp went up and down with demand, especially with the price of iodine in Phase 2, but only reached a maximum of £9 per ton. In the 1860-70s between 450 and 750 tons kelp were exported per year from the Aran Islands, from around 6,000 tons of wet weed.

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Figure 1. Map showing the locations of iodine works in Ireland—in Donegal, Galway and Clare.

Production revived in the 1890-1900s, when kelp made £4/ton, and finally ceased in 1948 (16). At the height of the industry in the late 1800s there were three kelp factories on Aran: *Teachan Smail*, The House of the Ash; *Port Chonnla*; and *An Teach Mor* at *Port Chorruch* (the largest one). The industry survived on the Aran Islands longer than in most places probably because it was the only source of cash income. For some of that period kelp was imported into Galway for processing into iodine, from ~1850 to 1877, revived briefly again around 1930 (see below).

Several contemporary accounts are available from the early 20th century, which describe the collection of seaweed and the burning of kelp on the Aran Islands and in Connemara. The process hadn't changed for at least 100 years by then. John Millington Synge's long account was published first in *The Manchester Guardian* (1905) (17) (later in his *Collected Works*) and a shorter piece in his book *The Aran Islands* (1907) (18). An extract from this contemporary account is given below:

The people had taken advantage of this dry moment to begin the burning of the kelp, and all the islands are lying in a volume of grey smoke. There will not be a very large quantity this year, as the people are discouraged by the uncertainty of the market, and do not care to undertake the task of manufacture without a certainty of profit.

The work needed to form a ton of kelp is considerable. The seaweed is collected from the rocks after the storms of autumn and winter, dried on fine days, and then made up into a rick, where it is left till the beginning of June.

It is then burnt in low kilns on the shore, an affair that takes from twelve to twenty-four hours of continuous hard work, though I understand that the people here do not manage it well and spoil a portion of what they produce by burning it more than is required.

The kiln holds about two tons of molten kelp, and when full it is loosely covered with stones, and left to cool. In a few days the substance is as hard as the limestone, and has to be broken with crowbars before it can be placed in curraghs for transport to Kilronan, where it is tested to determine the amount of iodine it contains, and paid for accordingly. In former years good kelp would bring seven pounds a ton, now four pounds are not always reached.

In Aran even manufacture is of interest. The low flame-edged kiln, sending out dense clouds of creamy smoke, with a band of red and grey clothed workers moving in the haze, and usually some petticoated boys and women who come down with drink, forms a scene with as much variety and colour as any picture from the East.

The men feel in a certain sense the distinction of their island, and show me their work with pride. One of them said to me yesterday, "I'm thinking you never saw the like of this work before this day?"

"That is true," I answered, "I never did."

"Bedad, then," he said, "Isn't it a great wonder that you've seen France, and Germany, and the Holy Father, and never seen a man making kelp till you come to Inishmaan."

Although written 200 years or so after the start of the industry, this account agrees with other descriptions of the process, in both the soda and the iodine ages, for example that in Muspratt (1860) (19), or accounts written in the early 1800s in Scotland. Other contemporary 20th-century accounts exist by Pat Mullen (1930) (20), Thomas O'Flaherty (21) and Seamus Mac an Iomaire (3). There are also a number of contemporary photographs, drawings and paintings showing the collection of seaweed and the burning of kelp, in Ireland and Scotland, so we can see the kelpers in action in both reality and in artistic imagining (e.g., Figure 2).



Figure 2: Burning seaweed on the Aran Islands 1922, Photo: A. W. Cutler. Image ID: BJT02T The Print Collector / Alamy Stock Photo.

Phase 1: Alkali from Seaweed (~1700-1820)

Alkalis were traditionally made from imported plant ashes (e.g., barilla, largely obtained from Spain) and wood ashes (potash, mainly from North America and the Baltic states), as well as from mineral deposits (e.g., natron). The origin of the use of seaweed as a source of alkali is unknown, but it goes back at least to the 17th century. Selby refers to kelp-burning at Holy Island as early as the 13th century (22). Singer notes the use of kelp as well as urine in making alum in England around 1620 (23). Warren mentions that kelp was used in glassmaking in Prestonpans in 1662 (24), and the earliest mention of kelp production in Scotland, according to Clow & Clow is in 1694 (25). It would appear to have been well-established in the 17th. century in Ireland as a source of alkali and probably goes back earlier than that. The technology was imported into Scotland from Ireland.

Kelp, the ash obtained by burning dry seaweed, is a mixture of salts and Walker (1799) (26) says "Kelp is a lixivial salt and is always mixed with other salts, sea salt, Glauber's salt, etc." Although the percentage of alkali was low (about 5-10%) the mixture of salts was not always a disadvantage. The salt was extracted as a by-product in soap making and used for salting out. Glassmakers skimmed off the salt that rose to the top of the melt and sold it off. The alkali content was the main factor for soap making but in glass manufacture the other salts helped the process. The alum makers used kelp for the potassium it contained (about 3% potassium chloride) and kelp was being used in alum making at Whitby as late as 1845. Estimating the quality of kelp was largely done empirically, for example, as Angus Beaton described it in 1799 (27):

It is estimated to be of good quality when on breaking a piece, it is found to be hard, solid and resembling good indigo, that is, when it has some reddish and light blue shades running through it. When it has none of its peculiar salt taste it is unfit for making ley [28], though it may be of use to glass-makers.

Not a very reliable method of quality control! The first person to assess the alkali content of kelp chemically was the Irish chemist Richard Kirwan (1789) (29), again illustrating the importance of the industry in Ireland. At that time kelp was mainly used as an alkali in the linen industry. Joseph Black in Edinburgh devised a better method of analysis, which showed that there was no connection between the price paid and the chemical content: samples had the same selling price when one had over eight times the alkali content of the other. Chemical analysis also enabled the alkali content of kelp and barilla to be compared, showing the superiority of barilla (30). This problem of payment in relation to chemical content was a permanent problem of the industry until well into the iodine phase, and payment was largely by guesswork and prejudice and sometimes showmanship. Although accurate analysis was possible it was still being done by "rule of thumb" in the early 20th century.

Kelp production started in the Orkneys around 1720 and was sold to bottle-makers in Newcastle. In 1732 Richard Holden introduced bleaching with kelp into Scotland and the Board of Trustees for Manufactures, Fisheries and Improvements in Scotland helped him to set up a bleachfield at Pitkerro, near Dundee. Around 1730 kelp-burning began in the Hebrides and it was said to have been introduced from Ireland. Kelp-burning was well established in both Ireland and Scotland by the middle of the 18th century.

The earliest account of kelp burning may be that of Daniel Colwall, in his 1678 description of making alum (31):

Kelp is made of Sea-weed. Being dryed, it will burn and run like Pitch. This is beaten into ashes, steeped in Water and the Lees drawn off.

There was regular trade in kelp in and out of Irish ports in the 18th and 19th centuries, as described by L'Amie (32). From 1764 to 1800 53,074 tons of kelp were exported through Irish ports (Figure 3), an average of 1,434 tons per year. This does not include kelp that was used within Ireland, and total kelp production would have much higher than the recorded exports. Producing 1 ton kelp required the collection from 20 tons upwards of wet seaweed. The exports of kelp over these 37 years involved the collection of over a million tons of seaweed. The maximum export in 1797 amounted to 3,561 tons, equivalent to at least 71,220 tons of wet seaweed.



Figure 3. Exports of Kelp from Ireland (1764-1800), based on data in Ref. 32.

Figure 3 above shows only exports from Ireland at the end of the 18th century and does not include the large amounts consumed locally by the linen, soap and glass industries. Production and prices of kelp peaked in the early 1800s due to the shortage of imported barilla during the Napoleonic Wars, after an earlier peak during the American Revolution, which cut off supplies of potash. This period, from 1790 to 1815, was to be both the high point and the golden age of kelp burning in Ireland and Scotland. It also seemed it was to be the end-game of the Scottish and Irish kelp industries as prices fell from a high of £20 a ton in 1810 to £4 in 1820. The resumption of barilla supplies and repeal of taxes after the defeat of Napoleon and the introduction of synthetic soda processes from 1823 onwards, sounded the death-knell of the kelp industry as a source of alkali, although it struggled on into the middle of the century.

A viable process to produce synthetic soda made from salt had been patented by Nicholas LeBlanc in France in 1791, and small-scale production of soda was already underway in Scotland and England from the last decade of the 18th century (33). James Muspratt (1793-1885), an Irishman born in Dublin, who had started as a chemical manufacturer in Dublin, moved to England and started making synthetic soda on a large scale in Liverpool in 1823 (34). This date is usually taken as the foundation of the alkali industry in the United Kingdom, which was synonymous with the chemical industry until 1856. Although Muspratt initially had to give away his product to the soap boilers, eventually his superior product ousted barilla and kelp as the source of alkali. The synthetic product was purer, more concentrated, cheaper and more reliable in supply than the impure, dilute and seasonal soda from kelp and ashes. Fyfe (1820) writes of (35)

a time when kelp manufacture is threatened with a total overthrow from the introduction of alkali matter made by the decomposition of sea salt.

There is much more information on the Scottish kelp industry than the Irish industry (10, 36) but in many respects they developed in the same way. However, it would seem that the Scottish kelp industry collapsed more completely than that in Ireland from 1820 and by 1860, when Stanford reported kelp production statistics for Scotland and Ireland (then used mainly for iodine production): annual production in the United Kingdom

was around 10,000 tons with 60% being made in Ireland (37). Note that this nearly doubles the maximum amount exported in the 18th Century (shown in Figure 1), so the industry was far from dead. However, Scotland remained the major center for the processing of kelp, located mainly in Glasgow and surroundings, and eventually the Scottish industry absorbed the Irish kelp-processing industry and took most of its kelp exports, as it still does.

In County Down, Harris reports that 300 people were involved in the industry in 1744, giving the proprietors profits of over \pounds 1,000 per annum (38).

This Peninsula produces large Quantities of Barley, and a kind of Oats, called the Light-Foot-Oats, as well from the Help of Marle abounding in the marshy grounds, as from Ore-Weed, which they have in great plenty, both from the Islands in the Lake, and the Eastern Shore. But this Vegetable is too precious to be used much as Manure; for they turn it to a better Account by burning it into Kelp, which they do in great Quantities, that they not only supply the linen manufacturers in this and neighbouring counties, but export it in abundance for the use of glass-houses in Dublin and Bristol, as appears in the custom-house books of Portaferry.

In his *History of Galway* Hardiman (1820) (39) reported export figures for Galway as: in 1808, 4,000 tons of kelp at an average cost of £16/ton; in 1820, 2,500 tons at £4/ton. These figures show both the collapse in the price of kelp in the early 1800s, and also the importance of the coast around Galway (which includes the Aran Islands) to the Irish kelp industry. The export figure for Galway in 1808 is greater than the maximum annual exports for the whole of Ireland from 1764 to 1800. On the Aran Islands alone there was an annual production of kelp of 120-200 tons/yr in the 1820s.

In the first phase of the seaweed industry kelp was used by many other industries as a cheap, indigenous source of alkali: for making glass, soap, paper, alum and in bleaching textiles, e.g. (40)

Kelp is used by the Irish bleachers, and is made along the coasts of Clare, Galway, Mayo, Sligo and Donegal.

In fact, some end-users continued to prefer kelp into the 1830s and after, long after synthetic alkali had swept the market, as this quotation from 1835 Ordnance Survey Reports shows (41):

Kelp (an impure kind) mixed with much sand and earthy matter was formerly obtained in great quantities from different species of Fucus but the price of the article has declined so much of late as scarcely to defray the cost of preparing it and bringing it to market. Soap boilers in the neighbourhood still use it in preference to barilla. Barilla is not manufactured, as the plant by the burning of which it is obtained (the Salsola kali) grows very sparingly along the coast.

As well as being exported, kelp was also imported into Irish ports from Scotland, the Scillies and the Channel Islands as a source of alkali and there was a vigorous trade in this commodity. L'Amie (42) gives some of the advertisements in the Belfast papers for renting kelp shores and for selling kelp, and Table 1 shows some typical 18th century advertisements. Such advertisements continued to appear well into the 19th century.

Table 1. Some 18th century adverts for kelp (42)

Friday, 5th. August 1763 Belfast Newsletter

Cargo of excellent new kelp made last May on the Western coast near Sligo, remarkable for good strong Wrack is arrived to be sold on the Kay out of the ship by James Hamilton at the corner of Linenhall Street.

Tuesday 12th. July, 1768 Belfast Newsletter

40 tun of kelp, pure and well made now lying at Gransha shore, in the Barony of Ardes and County of Down, to be disposed of. Apply the Reverend Nicholas Hamilton, Ballyabigin or Mr. James Neill, Greyabbey.

Friday, 28th. January 1780 Belfast Newsletter

About 30 tons Galway kelp and the like quantity of Kelp made in the Lough of Strangford to be sold exceedingly cheap by a person leaving this Kingdom. Apply William Johnston, Co. Down.

Tuesday, 16th. August 1785 Belfast Newsletter

To let from November next Island Mahee with the kelp shores thereof; the particular good qualities of its kelp and Grazing are well known. Apply Robert Hamilton, Ardmillan

Phase 2: Iodine from seaweed 1811 - ~1940

The end of the Napoleonic wars and the manufacture of purer synthetic alkali from the early 1820s meant that kelp production for alkali was no longer profitable, as its price collapsed. It was also hard, back-breaking work and the rewards were small for the effort and time involved. Kelping had resulted in population growth in Scotland in coastal areas, and also in Ireland, and the collapse of the industry led to starvation and emigration. Contemporary commentators also deplored the fact that kelp-making meant that people were not working their land, and the "manurial" value of seaweed was also being lost. It was literally going up in smoke.

Just when all seemed lost for the kelp industry, a fortuitous discovery by Bernard Courtois in 1811, a French saltpeter (potassium nitrate) manufacturer, saved the day. He was extracting potassium salts from kelp liquor as part of the process of making saltpeter. Shortage of saltpeter for gunpowder, due to the British naval blockade curtailing imports from India, had led to kelp being used as a source in France. He noticed that his copper pans were corroding and after some investigation and treating the residue with concentrated sulfuric acid, he observed the production of a violet vapor, which condensed to blue-black crystals (43). The new substance was quickly identified as a new element by Gay-Lussac (who named it) and also by Humphry Davy, who competed with Gay-Lussac for the priority of discovery, naming and characterization of this new element. One of the surprising things about this serendipitous discovery was that it hadn't happened before, as iodine is easily liberated from its compounds.

When saltpeter manufacture from this source became unprofitable, due to renewed imports from India, Courtois started making iodine on a small scale around 1822 by displacing iodine from solution using chlorine. (44, 45). Other French manufacturers started up soon after and France became an important producer of iodine from kelp until the early 20th century, only rivalled by Scotland. Courtois, like Le Blanc before him, didn't make a financial success out of his discovery. In 1817 Andrew Ure discussed the production of iodine from kelp using a modification of Courtois' original method, and suggested that kelp residues from soap boiling might a valuable source of iodine. This quotation also indicates the value placed on kelp by soap boilers (46):

As many of the Scotch soap manufacturers use scarcely any other alkaline matter for their hard soaps except kelp, it occurred to me that in some of their residuums a substance might be found, rich in iodine. Accordingly, after some investigation, I found a brown liquid of an oily consistence, from which I expected to procure what I wanted. This liquid drains from the salt, which they boil up and evaporate to dryness from their waste leys for the soda manufacturer.

Ure goes on to describe how he discovered that acidifying the liquid with concentrated sulfuric acid (diluted to 50%), cooling and filtering, removed crystallized salts and precipitated sulfur. He then added solid manganese dioxide as an oxidizing agent (suggested by William Wollaston) and heated the mixture, whereupon iodine sublimed over. He reports how he optimized the procedure with regard to the amount and concentration of acid, the amount of manganese dioxide used and the temperature. This method was to become the most common method for extracting iodine from kelp liquors in Scotland and Ireland. The French continued with the chlorine-displacement method. It is not clear when iodine was first made commercially in Scotland, but there are hints that Ure bought up the kelp residues from soapboilers to make iodine. By mid-century Glasgow had become a major center of iodine production with up to 20 manufacturers in 1845. One of these was a J. Ward who presumably was the same John Ward who started a factory in Rathmelton (now known as Ramelton), County Donegal in 1845.

There was no initial demand for iodine, except as a chemical curiosity and a subject for chemical research, but it quickly found uses in medicine, as a cure for goiter and as an antiseptic. It was used in the early photographic processes and in the production of dyestuffs, and demand grew steadily from the 1840s onwards.

The Extraction Process for Iodine

In 1853 Sheridan Muspratt, son of James Muspratt, started publishing his successful encyclopedia on industrial chemistry, *Chemistry: Theoretical, Practical & Analytical* in monthly parts and in it he describes the current methods used for extracting iodine from kelp and mentions the Donegal factory (19, 47):

The course pursued in its manufacture is simple. The several fuci and algae which contain it, are collected by inhabitants of places adjacent to the sea-shore, and dried in the air, after which shallow rectangular pits are dug wherein the dried material is burned. The semi-vitrified ash that remains is broken up by sprinkling a little water upon it while it is hot. This is the kelp of the Scotch and Irish, and is the same as the varec of the Continental producers; it is purchased by the several manufacturers, in order to extract from it the iodine and other salts. For this purpose it is reduced to a coarse powder, which is placed in rectangular filters, having an inner perforated bottom of sheet-iron.

Several manufacturers ... may be found, among whom may be mentioned Mr. Whitelaw of Glasgow, and Mr. John Ward of the country Donegal, Ireland.

William Paterson had become the dominant Scottish manufacturer of iodine from kelp by 1862, processing 80% of the kelp, and he bought kelp from Ireland for his Glasgow factory into the 1880s.

The process can be summarized as follows (see Muspratt (48) for more details). Seaweed was collected, dried and then burnt on the seashore in primitive open kilns to form a glassy mass, known as kelp (Figure 2). This was then shipped by sea to the end-users, and when iodine became the major product, these manufacturers (also known as lixiviators) were mainly located in Scotland and Ireland. The crushed kelp was lixiviated (leached) in cast-iron baskets in order to extract the soluble salts. This was done is a series of interconnected tanks. Concentrated liquor was taken off at the bottom and water added at the top, in what was known as a Shanks' battery.

In a series of evaporations of the resulting concentrated kelp liquor, potassium chloride, potassium sulfate, sodium chloride and sodium sulfate were removed by crystallization. These were filtered off separately and sold as by-products. The potassium salts were especially valuable up to the 1870s for use as fertilizer and in gunpowder, after which cheaper supplies became available from Germany. The residual liquor contained iodides, bromides and sulfur compounds. Concentrated sulfuric acid was added (1 part in 7) and allowed to stand for 36-48 hours. The sulfur compounds (sulfides and sulfites) decomposed, H₂S and SO₂ gases were given off and sulfur was deposited, together with more salts. Sulfur was another saleable by-product. After filtering, the acidified liquor was placed in an iron retort (with a lead still-head) and heated to 60 °C (140 °F). Manganese dioxide (MnO₂) powder was added as the oxidant and the solution boiled to expel the iodine as vapor (~100 °C). This was condensed in a series of connected glass or pottery receivers called udells. The iodine was purified by sublimation as required. The solid iodine was packed in small barrels known as kegs, each containing 1 cwt (112 lb.).

Muspratt describes other processes that had been developed as alternative methods of treating kelp to extract iodine, as do Muspratt and Molinari (47) and Mellor (45). The variety of methods that had been developed indicates the importance of this industry by the middle to late 1800s, when kelp was still the main source of iodine. (The detail of the various processes will be discussed in a future article.) From 1874 iodine started being imported into Europe as a by-product of the Chilean nitrate industry, and eventually this came to dominate the iodine industry. Iodine was available from this source in vast quantities—Chile could produce 5,100 tons a year when total world consumption was only 500 tons. However, a cartel was set up between the iodine producers to "fix" iodine prices, which lasted 61 years and served the interests of Chile as well as European producers, by regulating prices (49). This allowed the uneconomic production of iodine from seaweed to stagger on until around the 1930s in Glasgow, although it only finally ceased in France around the mid-1950s. It is interesting to note that China still has factories today extracting iodine and other chemicals from seaweed, as a by-product of algin production.

In 1862 the young English chemist Edward Stanford published an important paper describing improved methods of obtaining iodine from seaweed (13), the first of many papers he produced on the utilization of seaweed (50). In this paper he reviewed the history and uses of seaweed, and then went on to describe his improved process, known as the char process, using destructive distillation of dry seaweed in a kiln, to extract increased amounts of iodine and other useful by-products from seaweed, which he hoped would make the industry economically more viable. He comments on the state of the iodine from kelp industry in 1862 (13):

Kelp, however, is the only commercial source for its production, and the immense value of iodine, in photography and medicine particularly, has given an impulse to the manufacture of kelp, which renders it by far the most important of all the applications of seaweed.

As at present carried on, it has many disadvantages; these are well-known to chemists, but probably from the fact that it is conducted on desolate shores, at a considerable distance from centers of civilization, it has not yet received that attention its importance demands...

He goes on to say that

The manufacture is at present limited to a few parts of Great Britain, the western and northern islands of Scotland, the north-west coast of Ireland, and Guernsey.

At that time Mr. William Paterson of Glasgow processed nearly 80% of the kelp produced in Ireland and Scotland, a total of 10,000 tons in 1860-61, worth on average £4 a ton. 60% of the kelp came from Ireland. Stanford notes that only a small portion of British kelp is lixiviated (that is extracted) outside Scotland, in Ireland and Guernsey. He also gives statistics on French production of chemicals from seaweed in seven factories.

Irish Iodine Works

Figure 1 shows where kelp was lixiviated and iodine extracted in Ireland. Muspratt had mentioned John Ward of Donegal, and in the Great Exhibition of 1851 in London there was a display of Irish chemicals obtained from seaweed (51):

I observed in the great exhibition a case of chemical stuffs produced from Irish sea-weeds-viz., iodine, chloride of potassium, sulphate of potash, and alkaline, or kelp-salt-manufactured in the Ramelton Chemical Works, by the exhibitor, Mr. John Ward. These works, the first of their kind started in Ireland, were established by Mr. Ward, in March 1845, in Ramelton, a small town on an arm of Lough Swilly, county Donegal. Previous to their establishment the people of the north-west coast of Ireland had comparatively no home market for the produce of their industry, in so far as regarded the manufacture of kelp from sea-weed, consequently but little was produced; but since the opening of the works in Ramelton by the enterprising exhibitor, who was generally considered at the time to be making a rather bold experiment, a large annual consumption of kelp at the works has caused it to be made in much greater abundance, and the prices raised to such an extent, causing thereby not only a large circulation of money in that part of Ireland, but has conferred great benefits on the neighbouring coast, by the extensive employment it affords to the poorer classes round the districts, who, but for this field of commerce having been opened up almost at their own doors, would, in many cases, be unemployed, and in desperate circumstances.

In the town of Ramelton the chemical works have been of the greatest benefit, by the number of workmen and labourers employed in and around it, and the very considerable shipping trade, in vessels ranging from 50 to 120 tons, which the importation of manufactured stuffs has been the means of bringing to Lough Swilly.

Before concluding these brief remarks, I cannot refrain from expressing my high opinion of the talent and energy displayed by Mr. Ward in founding and carrying on such an extensive undertaking, where few would have hazarded such an enterprise.

The cultivation of national industry must, at all times, be regarded as of the utmost importance in every country, but more especially in Ireland; and it cannot fail to be looked upon as reflecting the highest credit on all who have contributed so largely as Mr. Ward has done to this important end, and the well-known and widely-spread liberality of that gentleman has brought its own reward in the increasing and flourishing state of the works, and also, the high name that his manufactured stuffs, viz., chloride of potassium, sulphate of potash, &c., has gained in the London and continental markets.

In the catalogue for the Great Exhibition of 1851 seven British and two French companies displayed their products from seaweed, and as well as John Ward, an E. Bullock & Co., Galway is also listed. J. Ward of Glasgow was bought by the British Seaweed Co. Ltd. in 1867 (Stanford's company) (52). In 1887 the company was still in existence, but it was now owned by James O'Mahony. The site of this factory in Green Lane, Ramelton is still known and the remains were only demolished 30 years ago, though some traces still remain (7). I have not yet managed to find out anything about the firm of E. Bullock in Galway, although it was obviously well known in 1851-2 and also displayed at the Cork Exhibition in 1852 (53):

Iodine is manufactured almost exclusively from kelp, which is the ash resulting from the burning of sea weeds. The iodine in a ton of sea weeds might be put into a small bottle; and the other products of value, sulphate and muriate of potash are very small compared to the bulk of the material from which they are obtained.

The ingredients for extracting the iodine, are comparatively few; therefore the importance of the manufacture of these products, as well as iodine of potassium, by Messrs. Bullock of Galway, and in the County Donegal by Mr. John Ward, at Ramelton, within a few miles of where the kelp is burned, is an interesting feature of the advancement of Irish chemical manufactures. Formerly iodine was almost altogether prepared in England, Scotland, and on the continent.

At least two other enterprises existed in Ireland for the chemical utilization of seaweed in the 19th century: in Galway and in County Clare. Robinson (1986) describes the kelp industry on Aran and the role of the Irish Iodine & Marine Salts Mfg. Co. Ltd. (54) based in Galway, later relaunched as the Marine Salts Company. A site on the bank of the Corrib in Galway is still referred to locally as "The Iodine," though this refers to part of the factory set up in 1863 by the Irish Iodine and Marine Salts Manufacturing Company (55) and used for converting the waste from iodine extraction into fertilizer (56).

This company was founded in 1863 by Thomas H. Thompson, Sir James Drombraine and Richard Young. They may have been operating Stanford's char process according to Booth (50), though initially they were using



Figure 4: The iodine works on Long Walk in Galway, ca. 1865, courtesy National Library of Ireland.

McArdle's patent wet process. Certainly, Stanford was well aware of their activities, as the cuttings in his notebook shows, and he complained that they were infringing his patent (57). By 1865 they had a factory operating in Galway on Long Walk (Figure 4), and were building one at Port Chorrúch on the Aran Islands, across the water from Galway. The 1860s was a boom time for the iodine industry, just before Chilean iodine arrived on the scene, which would sweep the board of kelp-derived iodine. The new enterprise was reported in the local paper (58):

Iodine Manufactory. The Marine Salts Co. of Ireland (Ltd.) want to increase their operation. They have a factory at Long Walk, Galway, and buildings in Arran for drying and burning kelp to be taken as ash to Galway. The Company has originated a process of converting seaweed to ash which is patented. There are twenty-six men employed under Mr. Glassford in Galway. The following substances are produced in abundance: Muriate of potash (used in the manufacture of powder, for which there is a brisk demand in Liverpool), Sulphate of potash (used in the manufacture of fine glass), Glauber salts, Soda salts (for the manufacture of coarse glass). The grand result produced from the factory is Iodine, with a standing order from London for as much as possible. The refuse makes manure.

The works manager Mr. Glassford was the same person who described the kelp industry in 1848 (12). By 1867 the Marine Salts Co. claimed to be the third largest iodine manufacturer in the United Kingdom. The Aran Islands produced around 700 tons of kelp a year and this had previously been sold to agents of Scottish manufacturers like William Paterson. The competition for the kelp production was solved by the land-agent on Aran, Mr. Thompson, declaring that kelp could only be sold to him, effectively setting up a monopoly, where he decided what price should be paid and defining his own 22.5 cwt. ton (rather than 20 cwt.). This sounds bad but the "long" ton of 21 cwt was normal practice in the kelp industry in Scotland and Ireland, due to the accidental, and sometimes deliberate, adulteration of the kelp by sand and stones. Robinson (1986) has a good discussion of this unsavory episode, which ended when the factory on Aran closed in 1870 after the fall in iodine prices, and in 1872 Thompson was forced to relinquish his monopoly. Robinson writes (59):

At the time of the iodine boom... there must have been lines of shore-workers trudging up the shingle with weed to feed the machinery of the factory.

The workers were paid a penny a basket for seaweed. The ruins of a kelp factory can still be found at Port Chorruch on Aran's best kelp shore, a decayed "outpost of Victorian industrialism," as Robinson expresses it. The Irish Iodine and Marine Salts Mfg. Co. finally closed in 1876, having gone into liquidation.

Booth (1978) (50) refers to the setting up of an iodine factory in Freagh, County Clare in 1878 by the North British Chemical Co. Ltd. (Stanford's company), and quotes a letter in Stanford's papers dated 1884 which refers to

Mr. Ross ... who thoroughly understands their patent process by retort, is to superintend the Freagh chemical works which are now to commence.

However, letters in the local papers in 1878 indicate that the factory was built and about to start production in early 1878 (60). In 1878 Robert Galloway said in a paper that no iodine was then being made in Ireland. The Galway works had closed, the Freagh plant had still to produce and he seems to think that the Ramelton plant had also ceased production by this date (61). The remains of this factory at Freagh were only demolished in 1999 (62). It is not certain when it closed, but the local story is that it was closed after a worker, the worse for drink, fell into the hot ash and was killed (63). Certainly by the end of the 19th century it seems that none of the Irish iodine factories was still in production, the one in Ramelton being the first to start and the last to close.

Kelp production still continued on a small scale into the 20th century, but the kelp was now all exported. Kirby (1953) records that the burning of kelp for iodine manufacture in Ireland only stopped in 1953 (64):

Up until 1953, kelp also continued to be burnt for iodine in Eire, the amount of ash produced ranging

from 330 tons to 1,335 tons annually with a value of ± 3 15s. 3d. to ± 8 11s. 4d. per ton.

The kelp was usually exported to Scotland, and when that industry closed in the 1930s, it was then sent to France for extraction of the iodine. Chapman (1970) writes, "In the 19th. century much of the Irish kelp was shipped to Glasgow for the extraction of iodine" (65).

It would seem that the Scottish iodine industry, which had started sometime before 1840, closed in the 1930s (at the collapse of the iodine cartel) and the last Scottish kelp was made around that date. The last shipment left N. Uist in 1934. The industry survived in France until mid-1950s. Kelp continued to be burnt in Ireland until the 1940s.

As was the case with other industries in the 19th century, the stronger Scottish or English companies bought out and closed smaller Irish companies to consolidate their own markets. As we have seen there was fierce competition for the kelp from Aran in the late 1860s between the local Irish company and agents for Scottish companies (66).

Payment for kelp was always a problem as the buyers appear to have used chemical sleight of hand rather than proper analysis to determine payment, as this passage from Robinson's book indicates (67):

Before he would buy, the agent would test the kelp for iodine content. He would crumble together two or three little pieces taken from different parts of the lot, put a pinch of the powder into a test-tube and do something mysterious with a drop of sulphuric acid; the islanders would take it as a hopeful sign if when the treated sample was thrown on the ground they saw a smoke of iodine vapour arising from it. Then after a calculation the agent would announce his verdict, acceptance or rejection, good price or bad.

Seamus Mac an Iomaire gives a similar, contemporary account (3):

The sampling man goes around with a hammer and bucket, taking a small bit off each slab. The kelp makers know him as well as a bad halfpenny. When the sample is taken he brings it into the assayer's office, and the name of the person who owns the pile is on the ticket on the bucket. The man inside has a glass as a means of assaying, and according to what the glass shows he will pay its value to the kelp maker.

However, if chemical analysis was not properly carried out by the agents, they had only themselves to blame as they were as likely to pay over the odds as under the odds for kelp. The problem of accidental or deliberate adulteration of the kelp was always a problem and adding sand, stones, even varnished rocks, was sometimes considered fair game by the kelpers, if they could get away with it.

Phase 3: Alginates from Seaweed ~1880-Today

The last, and still continuing phase, of production of chemicals from seaweed is the extraction of alginates and related compounds. This originated from the researches of E.C.C. Stanford (68), who was the first to extract impure algin from seaweed in 1881. He patented the process and published articles describing it and its potential uses. Krefting (1896) (69) later made a pure sample. Chapman has a useful chapter on "Algin and Alginates" (70). Alginic acid and its salts (the sodium salt is known as algin) are polysaccharides found in brown seaweeds, and comprise between 15-40% of the dry weight. As with almost all chemicals in seaweeds, the percentage varies from species to species, from sample to sample, and with the season! Norway has become an important center for alginate research.

Although Stanford suggested many uses for alginates and continued to work on seaweed until the end of his life in 1899, their potential was not realized for nearly half a century. In Canada and the USA the Kelco Company started extracting alginates from seaweed in 1929 and was still a major producer until 1999 when it was taken over by Monsanto, and later by ISP Alginates. The first company to produce alginates from seaweed in Europe was started in Scotland in 1937 and it took some time for the alginate industry to grow.

The simplest method of extracting alginates is based on Stanford's original process, which involved adding dilute acid to macerated seaweed, extracting the soluble salts, and leaving the organic residue, composed of algin and cellulose, behind. The alginic acid is then dissolved out in sodium carbonate to give sodium alginate, which when acidified yields pure alginic acid. The original kelp products—iodine and potassium salts—are obtained as a by-product in maximum yield because no heating is involved. This is known as the wet process.

Thomas Dillon and Vincent Barry of University College, Galway did important work on methods of extracting alginates from seaweed in the 1930s. Dillon had earlier written an article (71) encouraging a revival of the Irish iodine and potash industry:

For about two hundred years seaweed has been a raw material for chemical industry along our west coast.

For not less than that period, the enormous quantity of seaweed thrown up on our shores has been collected, dried and burned, to obtain the ash known as kelp.

He points out that in 1930 Ireland was the only kelpproducing country that didn't have its own iodine industry, and he compares the neglect of seaweed in Ireland to the relative importance of the industry in Brittany. He goes on to recommend that the industry be revived not solely for iodine production, where competition was strong, but to produce potash for agricultural use in Ireland. It would seem that his words fell on deaf ears in Ireland, but from 1910-1930 potash was extracted from seaweed on the Pacific coast of the USA (72).

In fact the revival of seaweed collection in Ireland after World War II was due to the demand for alginates for food, cosmetics, textiles and other uses. Alginates have become an important ingredient of many foods, including ice-cream. It also has important medical and pharmaceutical uses, for example, as wound and burn dressings. The government set up Arramara Teoranta in 1947 to collect and process seaweed into meal, which was exported to Scotland for processing. The company is currently owned by a Canadian company, Acadian Seaplants. World production of alginic acid is around 25,000 tonnes a year, with China, Norway and Scotland being the main producers. Thus Stanford's vision has come to pass at last.

Conclusion

This brief survey of the Irish "chemicals from seaweed" industry has covered more than three centuries. Happily seaweed is still being collected on Irish shores in the 21st century and processed into saleable products, creating jobs. Seaweed is collected by part-time workers in Connemara and shipped to the Arramara Teoranta factory for converting into seaweed meal. Some small companies produce liquid fertilizers and other high-value products from seaweed. Seaweed is still collected for use an as a green manure, its original use, going back centuries. There is an active Irish Seaweed Industry Organisation (73) based at National University Ireland, Galway.

Seaweed is still a largely unutilized natural resource and massive quantities are produced each year in the oceans of the world and swept ashore on to stormy shores. History has shown what materials can be obtained from seaweed, and it has also been demonstrated that it can be cultivated in seaweed farms, particularly in Japan. Even in Ireland one can see the remains of these seaweed (fucus) farms at several places around Irish coasts, where seaweed was cultivated on stones in shallow waters along the northern coast.

Ireland has suffered in the past by having the local seaweed industry dominated and directed by outside companies, where Ireland exported low-value bulk products (like kelp) and foreign companies produced the value-added products (such as iodine and its salts.) The demands for a sustainable economy and for greener industries, and for job creation, suggest that we should look again at this abundant but underutilized natural resource and develop new industries with 21st century technologies.

In subsequent articles I hope to look specifically at the iodine industry in Glasgow, the fascinating career of Edward C. C. Stanford, and the chemistry of the various processes used for extraction iodine from seaweed.

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About the Author

Dr. Peter Childs taught Chemistry at university level from 1970 until retiring in 2009, at Makerere University, Kampala, Uganda (1970-76) and later at the University of Limerick, Limerick, Ireland (1978-2009). He became interested in the early Irish chemical industry and has been researching this for the past 20 years. He has worked extensively with Irish chemistry teachers—producing *Chemistry in Action!* magazine since 1980, starting the annual ChemEd-Ireland conferences, and running inservice courses and workshops. He is a past President of the Irish Science Teachers' Association and also of the Institute of Chemistry in Ireland. He is still active in chemical education, nationally and internationally, and is a past chair of the EuCheMS Division of Chemical Education (2002-2008). He has supervised a number of Ph.D. and Masters students in chemical education and been involved since 2010 in three EU-funded science education projects (SALiS, TEMI and ARTIST). He was a member of the first EuChemS Historical Landmarks Selection Committee (HLAC), 2017-2021.

Call for Nominations for 2022 HIST Award

The Division of History of Chemistry (HIST) of the American Chemical Society (ACS) solicits nominations for the 2022 HIST Award for Outstanding Achievement in the History of Chemistry. This award, formerly known as the Dexter Award and then the Edelstein Award, continues a tradition started in 1956. The award is international in scope, and nominations are welcome from anywhere in the world. Previous winners of the Dexter and Edelstein Awards include chemists and historians from the United States, Canada, Germany, France, the Netherlands, Hungary, and the United Kingdom.

For further information on the award and how to nominate, see acshist.scs.illinois.edu/awards/hist_award.php.

Society for the History of Alchemy Chemistry: Morris Award 2021

The SHAC Morris Award for 2021 has been given to Ernst Homburg for his outstanding work on the history of the chemical industry. His contributions include major studies on the history of the madder industry, his seminal paper on the early history of industrial R&D laboratories and his comprehensive history of twentieth-century chemistry and chemical industry.

The Morris Award honours the memory of John and Martha Morris, the late parents of Peter Morris, the former editor of Ambix and recognises scholarly achievement in the History of Modern Chemistry (post-1945) or the History of the Chemical Industry. The next award will take place in 2024. A call for nominations will be circulated in 2023.

A COMMEMORATION OF ERNEST RUTHERFORD ON THE 150TH ANNIVERSARY OF HIS BIRTH PART I: 1871-1907

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Introduction

If any one person can take credit for splitting open the atom, taking a look inside, and then defining the terms for its self-destruction, that individual is Ernest Rutherford (1871-1937). Rutherford accomplished all three of these stupendous feats, albeit in reverse chronological order. For this, and many other achievements, his name has become legendary. He was incorporated into the most exclusive club in the world, the periodic system, as element 104, rutherfordium (Rf). He is recognized as New Zealand's most famous native son, a first-generation child of an immigrant father from the city of Dundee, Scotland, and an immigrant mother from England. He received the 1908 Nobel Prize in Chemistry "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances" (1). Almost a dozen of his former students went on to win their own Nobel Prizes.

In 1971, the Royal Society of London organized a centennial commemoration of Rutherford's feats with several presentations of recollections by persons who had worked with him. Their remarks were collected into an issue of the *Notes and Records of the Royal Society of London* (2). Fifty years later, while it is not possible to record personal recollections, it is certainly appropriate to commemorate this great scientist by reminding our con-

temporaries of his life and accomplishments, which this contribution and a second that will follow, attempts to do.

Rutherford, often called the "Father of Nuclear Physics," (after all, he did discover the atomic nucleus!) clung to the notion, to the last, that hard work, close attention to detail, and minimal equipment would lead inevitably to great discoveries. While this may have been true in his own case, the juggernaut science modeled by E. O. Lawrence (1901-1958) soon overcame this view and transformed the way science was done—from benchtop to Bevatron (3). Nevertheless, Rutherford's method led to major discoveries in the fields of what we now call atomic physics.

A native New Zealander from a farming family based on the rugged South Island, Rutherford became a transplant to England somewhat by chance. In 1895, he, in his mid-20s and working in a laboratory at Canterbury College in Christchurch, and a young chemist named James C. Maclaurin, were the two top candidates for the 1851 British Exhibition Research Fellowship awarded to promising young men from the far reaches of the British Empire for study in the "home country." Maclaurin was chosen, but declined because of family obligations. When the mailman brought the news of his (second place) selection to Rutherford, who was digging potatoes at his father's farm, he is said to have thrown down the shovel and exclaim, "That's the last potato I'll ever dig" (4). Little did he know that he would be digging in a different, and far more intransigent, "topsoil" for the rest of his life. Upon his arrival in Cambridge, Rutherford was looked upon as something of an intruder from the provinces, an "alien" because he did not have a Cambridge degree. His bluff manner, earsplitting voice, and strange Scottish burr-colonial accent did not endear him to his colleagues. They were especially jealous because he was assigned to study with J. J. Thomson (1856-1940), the discoverer of the electron. Thomson recommended Rutherford for an open position at McGill University in Canada, a post that he held for 9 years.

When news of Henri Becquerel's (1852-1908) discovery of radioactivity reached Canada, Rutherford began to study this phenomenon with a young assistant named Frederick Soddy (1877-1956, eventually the Nobel Laureate in Chemistry in 1921 "for his contributions to our knowledge of the chemistry of radioactive substances, and his investigations into the origin and nature of isotopes" (5). In 1902 they published their finding that radioactivity was evidence of the spontaneous disintegration of one type of atom into another, a virtually unacceptable and counterintuitive idea at the time (6), first intuited by Marie Curie (1867-1934) (7). They also investigated and named the three common types of radioactive emanations, α , β , and γ emissions, first recognized by Pierre Curie (1859-1906), defined the half-life of a radioactive species, and proved the succession of radioactive species descending from uranium, thorium, and radium. For these achievements, Rutherford was awarded the 1908 Nobel Prize in Chemistry, an ironic twist given the fact that he famously (and perhaps chauvinistically) once remarked: "In science there is only physics; all the rest is stamp collecting" (8).

Meanwhile, in 1907, he had transferred to Victoria University (now the University of Manchester) in Manchester, England, where he took up, with Hans Geiger (1882-1945) and Ernest Marsden (1889-1970), his famous gold foil experiments that led to the discovery of the atomic nucleus. In 1919, Rutherford succeeded his former mentor, Thomson, to the Chair of the Cavendish (9) Professorship at Cambridge. Eleven of his former students became Nobel Laureates because of their work in discovering the neutron, splitting the atom, and demonstrating the existence of the ionosphere. Many volumes have been written elaborating on the life, work, and legacy of Ernest Rutherford; let us be content to say here that he changed the way we view the world and how it works.

Ernest Rutherford, Rutherfordium's Namesake

Origins. Family Background and Education (1871-1892)

In 1843, James Rutherford (10) (1838-1928), aged three, emigrated with his family from Perth, Scotland, to New Zealand where his father, George, had been hired to set up a mill at Motueka, on the South Island. Another emigrant family, the Shuttleworths of Essex, England, together with their widowed daughter Caroline and twelve-year old granddaughter, Martha Thompson (1843-1935), arrived at Auckland in 1855. Later, force of circumstances caused Caroline and Martha to move to Nelson, also on the South Island, about 30 miles from Motueka. And eleven years later, in 1866, James, by now a skilled wheelwright and mechanic like his father, and Martha, the elementary school teacher in the town of Spring Grove (later Brightwater), were married. Martha brought to her marriage a cultured background, as evidenced by the possession of rare commodity in New Zealand, a Broadwood piano, a make favored by Ludwig van Beethoven and Frédéric Chopin. Now a full-time mother, Martha was destined to give birth to twelve children, nine of whom survived to adulthood. Ernest, born on August 30, 1871, was the fourth child and second son in this growing family.

Ernest's first and most influential teacher was his mother, who took great care to prepare each of her children for entry into formal education. Martha Rutherford was one of the first women schoolteachers in New Zealand and she passed her cultural background on to all of her children by her lived example and constant attention to their intellectual growth. The happy and carefree atmosphere of the Rutherford household, combined with a healthy and constructive environment presided over by parents who valued education, and pursued it at great sacrifice, provided the solid basis for all of Ernest's future endeavors.

The family experienced some re-locations due to James Rutherford's work and the growing size of the family: first to Foxhill in 1877 and then to Havelock in 1881 where James ran a flax mill. Young Ernest, now eleven years old, attended Havelock primary school (11) where he met the second of several influential teachers, Mr. Jacob H. Reynolds, a Latin language enthusiast who used to teach it to some of his students, including Ernest, before classes began in the morning. In 1886, this extra tutoring paid off for young Ernest in the form of a scholarship that, at the age of 15, enabled him to attend Nelson College from 1887 to 1889. But over this happy event hung a curtain of tragedy, for in that same year, two of Rutherford's younger brothers were lost in a boating accident on Pelorus Sound (12).

The move to Nelson, 45 miles distant from Havelock, meant that Ernest would have to be a boarder, a not uncommon situation in a country that was mainly rural and had few secondary schools. The city of Nelson, itself, was the largest population center in the area: it counted about 5,500 residents at the time that Rutherford attended school there. It was here that he began to enjoy playing cricket and developing proficiency in first aid and survival skills as a member of the Cadet Corps. Nelson College, likened to an English "public school," and the oldest state secondary school in New Zealand, would be Ernest's intellectual home until the age of 18. It provided the broad education that fostered the inventiveness, imagination and creativity that were later to become Rutherford's hallmarks. William Justice Ford (1853-1904) was Headmaster from 1886 to 1888, and his enthusiasm for field sports was infectious for Ernest. Perhaps the greatest influence on Ernest while at Nelson was William Still Littlejohn (1859-1933), also an enthusiastic cricket player, but more importantly, a classics scholar and the mathematics and science master. It was from him that Ernest got his excellent foundation in physics, often in a class by himself. In his first year at Nelson, Ernest won prizes for history and reading, and later in his career, other prizes in classics, languages, English literature and mathematics. Science does not seem to have interested him at this stage, but his education was very well-balanced nonetheless.

During school vacations, Ernest enjoyed being with his large family, teaching his younger brothers and sisters, and reveling in the magnificent countryside where he hiked, fished, flew kites, bird-nested and honed his skills as a marksman. He had all the interests of most boys in their teens: guns, and models and mending things, such as clocks or toys. He even constructed his own cameras and became a very good photographer (13). His keen mind was interested in everything around him and he especially wanted to learn how things worked. He also enjoyed reading to and teaching his younger siblings, sometimes tying his sisters' pigtails together so they would sit down and listen. However, he was also very goal-oriented and excelled in his studies, leading to a series of scholarships that enabled him to pursue his education. Although he had worked on a farm all his life, he was not destined to remain in agriculture. He had a far more expansive

vision of where his future lay. It is probably no accident that at this stage of his life, he became a voracious, and lifelong, reader.

Another scholarship, and a very important one, was the means by which Rutherford matriculated at Canterbury College, Christchurch, in 1890: he placed fourth among all students in the country to win a coveted New Zealand University scholarship. Were it not for this award, Ernest could have remained a farmer or a minor civil servant for the rest of his life: his family did not have the means to send him to university. And once again, he encountered two excellent teachers who greatly influenced his career. The first was Professor Charles H. H. Cook (1843-1910), Chair of Mathematics and Natural Philosophy, who held this position for thirty-three years until ill health forced his resignation in 1908. To this day, his services are recognized by the annual Cook Memorial Prize. Ernest's physics teacher, Alexander William Bickerton (1842-1929), promoted discovery of the unknown; he was enthusiastic, versatile, and research oriented. He had excellent credentials, having himself studied with Edward Frankland (1825-1899), John Tyndall (1820-1893) and Thomas Huxley (1825-1895). To attract students to his classes, he adopted the attitude that science should be taught in an atmosphere that mimicked both a music hall and a circus. Eventually, immensely successful as a teacher, he was offered the chair of chemistry at Canterbury College, New Zealand, where he arrived with his wife and four children in 1874. Since science was not taught in secondary schools in New Zealand, Bickerton ended up with very few students, an initial disappointment that he soon overcame by branching out into giving night classes for adults and basic chemistry classes for elementary school children. His reputation as a brilliant teacher grew, but this was not enough to keep him from alienating himself from the school authorities by his socialist beliefs and eccentric, actually baseless, astronomical theories. He was removed from his professorship in 1902. For the next dozen years, he turned his home into a theme park called "Pleasure Gardens" to augment the family income; it closed due to financial difficulties in 1914 (14). He called upon his most famous student, Rutherford, to support him in his attempt to gain recognition for his theory of how bright new stars (novae) developed. Although Rutherford spoke up for his former teacher, he carried no weight since he was not an astronomer. Despite this failure, Rutherford had great affection for his mentor, and the two remained close friends for the rest of Bickerton's life. Rutherford wrote Bickerton's obituary for The Times (of London) in 1929 (15).



Figure 1. The "tin shed" that served as the chemistry and physics building at Canterbury College (left); Rutherford's "den" where he carried out his most sensitive experiments (right).

While Ernest was sitting for and passing his examinations with distinction in varied fields such as history, physics, French, Latin, English, and pure and applied mathematics, he also found time for a number of extracurricular activities such as the debating society, the science society, and rugby. And so it was that he took his B.A. degree in 1892, earning a "first" in mathematics under Cook's tutelage. To continue his study towards the M.A. degree, Rutherford needed yet another scholarship, which he handily won, returning him to Canterbury College for an additional year. To complete this higher degree, he was required to carry on original research in a setting where a physics laboratory was non-existent. He had to a find suitable space, finally settling on an unused cloak room with a solid concrete floor that rendered any vibrations minimal, an important feature because of his sensitive equipment. This "den," now known as "Rutherford's Den," is maintained as a museum in the clock tower of the Arts Centre; it runs multisensory interactive programs for children (16).

Early Research (1893-1895)

The subject of Rutherford's first research project was dictated by his interest in a sensational discovery by Heinrich Hertz (1857-1894) in 1888: electromagnetic waves, or more specifically, radio waves, that had been theoretically predicted by James Clerk Maxwell (1831-1879) in 1865. Though Hertz himself could perceive no use whatsoever for these waves, they gave rise to a flood of research reports by scientists wanting to know more about how these waves could be detected and how they interacted with matter. Rutherford's attention was drawn to the fact that an alternating electromagnetic field could induce magnetism in iron, a subject that gave rise to his very first publication (17). In this paper, he first identifies himself as E. Rutherford, M.A. (18) and then, appropriately, cites previous reports on the topic including Hertz, J. J. Thomson, and works by Oliver Lodge (1851-1940) and John Ambrose Fleming (1849-1945) (19). Well into the experimental work, he states (17),

Before starting this research, I was uncertain whether iron was magnetic in very rapidly oscillating fields or not. The only information I could obtain on the subject is given in the opening pages. What experimental evidence there was seemed vague and contradictory. In this research ... it has been shown that iron is magnetic for frequencies up to 500,000,000 per second.

A little farther down the page, he states

The use of magnetized steel needles as "detectors" and "galvanometers" has been explained, and their possible use also for measurement of the intensity of electro-magnetic waves.

In one fell swoop, Rutherford put to rest the uncertainties surrounding the magnetization of iron in high frequency fields and developed a possible use for magnetized iron as a detection instrument. But we must not forget that these results were hard won. Working in a tin shed that served as a science lab and a cold and drafty basement "den" (Figure 1) with self-designed instrumentation completely made by hand without benefit of mentor, budget, machine-shop, any supplies, or expert assistance, he achieved wonders. His first definitive results were made using knitting needles and piano wire!

We must remember, too, that his sources of electricity also had to be made by hand. This involved making an induction coil, sometimes called a Ruhmkorff coil (20) by winding thousands of turns of wire around a solid core, an operation that could take an enormous amount of time and had to be repeated about every three weeks.

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Rutherford's source of direct current was also difficult to construct: each day he had to fashion new Grove cells which required amalgamating zinc plates, the anodes, immersing them in dilute sulfuric acid, and then constructing the other half-cell, the platinum cathode immersed in concentrated nitric acid. A single Grove cell provided a voltage of 1.9 volts but deteriorated rapidly after a few hours, as Rutherford had observed in his experimental notes (21). At every turn, he had to invent in his mind's eye and then construct the apparatus needed to investigate a phenomenon. For example, in proving the magnetization of iron, he also wanted to know if this was a surface effect or not. To find out, he used a home-made small mirror magnetometer to measure the diminishment in deflection caused by a magnetized steel needle over time while it was being gradually consumed by boiling nitric acid. He was able to show that the depth of penetration of the magnetic field in a steel needle 0.032 inches in diameter was 0.0095 inch. From his calculations, he deduced that there was a thin surface layer magnetized in one direction, and a thicker interior layer magnetized in the opposite direction.

Ernest also found that playing with electromagnetic waves, popularly called "radio waves," was fun. He showed his fellow students how he could generate spectacular sparks and send the waves fairly long distances and yet be able to detect their signals through stone walls. These experiments were a source of great entertainment for both students and the folks from town who packed auditoriums to see the show.

In his second paper on "magnetic viscosity," i.e., the delay in the magnetization of iron following application of the magnetic force (22), Rutherford identifies himself as E. Rutherford, M.A., B.Sc., 1851 Exhibition Science Scholar. So, a lot has happened since the publication of his first paper: he was awarded a B.Sc. degree, for studies in geology and chemistry, as well as the scholarship that was to shape his destiny. The latter, using the proceeds from the London Great Exhibition of 1851, was awarded every two years to the most outstanding New Zealand student engaged in some branch of scientific research. Although Rutherford placed second-best, the original awardee, James Maclaurin, was unable to accept the obligatory conditions of the award, and the prize fell to Ernest. It would enable him to continue his research at an academic institution outside his home country. Since one of the major centers of gravity of scientific research toward the end of the 19th century was England, that is where Rutherford would betake himself the following year.

Meanwhile, Ernest was not spending 100% of his time in his research laboratory. Looking toward the future, he applied, unsuccessfully, for several teaching jobs, and in 1894 took on a temporary position at Christchurch Boys High School where his performance was judged less than stellar. It was actually a train of such failures that drove him to apply for the Exhibition Scholarship. Another facet of his life at this point was his growing relationship with Mary Georgina Newton (1876-1945), the daughter of his landlady; they secretly became engaged shortly before he left for England in 1895, but they were not to marry until 1900.

Returning to magnetic viscosity, Rutherford found that he had to measure very short time intervals, as short as 1/100,000 of a second. It is worthwhile to have a look at the ingenious, yet simple, device he conceived in order to accomplish this task. Figure 2 is a line drawing showing the basic arrangement:



Figure 2. Rutherford's timing apparatus (Ref. 22, p 183).

When the weight LM falls along the wire WG, it displaces the two copper levers, AB and CD, simultaneously. However, if the screw S initially displaces lever CD slightly downward, then the falling weight will first encounter AB and then after a short interval, CD. Using a simple geometric calculation, Rutherford showed that the time interval corresponding to one turn of the screw, S, was 0.000192 seconds. Since S was divided up into 20 divisions, he stated that (22)

the apparatus was quite delicate enough to show a difference for every division of the screw-head when determining the times of rise of currents of very short duration. The apparatus could therefore measure intervals of time up to 1/100,000 of a second.

Clever as the device may be, we must also marvel at the precision machining of the set screw and the falling weight.

All the characteristics that brought Rutherford this far in his career were to be manifested in the groundbreaking discoveries that punctuated his life's work in the years to come: simplicity, insistence on experimental evidence, creativity in experimental design, insight, attention to detail, cutting-edge research on new phenomena, thinking outside the box, imagination, attention to anomalous observations, and very hard work. One of his biographers, Edward Neville da Costa Andrade (1887-1971), remarked (23)

Altogether, these two papers, if they do not announce a genius, as Newton's first published papers did, show an experimenter of outstanding ability, able to pose and answer definite problems without either technical aid or apparatus other than that made by himself.

Cambridge I: Work with J. J. Thomson (1895-1898)

In August of 1895, E. Rutherford, 1851 Exhibition Science Scholar, set sail for England with his passage paid by borrowed money from his brother, George. On the way, the ship berthed in Australia for enough time to enable Ernest to meet with William Henry Bragg (1862-1942) of the University of Adelaide, another scientist interested in long-distance transmission of electromagnetic waves. His discussion with Bragg bore fruit: a letter of introduction plus an acquaintance that would blossom into a great personal friendship and a mutually supportive scientific comradeship (24). His arrival in London on a gray day in September did not bode well: pollution and a damp climate sent him to his boardinghouse bed for days and his future was still uncertain. He had previously sent copies of his research work and his letters of recommendation to the Cavendish Laboratory in Cambridge and was awaiting a reply. Finally, in late September, a welcoming letter from J. J. Thomson, Director of the Cavendish, arrived. This upswing in Rutherford's fortunes was to continue, seemingly unabated, until his dying day.

Thomson's open, immediate and unreserved hospitality for this virtual unknown from "the antipodes" ran counter to the prevailing attitude at Cambridge in that period. The university had recently created a research degree that enabled graduates of other universities to become candidates for a Cambridge B.A. after two years' residence and an acceptable thesis. This arrangement was unwelcome to both the Cambridge insiders, who considered the newcomers intruders, and the graduates themselves, many of whom arrived with advanced degrees from very prestigious institutions. Rutherford recognized the situation almost at once, realizing that he was not in-the-club and believing that he never would be. Nevertheless, despite the snubs and bullying, he set right to work in the laboratory, and after about two months, people began to take notice that here was no ordinary farm boy from the backwoods. In fact, they found that they had a hard time keeping up with him with respect to brilliance, insight, ingeniousness and hard work.

Rutherford's first piece of work at Cambridge was a continuation of the work accomplished in his two previously published New Zealand papers, namely, perfecting his magnetic detector of Hertzian waves and trying to increase its effective range to beyond a half-mile (25). Using this detector, he was able to estimate the wavelength of the radio waves, about six or seven meters, and observe the fact that their signal was not diminished even when passing through multiple layers of stone walls and buildings. He was also able to determine the resistance of iron wires for high frequency alternating current and the absorption of energy of various conductors measured in terms of increased resistance of the discharge circuit. He also described a simple method to obtain the period of oscillation of a discharge circuit for a wide range of frequencies (26). While the published work appeared in 1897, Rutherford also gave an oral report at the 1896 meeting of the British Association for the Advancement of Science that was reported in the proceedings (27). This research seemed to be moving along a fruitful path that, as Rutherford recognized, might even have commercial value, but an astounding discovery announced in December of the very year that Rutherford arrived in England transformed his life forever. He seemed to have no regrets in abandoning radio waves to Guglielmo Marconi (1874-1937) even though he had to penny-pinch for many a year thereafter.

On 28 December 1895, Wilhelm Conrad Röntgen (1845-1923) of the University of Würzburg discovered a phenomenon now called X-rays (28). He gave his oral report at the 23 January 1896 meeting of the Würzburg Physical-Medical Society, which was also subsequently published in that society's journal (29). An English translation of the original paper was published at the same time as Röntgen's oral report (30). There is no substitute for the actual words expressed at that historic meeting that will convey the excitement surrounding this discovery (31):

Mr. Röntgen, greeted by lively, long-lasting applause, gave his lecture on: "A new kind of rays." Towards the end of the presentation, the silhouette of the skeleton of a human hand was photographed using the new method, actually the right hand of the Honorary President of the society, Mr. V. Kölliker, who thanked the lecturer, in the name of the Society, for the communication that had never had an equal in the annals of the meetings, and stood Mr. Röntgen up on the podium, at which the members and the entire auditorium, crowded into the physics institute lecture hall, gave three cheers and burst into rapturous applause. Mr. V. Kölliker's proposal to call the new X-rays "Röntgen rays" from then on unleashed a new round of cheers.

The whole scientific world greeted Röntgen's announcement with as much excitement as the Würzburgers, including the Cavendish Laboratory. Röntgen's announcement was the first of a chain of developments that threatened John Dalton's doctrine that atoms were indivisible and immutable. And within a year of his departure from New Zealand, Rutherford found himself at the forefront of this new frontier.

Following up on Röntgen's astounding discovery, Rutherford and his mentor, J. J. Thomson, immediately set to work examining the effect of these new rays on gases. In their first co-authored paper, they exposed a gamut of common gases to the rays and looked at their resulting electrical conductivity. The first thing they observed was that gases retained their conductivity for a short time after being irradiated, that the conductivity was not impaired by heating the gas, but that it disappeared entirely when the gas was passed through water or through glass wool. They also found that "the analogy between a dilute solution of an electrolyte and gas exposed to Röntgen rays [held] through a wide range of phenomena...." (32).

In 1887, a Swedish chemist, Svante Arrhenius (1859-1927), had proposed a controversial theory of conductivity in aqueous solution: salts and acids actually broke up to form charged species called ions without any intervention in the form of imposition of a voltage across the solution (33). That Thomson and Rutherford found an analogous situation for gases, albeit under the external influence of high energy rays, was a great step forward in understanding the nature of the particles that made up the gas. When Thomson continued Arrhenius's line of reasoning with respect to electrical discharges through gases in the following year, he was to make the most astounding breakthrough of the century: the discovery of the electron (34).

Meanwhile, Rutherford continued to pursue the interaction of Röntgen rays with gases, finding that a charged gas contained "an excess of ... positive or negative conducting particles, whatever they may be, to which conduction in gas under the Röntgen rays is due" (35). He also succeeded in measuring the velocity and rate of discharge of these particles, by now calling them "ions" (36). He called them "jolly little beggars," claiming that he could almost see them (37)—such was his extraordinary scientific imagination. Although Rutherford was soon to discard his work with Röntgen rays in favor of

the strange new rays emanating from newly-discovered radium, this work was critical to the coming discoveries in the sense that he learned how to design and perform discharge experiments and also learned ionization theory, proving Thomson's idea that the rate of ionic recombination was proportional to the square of the total number of ions in the system (38). But more importantly, he succeeded in laying "the foundations of precise and mathematically expressible work on the conduction of electricity in gases" (39). This latter achievement was to be the foundational experimental method used in his celebrated 1902-1903 development of the theory of radioactive disintegration (40). Andrade goes on to say that this work was typical of Rutherford's approach-"a search for a simple theory, expressing processes that can easily be pictured, and accounting for precise physical measurements" (41).

The end of the 19th century bore witness to, in addition to two "new" forms of energy, "Hertzian waves" and "Röntgen rays," an entirely new type of energy emanating from uranium which literally electrified the world. Uranium had been known since its discovery by Martin Heinrich Klaproth (1743-1817) in 1789. Working as an apothecary in Berlin, Klaproth treated a sample of pitchblende (42) from the Joachimsthaler mine (now in the Czech Republic) with nitric acid, followed by potash (impure potassium carbonate and other potassium salts) and observed a yellow precipitate that signaled a new element to him. He heated the precipitate strongly in a carbon crucible, thinking to reduce the compound to a metal, and he obtained a black, metallic-looking, powder that he took to be the pure element. He named the substance uranium after the newly discovered planet, Uranus. It was only 52 years later that the elemental metal was isolated by the French chemist, Eugène Melchior Peligot (1811-1890).

For over a hundred years from its discovery until 1896, uranium's radioactive properties lay hidden under the guise of an element good only for coloring glass. In that year, the French physicist, Henri Becquerel, announced a discovery that initiated energetic research on the part of many scientists. Uranium, he found, emitted a silent, invisible aura capable of reacting with silver salts even when they were shielded by some layers of metals. He realized that this astounding phenomenon was a property of uranium itself, that it seemed to resemble Röntgen rays (but not quite), and was not light-induced phosphorescence or fluorescence. Marie Curie eventually dubbed this phenomenon "radioactivity" (43). By the time Rutherford made his move to McGill University in 1898, research on radioactivity was feverishly under way all over the world. And as is well-known, Curie herself made the most significant advances in this research, discovering, in the process, two new radioactive elements.

McGill University (1898-1907)

Rutherford, himself, as was his wont to pursue the most recent and significant problems (44), immediately set to work to measure the extent of penetration of the uranium rays by using his tried and true method of the degree of ionization produced. He found that (45)

the uranium radiation is complex, and that there are present at least two distinct types of radiation—one that is very readily absorbed which will be termed for convenience the α radiation, and the other of a more penetrating character, which will be termed β radiation.

By the time that this paper was published, he was already ensconced in Montréal, Canada, as the Macdonald Professor of Physics at McGill University.

Rutherford's time of residence at Trinity College, Cambridge, had always been an uneasy affair. As an outsider from the antipodes, he knew that he would never be accepted as a full member, to say nothing of being elected a Fellow (46)—he realized that insiders doing less than half the work at half the quality as his own work were easily and quickly welcomed into that august society. At the same time, he realized that his time at Cambridge was coming to a crossroads-he had to move on in order to establish his own career and to make a living that could support a family. His engagement to Mary Newton had already stretched out into several years. So, when he realized that the physics professorship at McGill would soon be vacant due to the resignation of its incumbent, Hugh L. Callendar (1863-1930), he decided, with J. J. Thomson's enthusiastic recommendation, to apply. Not least in forming this decision was the knowledge that the physics laboratory, outfitted lavishly by its sponsor, tobacco millionaire Sir William Macdonald (1831-1917), was the most advanced in the world $(47, ^{48})$. And as one of Rutherford's biographers, David Wilson, remarks, "... one of the chief reasons for accepting the post when it was offered to him was that there was no very great emphasis on the teaching duties" (49). In early August he received word of his appointment and on September 8, 1898, at the age of 27, he set sail for Canada.

Rutherford knew from the start that great things would be expected of him at McGill, including having to fill the shoes of his predecessor, Callendar. He knew that he would be expected to form an excellent research team, that he would have to produce original work, and that he would have to work hard to stay at the forefront of scientific research. With this in mind, he plunged right into his task and made the same mistake as generations of teachers before him and following after him: he started lecturing over the heads of his students, assuming a level of mathematical knowledge that was beyond them. However, he quickly caught himself and soon projected a mellower persona in the lecture room (50).

Anxious to get his research started, he soon assembled some of his key equipment, electroscopes and electrometers, and sent urgently to Cambridge for the uranium and thorium essential to his experimental work. He had already established two types of uranium radiation and knew from Becquerel's work that the beta rays carried a negative charge and from Thomson's that their mass was about 1/1850 of a hydrogen atom. The alpha particles were more of a mystery. Their measured energy far exceeded that of beta particles, but their penetrating power was much less. His "love affair" with alphas over the next nine years would lead to proof of the nuclear atom and transmutation of the elements.

Rutherford's first major discovery at McGill occurred when a colleague, Professor of Electrical Engineering, Robert Bowie Owens (1870-1940), found that thorium behaved in a most peculiar manner: it gave off, in addition to α and β particles, an uncharged, chemically inactive, radioactive substance that was unaffected by heat but that could be condensed by extreme cold (51). When confined, this gaseous material lost half of its radioactivity every 54 seconds, falling to one-quarter of its original activity in 108 seconds and to one-eighth in 162 seconds, and so forth. Mathematically, Rutherford established that this new substance, which he dubbed "thorium emanation," obeyed the exponential decay law, a characteristic of every radioactive substance, the length of its so-called "half-life" dependent upon the nature of the active species (52). Put succinctly, "the rate of change of the system at any time is always proportional to the amount remaining unchanged" (53).

A year later, Friedrich Ernst Dorn (1848-1916) published a paper in which he described a new substance that he called "radiated emanation;" radium was the parent of this gas. He gave due credit to Rutherford and Owens for their discovery of "thorium emanation" the year before (54). In 1902, Friedrich Giesel (1852-1927) (55) described an emanation given off by actinium; it was later studied by André-Louis Debierne (1874-1949), discoverer of actinium, in 1904 (56). Subsequently, all three of these "emanations" were shown to be different isotopes of the same element, radon, the heaviest of the naturally occurring noble gases, although Dorn continues to be recognized by some as the sole discoverer (57). Marshall and Marshall point out that this was a citation error by George de Hevesy (58). Rutherford and his graduate assistant, Harriet Brooks (1876-1933), continued to examine this emanation together (59, 60), showing that it was a gas with a much lower atomic weight than the parent material. Brooks also observed the nuclear recoil effect (later interpreted as such by Rutherford) and the sequential nature of radioactive decay (61).

Initially, neither thorium nor uranium appeared to lose any activity, but it was later found that their half-lives were so long that they far exceeded any human lifetime, 1.4×10^{10} and 4.5×10^{9} years, respectively.

Thorium emanation gifted Rutherford with another surprise: whenever it came into contact with anything, such as a glass container or a metal rod, it made that object radioactive. Careful work soon showed that this effect was due to an invisible, miniscule, positively charged radioactive film left on the surface. He called it "active deposit" for lack of any better name (62).

With the publication of the short note co-authored with Owens and two major papers appearing in the Philosophical Magazine shortly thereafter, Rutherford considered that his first two years at McGill were quite productive. He had shown that "thorium emanation" was a material substance, he found that the rays emanating from uranium were not reflected or polarized, and he had confirmed the existence of an additional type of high energy, penetrating rays discovered earlier in 1900 by the French chemist, Paul Villard (1860-1934) (63) calling them "gamma rays" (64). This seemed like enough justification to take the summer of 1900 off for a very important project: his marriage to Mary Newton. This duly took place in New Zealand in July, and the newlyweds arrived back in Canada in September via Honolulu, Vancouver, and the Canadian Rockies. In March 1901, the happy couple's first and only child, Eileen, was born; she was to predecease her parents, dying in 1930 in childbirth at only 29 years of age.

While Rutherford was away on his honeymoon, a young chemist from Oxford University, Frederick Soddy, had arrived at the McGill chemistry department, attracted as Rutherford had been, by the university's excellently equipped laboratories. It had become obvious to Rutherford that his unruly emanations and ions were shedding parts of themselves, shape-shifting out of control into new and elusive substances. He had already intuited this phenomenon of transmutation (65), a reality that ran counter to everything that any scientist of his day had ever been taught. At this point, he needed a chemist to help sort out the changes he was observing, to separate and identify the products, to prove their origins experimentally, and to formulate a model that explained their nature and behavior. Their collaborative work (Figure 3) was to produce "a revolution in the accepted notions concerning the [immutable] nature of the atom" (66). Their overwhelmingly convincing evidence dispelled any hint of accusations of "alchemy."



Figure 3. Portrait of Frederick Soddy (left). Ernest Rutherford in his Laboratory, McGill University, 1905 (right).

Rutherford and Soddy co-authored numerous papers during the course of 1902-1903, many of which appeared in the Philosophical Magazine. Two of the most important, entitled "The Cause and Nature of Radioactivity" in two parts (6, 67) dealt with their investigations on the behavior of thorium. They first found that the greater part of thorium's radioactivity could be removed by chemical means, but once removed, thorium shortly thereafter, in four days' time, recovered half of its original activity. Meanwhile, the substance removed, which they called thorium X, lost half of its activity likewise in four days, according to the decay law previously established by Rutherford and Owens. They established that the mysterious thorium X was chemically distinct from its parent substance, thorium, with distinctly different chemical properties, but that the accompanying radioactivity was an atomic property that could not be changed or influenced in any way by the usual agents, such as application of heat or electricity. They wrote (6, p 395)

... radioactivity is at once an atomic phenomenon and accompanied by chemical changes in which new types of matter are produced; these changes must be occurring within the atom, and the radioactive elements must be undergoing spontaneous transformation.

They also showed that their ideas could be applied to the behavior of uranium and radium and their products (68, 69). In a piece published some years later in the *Chemical News*, Rutherford summarized (70):

... atoms of the radio-active bodies are unstable systems which break up with explosive violence ... expelling in many cases a small portion of the disrupted atom at high speed. The residue of the atom forms a new atomic system of less atomic weight, and possessing physical and chemical properties which markedly distinguish it from the parent atom. The atoms composing the new substance...are also unstable and break up in turn.

During the year following their two 1903 papers, they published "Radioactive Change" (71), in which they reiterated that radioactivity is "...the result of a process which lies wholly outside the sphere of known controllable forces, and cannot be created, altered or destroyed." It ranked, in their minds, with other fundamental properties of nature: electricity, magnetism, light, and gravity (72). They were also able to establish that uranium, thorium, and radium were the parent elements for a cascade of transmutations (73), each new product arising as a result of expulsion of an alpha or a beta particle. Although the amounts of these substances were extremely minute, far below the limits of sensitivity of balances or spectroscopes, they could be detected by the nature of their radiations, in terms of range, energy, and velocity, measured by the ionization produced. Realizing the great deal of heat that samples of radium emitted, they also went about measuring the total energy expelled by a gram of it: a remarkable 25,000 times the amount of chemical energy given off to form a gram of water from its elements!! By a similar calculation in terms of energy, they were also able to estimate the half-lives of these long-lived parents: about a thousand years for radium and billions for uranium and thorium. Finally, in estimating that the alpha particle traveled at about one-tenth the speed of light, they were convinced that radioactive decay was an enormously powerful source of energy (74). They thus concluded their paper on "Radioactive Change" with this astounding statement: "...the energy latent in the atom must be enormous compared to that rendered free in ordinary chemical change." This prescient remark foreshadowed the advent of the nuclear age with the creation of the first self-sustaining atomic pile by Enrico Fermi (1901-1954).

about ten years was the nature of the alpha particle and of gamma rays. Very early on, the beta rays could be seen to be analogous to J. J. Thomson's electron, and eventually they were realized to be identical. On the other hand, alpha particles remained elusive for about ten years from the time they were first discovered. Rutherford was able to show, with difficulty, that the alpha particle was positively charged. He measured the charge to mass ratio, and it was found to be roughly half that of the hydrogen atom. So, if both particles had a unit charge, this would mean that the alphas were twice the mass of hydrogen. Rutherford tried to make sense of this idea, bothered by the fact that helium, four times the mass of hydrogen, was often found in association with radioactive materials. In fact, he hypothesized, without proof, that alphas might be doubly-charged helium atoms. It was only when he was actually able to measure the charge on the alpha that he could show definitively that his hunch was correct-this confirmation was very difficult experimentally and could only be accomplished after he arrived in Manchester in 1908. It was then that he understood why so many of the radioactive products in the decay chains differed by a mass of four-helium's atomic weight-in their atomic weights (75).

When Rutherford traveled to England in mid-1903, he did not realize that he was living in the ante-chamber of the most eventful year in his life, 1904. In June of 1903, he received notification of his election to the Royal Society, a mark of honor rarely conferred on one so young-he was only 31 years of age. During his visit in England, he spoke at the annual meeting of the British Association for the Advancement of Science on his strange emanations and his ideas on the nature of radioactive decay-to a stubbornly skeptical audience, some of whom still believed in the "ether" and others who denied the existence of ions. Then a series of events punctuated the propitious year like so many movements in a symphony: Early 1904 saw the publication the first edition of Radio-activity, immediately considered a classic in its field; thence followed notice of his selection to deliver the Bakerian Lecture of the Royal Society, a great distinction hardly ever conferred on one so young and so new to fellowship in that august institution; in November, the Royal Society again honored him with the Rumford Medal, a biennial award to recognize exceptional work in physics; and again, in November, his invitation to deliver the distinguished Silliman Lectures at Yale University.

Rutherford's final two years at McGill went by in a flurry of activity. He found time to estimate the age of

the earth, offering the first cogent argument for using radioactivity as a means of measuring geologic time directly, first by his 20 May 1904 lecture at the Royal Institution (76), followed by many other interventions in this area (77, 78). In 1905, he hosted, among other able research physicists and chemists, the German chemist, Otto Hahn (1879-1968), who would eventually receive a Nobel prize for the discovery of nuclear fission. He also continued work on the alpha particle, this time estimating the number expelled from one gram of radium per second: an astounding 250 million! Also in 1905, he published a much enlarged second edition of *Radio-activity*, in which he emphasized the vast amounts of energy released per unit mass of disintegrating atoms, and also surmised, correctly, that the end product of the disintegration of Working at the periphery, Rutherford felt intellectually isolated, and even at a disadvantage regarding publication priority because of time lags across the Atlantic—he had actually been "scooped" by the Curies in 1899 (79). So, although he received numerous attractive offers of posts in the United States, among them Yale, Columbia, Stanford, and the Smithsonian Institution, he invariably rebuffed them, sometimes using them as leverage for a higher salary at McGill. He seemed to be waiting for the right moment to return to England and assume an acceptable chair there (80).

The propitious moment arrived in mid-1906 in the form of a letter to Rutherford from Arthur Schuster (1851-1934), the Langworthy Professor of Physics at Victoria University in Manchester. Schuster, a very able



Figure 4. Left: Portrait in oil of First Baron Rutherford of Nelson and Cambridge in 1932, aged 61; Artist: Oswald Birley. The apparatus is the artist's rendition of that used by Rutherford to demonstrate that alpha particles and the helium nucleus were identical. Right: Photograph of Ernest Rutherford in 1896, aged 25.

radium was lead. In 1906, another book, *Radio-active Transformations*, the content of the Silliman Lectures delivered in the previous year, was published.

McGill University, despite its excellent facilities, was situated at the outer reaches of scientific activity the center of gravity was geographically and philosophically somewhere midway between Cambridge and Paris. physicist who presided over the second most important and excellently-equipped laboratory in England, was considering early retirement; he had already given up experimental physics some half-dozen years before and wanted to devote more time to his interests centering around the Royal Society. But he also wanted to make sure that the Chair at Manchester would be filled by someone whom he held in the greatest esteem: that individual was none other than Ernest Rutherford. The latter's reply was swift and favorable, and by May 1907, Rutherford was on his way to the grime-covered manufacturing center of North West England that was Manchester.

Figure 4 shows two images of Rutherford at different stages of his life.

During his tenure at McGill, Rutherford built a reputation as both an inspired experimentalist and a theoretical pioneer. He placed the science of radioactivity on a sure and firm footing and at the same time completely dismantled the prevailing ideas on the nature of the atom. His former mentor at Cambridge, J. J. Thomson, gave this authoritative summary of his work there (81):

Rutherford's scientific activity was never greater than when he was at Montreal. In the years between coming to Cambridge and leaving Montreal to be Professor of Physics at the University of Manchester he had published between forty and fifty papers; a few of these were joint papers, but the great majority were about researches of his own which led to results of first-rate importance and which could not have been obtained by anyone who was not an experimentalist of the very first order.

This assessment was to be borne out in short order when, in 1908 as Langworthy Professor of Physics at Manchester, he was awarded the Nobel Prize in Chemistry for his Montreal work, namely "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances" (1). We will catch up with him in Manchester in Part II of this paper to learn more of his revelations on the nature of the atom.

Appendix: The Rutherford Museum at McGill University

When Ernest Rutherford left Canada for England in 1907, he left behind all the equipment that he had accumulated during his nine-year tenure. Most of it had been designed and built by Rutherford himself since he was investigating phenomena never before observed or even imagined. Following his usual mode, he first conceived of an idea of how to tackle a problem and then designed and built the apparatus deemed necessary: simple and at the same time highly sophisticated. Almost all of this equipment, therefore, was homemade and purpose-built. Fortunately, a colleague at McGill, Howard Barnes (1873-1950), perceived how important this collection was and to prevent its removal to the stockroom or the trash bin, he stored it all in a closet that wasn't opened again until 30 years later. The occasion was a request for photographs of the apparatus by Arthur Stewart Eve, Rutherford's official biographer. The collection was entrusted to Ferdinand Terroux, a member of the physics department, who eventually proposed the museum's creation in 1950. Nothing happened until a bequest in 1964 enabled construction to begin, and it was formally opened in 1967. The various cabinets contain important documents, some written in Rutherford's own hand. The equipment on display in six cabinets illustrates Rutherford's major achievements while at McGill: the nature of alpha rays, emanations from radium and thorium, excited radioactivity, heating effects of radiation, and ionization studies. The museum is excellently laid out and easily accessible online (82).

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HIST at Pacifichem 2021

The 2021 International Chemical Congress of Pacific Basin Societies (Pacifichem) will be an all virtual meeting, December 16-21, 2021. The conference is sponsored jointly by the American Chemical Society, Canadian Society for Chemistry, Chemical Society of Japan, Chinese Chemical Society, Korean Chemical Society, New Zealand Institute of Chemistry, and Royal Australian Chemical Institute. Seth Rasmussen, Yasu Furukawa, Ian Rae, and Gary Patterson have organized a symposium, "Hands across the Pacific: History of Collaborations and Exchange Programs between Countries of the Pacific Rim."

Further information about the Congress can be found at pacifichem.org.
FRITZ REITZENSTEIN: A LITTLE-KNOWN FIGURE IN THE WERNER-JØRGENSEN CONTROVERSY

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Introduction

Our lab has recently been examining the structural chemistry of metal-pyridine-sulfate complexes (1-4). In researching the history of these compounds, the earliest literature report that we could find of such a complex was from 1894 (5). The sole author on this report was Fritz Reitzenstein, of whom we had no prior knowledge. In reading his works, we discovered that the first metal-pyridine-sulfate complex was actually reported eight years earlier by Jørgensen, though (not surprisingly) a modern structure search, based upon Werner theory, does not point to this publication (6). As we dug more into this literature, we decided to research Fritz Reitzenstein, which led to his rather interesting Figure 1. Fritz Reitzenstein in 1909 at the University story which is described below.

Early Work

Fritz was born Friedrich Reizenstein (7) on January 14, 1868, in Mühlhausen, Aichach-Friedberg, Bayern, Germany. He was the fourth of eight children born to

Max Reizenstein and Lina Offenbacher, only six of whom survived infancy. Outside of his birth record, we could not find any information about him prior to his enrollment at the University of Würzburg for his graduate work. He performed the work for his inaugural dissertation in the lab of future Nobel laureate Emil Fischer, under the supervision of Wilhelm Wislicenus (8). Wilhelm was the son of the better-known Johannes Wislicenus, but was an accomplished organic chemist in his own right. At the time of his death, his obituary in Nature stated that (9):

organic chemistry lost one of its most fruitful research

workers, who contributed in no small measure towards placing the science on the basis which it now occupies.

The work performed in Reit-

zenstein's thesis focused on the condensation of 1,3-indandione to bindone, its characterization and reactivity, and was summarized in a single publication with Wilhelm Wislicenus (10).

of Würzburg. Public domain image from Wikimedia Commons, https://commons.wikimedia.org/wiki/ File:Fritz_Reitzenstein_1909_Wü.jpg.



Coordination Chemistry

Following his thesis, Reitzenstein began his independent work with his habilitation. The focus of this work was a shift from the organic chemistry of his inaugural thesis and examined the complexes formed by the reaction of metal salts with organic bases (11). The close resemblance of the compounds formed between metal salts and water with those formed between metal salts and ammonia had been recognized fifty years earlier by Heinrich Rose (12); this relationship was something that Mendeleev considered in his development of the periodic table (13). The theoretical explanation of the close resemblance of ammonia complexes and hydrates of metals was described at the time by the widely ac-

HCl ClH \mathbf{H} Pt-NH2.NH4.Cl; н- \mathbf{H} н, BERZELIUS GRAHAM 2NH_a.Pt+Cl_a CLAUS. ELTZIEN. $\begin{cases} Co \\ H, \end{cases}$ $\left. \begin{array}{c} \mathbf{H}_{5} \\ \mathbf{Pt} \end{array} \right\} \mathbf{N}_{2}. \mathbf{HCl}.$ GERHARDT SCHIFF NH₂ Cl NH₃-Cl NH_a.Cl Cl NH Platosamminchlorid, Platosamminchlorid. **BLOMSTRAND-JÖRGENSEN** WERNER Figure 2. Sample structures of metal amine complexes

cepted chain theory of Blomstrand and Jørgensen (14). When Reitzenstein began his habilitation, Werner had just proposed his coordination theory to explain the structure of these compounds (15).

Reitzenstein's habilitation is in two parts, with the first one being a summary of the theory of ammonia complexes to that point. This was published as an article in Zeitschrift für Anorganische Chemie (16) It begins with the discovery of metal ammonia salts from Tassaert and Torbern Bergman, then platinum ammonia salts from Magnus, followed by Gros, Reiset, Peyrone, Raewsky and Gerhardt. This leads into the description of theory that starts with Berzelius' conjugate theory, followed by Graham's ammonium theory and its modifications proposed by Gerhardt, Wurtz, Reiset, von Hofmann, and Weltzien. Claus's ammonia theory is presented, as well as its challenge by Schiff. Blomstrand's concept of nitrogen-water chains equivalent to hydrocarbon chains is put forward. Jørgensen's work on metal pyridine complexes, a tertiary amine without replaceable hydrogen atoms, helped to eliminate Graham's theory from consideration. Like much of Jørgensen's research in coordination compounds, his own data on pyridine complexes would later help to support an opposing theory. Reitzenstein then goes into an in-depth description of chain theory. This half of the habilitation is actually very similar to the beginning of Kauffman's "Coordination Chemistry: History" which does an excellent job of summarizing early coordination theories (17).

Reitzenstein then presents Werner's coordination theory and compares it to chain theory. He looks at the disparities in the two theories related to ion formation in different salts, and discusses isomerization in the two theories. He goes through the extensive work that Werner had done on platinum ammonia compounds. He emphasizes the distinction between coordination number

and valence number in Werner's theory, giving particular attention to the association of volume and energy to what we now know as steric effects. He describes Werner's "spatial" coordination number of 6, and his "planar" coordination number of 4. He describes thiocarbonic compounds of Hofmann and Weide as examples of Werner's theory. He presents a summary of the compounds prepared with organic bases including ammonia, piperidine, pyridine, aniline, toluidine, dimethylaniline, and naphthylamine. He contends that the results from these compounds strongly argue against chain theory. Many of the detailed arguments between Werner and Jørgensen are outlined. He concludes by stating that Werner's theory is definitely preferable. He seems to take a swipe at Jørgensen and allies Klason and Kurnakow, by stating that it is better to point out weaknesses in a theory than to cling to the most favorable examples that fit in a given framework.

The second half of Reitzenstein's habilitation focuses on the synthetic work that he performed during this time, and was published as a separate article in *Zeitschrift für Anorganische Chemie* (18). This included the prepara-

Figure 2. Sample structures of metal amine complexes drawn according to different theories. Images combined from Reitzenstein's paper on the topic (15).

tion of twenty-eight new pyridine complexes, including bromide, chloride, and sulfate salts of cadmium, chromium, cobalt, copper, iron, lead, manganese, and nickel. He pointed out that the compounds in the series with organic bases were of the same type, and in the same ratios as those observed with hydrates and ammonia complexes. Explaining why there was a repeated occurrence in the type of compounds formed from water to ammonia to pyridine was most easily explained by Werner's coordination theory. He also synthesized a number of quinoline complexes, and recognized that pyridine complexes can have up to six organic bases incorporated per metal atom, while quinoline complexes possess a maximum of only four. This is one of the earliest direct measures of steric bulk impacting coordination number identified as such in modern inorganic chemistry.

Reitzenstein's two articles, summing to 109 pages of text, garnered attention in the scientific community worldwide. The articles were highlighted in *Science* magazine in a "Notes on Inorganic Chemistry" feature in 1898, where attention was called to Reitzenstein's habilitation as important science for American readers. The article concludes its discussion on Werner's theory with the following statement (19):

The theory is too new to prophesy whether it will meet with general acceptance, but in its application to the platinum and cobalt bases it explains much that is difficult to account for on the valence theory as ordinarily accepted.

The *Science* paper is signed simply J. L. H., with no further description, though this appears to be James Lewis Howe, professor from William and Lee University, and Bibliographer of the Platinum Group Metals (20).

These results, and a reported friendship with Werner, made Reitzenstein an ardent, and important, supporter of the new theory (21). The two papers that come directly from the habilitation were supported by two prior publications (5, 22), and a note (23) to point out how Pincussohn (24) had overlooked his prior work. Reitzenstein's only other publication on metal-pyridine complexes was in 1902, looking at pyridine salts with organic bases including acetate, chloroacetates and thiocyanide (25).

Later Work & Students

After the work from his habilitation, Reitzenstein went back to the organic chemistry roots of his thesis. The majority of the work for the remainder of his career focused on the preeminent chemical industry of the time, the production of dyes. This included work on triphenylmethane based dyes, asymmetric- α , β -naphthazines (induline precursors), benzidines, and polynitroaromatics (26-41). He was also issued at least one German patent on his chemical dye efforts (Figure 3) (42).



Figure 3. The patent issued to Reitzenstein and Wilhelm Breuning on red basic dyestuff (41).

It was during this time period that Reitzenstein was training Ph.D. students in his lab. Perhaps the most notable of these students was Otto Runge, with whom he studied triphenylmethane dyes (25). Runge was a descendent of Friedlieb Ferdinand Runge, the famous analytical chemist who identified the action of belladonna, discovered caffeine, and made the first coal tar dye—aniline green (43, 44). Otto would go on to work in the dye industry and was involved in a major industrial espionage scandal. DuPont recruited dye chemists from Bayer, and Otto was one of the "four traitors" according to German newspapers (45, 46).



Figure 4. Headline from the Bloomington (IL) Pantagraph on February 21, 1921, regarding the international incident that brought Reitzenstein student Otto Runge to the US.

Music

Reitzenstein appears to have been very active in the Würzburg Chemical Society. As a member of the *Vergnügungskomité* (amusement committee), he helped to organize the entertainment for society events. In particular, he was well-known for putting together chemistry-based musical comedies which were generally performed at annual meetings of the society.

The first comic-opera that Reitzenstein prepared for a chemical society celebration was in 1890. He wrote a chemistry-based libretto to the melody of Gilbert and Sullivan's *The Mikado*, with the costumes and wigs borrowed from the city theater (47). The lead role in *The Chemikado* was played by Emil Fischer's nephew who was studying chemistry at Würzburg at the time. Fischer was a big fan of these musical events, and when he was unable to attend the 25th anniversary celebration of the chemical society, he expressed his regrets in the form of a poem, which he included in his autobiography (48).

During the 25th anniversary celebration, Reitzenstein prepared a chemical opera entitled *Musenkinder* based upon Englebert Humperdinck's *Königskinder*, the title page of which is shown in Figure 5 (49). He contributed at least six other chemical-based musicals to Chemical Society events, including ones based upon the work of Strauss, Leoncavallo and Lortzing (50-55). One of the musicals, "X-Strahldine" incorporated X-rays as a theme, which had been discovered in Würzburg only 14 months earlier (54).



Figure 5. Musenkinder. *The title page to the chemistry comic-opera that Reitzenstein prepared for the 25th anniversary celebration of the Würzburg Chemical Society.*

Music not only interested Fritz, but a love of and talent in music also ran in his family. His brother Albert

Reizenstein, served as a medic in World War I, and then as a practicing medical doctor in Nuremburg, where he died in 1925. Albert's son, Franz Reizenstein, was a musical prodigy, who studied composition under Paul Hindemith in Berlin. He fled Germany for England to escape the Nazis in 1934 at the age of 23. In London, he trained with Ralph Vaughan Williams, and would go on to become a renowned composer. He received his greatest critical acclaim for his piano quintet in D minor from 1949. He scored eight films, including the 1959 Christopher Lee/Peter Cushing feature The Mummy. His Concerto Popolare is also well loved, where the piano soloist "believes" they are hired to play the Grieg Concerto while the orchestra is playing Tchaikovsky. He also wrote a comic opera titled Let's Fake an Opera for a Gerard Hoffnung music festival (56). These whimsical pieces relate nicely to the tongue-in-cheek nature of Fritz's chemical-comedies. Franz Reizenstein is shown in Figure 6.



Figure 6. Franz Reizenstein. Noted composer and nephew of Fritz Reitzenstein (Image provided by John Reizenstein)

Last Publications & Death

Reitzenstein's last academic publication was in 1914 (41), with the onset of World War I likely interrupting his research. He did have two further publications that did not involve the report of new data or interpretation.

In 1915, he wrote the obituaries for Ludwig Medicus in *Berichte* and *Chemiker-Zeitung* (57, 58). Medicus is perhaps best known for first identifying the correct structure of caffeine. He served as director of the royal research institute of food and beverages, and attained the rank of full professor in applied chemistry and pharmacy at Würzburg. Medicus died soon after his only son fell on the battlefield in World War I. Reitzenstein's affection for Medicus and his grief at his loss are clear in these articles.

The only other publication from Reitzenstein was a 1920 article published in *Chemiker-Zeitung* where he defended the use of chemical weapons by Germany in World War I (59). The argument was centered around France using chemical weapons first, which is nominally true because the French used tear gas early in the war, before the German use of significantly worse chemical agents. Reitzenstein's patriotism is very clear in this editorial.

His appreciation for the German state is likely to have fallen off precipitously as the next regime took over. Fritz came from a Jewish family that was greatly impacted by the third Reich. The generation below Fritz (including Franz) mostly emigrated, and a number of those who remained were deported. Fritz's older brother Ernst took his life in 1942, about the time that his daughter was deported to the Theresienstadt ghetto-camp.

Fritz died on the 19th of April, 1940, of old age. As can be seen in post-World War II documents, he died indebted, as the guarantor of an existing mortgage. In these documents, his nationality is listed as "Deutsche Reich (Juden)." There is some indication that he was a Protestant convert, and that the use of the Reitzenstein surname rather than Reizenstein might have accompanied that conversion. His death certificate was handled by a synagogic community in Nuremberg, but has a handwritten note listing him as protestant. His remains were cremated and placed in an urn in a Jewish cemetery in Lauf an der Pegnitz to the east of Nuremberg.

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THE PROTOTYPE OF MOBILE LABORATORIES FOR CHEMICAL EDUCATION

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Abstract

Recently, mobile laboratories equipped with a variety of expensive equipment have been used in the world to perform laboratory work in schools. Mobile laboratories travel to various schools and demonstrate experiments to students and teachers. This article discusses the historical facts about the world's first mobile chemistry laboratory, organized by V. N. Verkhovskiy. In 1921, despite difficult political circumstances and devastation in Russia Verkhovskiy organized the carriage-laboratory ("Wagonlaboratory") and travelled to various schools in Petersburg province. The purpose of carriage-courses was to train provincial teachers in the technique and methodology of chemical experiment. The mobile chemistry laboratory was equipped and the simplest and most affordable instruments were developed for it. The authors claim that these trips to schools were the prototype of mobile chemistry laboratory that turns one hundred years old in 2021.

Introduction

Since chemistry teaching and learning are based on experimental skills, the experimental aspect of pedagogy in chemistry complicates the logistics of teaching chemistry. Studying chemistry requires laboratory equipment and hands-on activities are a successful way to promote chemistry learning (1). Already in the 18th and 19th centuries teachers showed chemical experiments during lectures at universities. However, since work in a laboratory is a main part of the chemistry curriculum, in the 1830s von Liebig began to move from a lecture model with demonstrations to the one that included laboratory experiments (2) that emphasized the development of laboratory skills and approaches to science (3). For over a century, chemists have believed laboratory-based learning to be an essential component of school and university chemistry education (4). However, chemistry teaching is expensive for universities and this is mainly due to the laboratory experiment component, which is a major part of undergraduate chemistry degrees (5). For example, in the USA it is required for a bachelor degree to have 400 hours of laboratory experience beyond introductory chemistry (6), while in Great Britain bachelor and integrated master degrees must include 300 and 400 hours of laboratory experience, respectively (7).

Among the applications of computers to education virtual chemistry laboratory experiments have been used successfully as replacements (8, 9) or preparatory activities (10, 11) for hands-on experiments in university and college chemistry courses. It has been determined, that university students have an equally positive attitude towards actual and virtual experiments; however, data that virtual labs in grade 9 did less to stimulate interest in chemistry than real laboratories has been reported (12).

In the second half of the twentieth century, positive attitudes toward the natural sciences in the world had changed, and since then the number of students choosing natural sciences has been decreasing steadily (13). After all, chemistry and physics are the two lowest ranked subjects compared to other subjects at school in Europe and the USA (14).

At present mobile laboratories equipped with a variety of expensive equipment have been used in some places to perform laboratory work in schools, defraying expenses to the schools and increasing student engagement. Universities deploy these mobile chemistry laboratories to visit different schools and show experiments to students and teachers. Examples of such projects include those organized by IPN-Kiel (Institut für die Pädagogik der Naturwissenschaften in Kiel, Germany) (15) and Virginia Tech University. During 2000-2004, Virginia Tech's mobile chemistry laboratory went to 38 schools, and 9,100 students performed 36,200 experiments (16). It is thought that the mobile chemistry laboratory program will increase the students' motivation in choosing natural sciences. The published data suggest that the mobile chemistry laboratory influences students' measured constructs: enjoyment, frustration, current interest and boredom (15). A stationary laboratory never causes a larger change in any of these constructs. Students rated the mobile chemistry laboratory better than stationary laboratories because it was an innovation and offered greater variety of lessons for them.

The usefulness of the mobile chemistry laboratory was illustrated by the facts listed above, but the question has arisen: when, where and who was the first person to use a mobile chemistry laboratory? Therefore, the aim of this article is to identify the pioneer of mobile chemistry laboratories after reviewing historical facts.

The Russian plague control system developed by Tsar Nicholas II in the 1890s used mobile laboratories in 1921 in the fight against the plague epidemic in the Russian Far East (17). In January 1921, on the initiative of V. N. Verkhovskiy, in the workshops of the Aleksandrovskaya railway (Moscow-Brest), a carriagelaboratory ("Wagon-laboratory") was made for training of the teachers who would later train adolescent students. In the absence of equipped labs, experiments were conducted in the railway carriage (18) (Figure 1). This latter was the prototype of the pedagogical mobile chemistry laboratory.

Under extremely difficult conditions V. N. Verkhovskiy not only put forward the idea of a carriagelaboratory to help provincial teachers, but also managed to implement it albeit to an incomplete extent.

The Situation in Russia and its Schools in the Late 1910s and 1920s

In Soviet Russia, the Civil War continued into the early 1920s, and during 1920-1922 the situation in Petrograd (Saint Petersburg) was difficult. These are a few of the crises of that period:

• Aid to the starving regions (June 1921 - June 1922);

• Kronstadt insurrection (armed uprising in March 1921 of the garrison of the Kronstadt fortress, the crews of the Baltic Fleet ships and residents of the city against the dictatorship of the Bolsheviks)

• Karelian insurrection (armed uprising of local residents, who received help from Finland in December 1921 - February 1922);

- The Revolutionary Tribunal was constantly working;
- Year-round problems of providing the city with fuel ("fuel front");
- Persistent problems with food (food cards introduced);
- Help for the army ("front week");
- Typhus (1920);
- Several cases of cholera (1920, 1921);



Figure 1. Copy of the first note about the Wagon-school trip in the newspaper (18).

• Tasks were set to eliminate illiteracy ("fight against illiteracy");

• The media constantly described the environment as hostile to Russia.

Before 1918, the Russian secondary school education system included the following schools for boys: A) 440 classical gymnasiums; B) 287 "real schools" (19); C) 60 technical schools of various types; D) 260 commercial schools; E) 29 schools for cadet corps. There were the following schools for girls: F) 873 female gymnasiums; G) 14 institutes for noble maidens (20). These educational institutions were headed by the Ministry of Public Education (A, B, C, D, F), the Ministry of War (E), the Ministry of Trade and Industry (D), or the Department of Empress Mary (F, G). There were about 2,000 schools in total (21). There were many gymnasiums (male and female), "real" and commercial schools (400 in all). The term of study was 8 years; students entered the school from the age of 10 (but not later than 12). At the same time, chemistry was studied in approximately 32% of secondary educational institutions ("real," technical, commercial schools, cadet corps).

In 1918, schooling in Russia became a single general educational system, which included two levels administered by the People's Commissariat of Education. Students began attending school at the age of 8. The first-level school was for students 8 to 11 years old, and the second-level school for those 12-17 years old. By the end of the 1920s there were about 1800 schools of the second level.

Chemistry as an academic subject was introduced into all secondary schools in 1920. The classes in which chemistry was studied changed: from 1925 in the 5th and 6th grades, from 1927 in the 7th and 8th years of study.

It should be noted that almost until the end of the 1920s, teaching chemistry was rather nominal, because due to the consequences of the world war, revolution, and civil war, there were no material resources for conducting chemistry lessons and there were no qualified teachers. By the way, the population of Russia during the period 1914-1926 decreased from 175 million to 147 million. That is why the work of teacher trainers in any form (courses, lectures, congresses, carriage courses) in preparing teachers for teaching chemistry was so important. This was especially important for teachers not working in cities.

here were no qualified ation of Russia during from 175 million to 147 (teacher trainers in any sses, carriage courses) ing chemistry was so important for teachers Table 1. Information about the educational training of

Although on April 1, 1921, there were 441 schools of the 1st and 2nd level in the Petrograd (St. Peterburg) province (22), the province's budget for education in 1922 was allocated as 4 million rubles in gold instead of the 24 millions needed. In newspapers of 1919-1923 the poor state of education in general was reported. Working conditions at schools were horrendous: "Temperature in the classrooms dropped to 10

higher education	1
gymnasium	18
teacher's seminary, pedagogical courses	4
diocesan school, theological seminary	14
secondary school	34
homeschooling,	10

Level of education

incomplete secondary

teachers, Dmitrovsky district (28)

Number of teachers

In his printed publications, V. N. Verkhovskiy (Figure 2) consistently pursued the idea that the successful teaching of chemistry and physics is impossible without experiments and that without experiments the pedagogical effectiveness of teaching these subjects is lost. Among his colleagues, there was a strong opinion that if chemistry is exclusively "chalk chemistry," then it is not necessary to study it at all in the school course. The absence not only of

°C, children were freezing, they got sick with bronchitis and pneumonia," there were no textbooks, children had no shoes, and many of them wore summer homemade rope shoes even in October, or even were barefoot (23). At the same time, efforts were being made to create a new educational system, since the old one was considered to be a school of study, i.e., a school isolated from life. The school had to be responsive to life. Therefore, a vocational school was needed (24). A questionnaire was conducted in order to determine the level of teachers' qualifications, their readiness to work under the new conditions (25, 26). In addition, strategies for how to improve teachers' qualifications were considered. In summer of 1922, the Moscow Department of Public Education implemented a kind of experiment in the form of sending 1800 rural teachers (about 30% of their total number) to two-month courses, which were held at Soviet party schools (27).

Summer courses were held in seven county seats and Moscow. They were devoted exclusively to theoretical issues including ideological ones. Exact data on students of military schools (cadets) are missing. Only fragmentary information that about 50% of teachers were young people with work experience from 1 to 5 years is available. There is information only about the level of education of teachers from one group (Table 1) and the conclusion can be made that this level was very low. classrooms and laboratories, but also of a minimum set of elementary manuals in almost all schools (both rural and urban) prompted Verkhovskiy to create the carriagelaboratory.



Figure 2. V. N. Verkhovskiy (1873-1947), photo 1938.

Realizing that in the coming years, the supply of schools would not improve and, in this regard, it would be necessary to temporarily abandon practical work and laboratory lessons, Verkhovskiy believed that even under these conditions it was necessary to make every effort to conduct chemical experiments. In his opinion, it was necessary to simplify the devices and manuals used as much as possible, and try to make the devices on the spot even by the teacher himself. He noted that the simplification of the experiment within certain limits did not contradict the methodological requirements. For several decades, flasks, funnels, spirit lamps, beakers, files, soldering irons, and

glass tubes had been widely available, and at that time they had become jewels that a teacher could only dream of. At the same time, there was a problem related to the fact that a very small number of teachers (primarily provincial) were prepared to carry out the experiments, that especially among the young people the number prepared to do experiments were few. Most often, teachers' knowledge of conducting an experiment was purely theoretical (29) (Figure 3).

To solve this problem Verkhovskiy with the support of the Department of Pedagogical Education of Petrograd Professional Education organized mobile laboratories. Everything needed for their work was placed in a specially equipped carriage, which was a laboratoryworkshop and in which classes were conducted with course

OBDEMEMMAS

Figure 3. Cover of the book in which V. N. Verkhovskiy's first instructions on a chemical experiment were printed (29).

Experimental Base of the Carriage-Laboratory

Verkhovskiy shared his experience of the experiments in the carriage-laboratory in an article (29), which was accompanied by 38 drawings of the simplest apparatus and devices that the teacher himself could make.

> Verkhovskiy then described in detail those simple devices and apparatus that was necessary for conducting a school demonstration experiment in a course about inanimate nature, in which course participants were taught specific methods of work. Some of these devices and simplifications were specially prepared by him for the carriagecourses. If there was a possibility that the device was available in a variety of forms from different manufacturers. then the teacher trainee was introduced to the methods of working on all samples of this device. At the same time, they made their own devices and demonstrated to the rest of the class how to perform the experiment with this device. Along the way, teacher trainees were given methodological instructions regarding the use of experiment in teaching. It was assumed

participants. Due to the fact that the carriage moved around the area, it was possible to cover a larger number of teachers with coursework than in stationary courses. The goals of the carriage-laboratory were (29): 1) to help teachers; 2) to teach them the most important techniques of work necessary to create the simplest devices from scrap materials; 3) to acquaint them with some examples of simplifications that could be used in the absence of the preferable equipment; 4) to show the path along which they could move in the future independently developing their inventiveness. To achieve these goals, a mobile chemical laboratory was equipped and the simplest and most affordable instruments were developed for it. that the teacher, who was familiar with the methods of work, in the future would be able to vary the device design himself and conduct the experiments he desired.

If the device was complicated and was not available at school, then work with it was not considered (e.g., experiments with a mercury barometer). At the same time, Verkhovskiy noted that the teacher needed a certain minimum number of auxiliary aids, without which it would be difficult or even impossible to carry out the experiment, and it would not be possible to prepare them on his own. This list included glass tubes, corks, rubber, thermometer, wire, file, pliers, knife, and scissors (at the same time Verkhovskiy noted that it was desirable that such a set could be received by every enrollee in the carriage-laboratory). Of course, this activity did not substitute the responsibility of the local education authorities for the material support for the chemistry classroom—only in this case, teaching would gradually be raised to the required level.

The article (29) consists of three sections: 1) description of experiments, 2) auxiliary aids; 3) methods of work, which were taught to teacher trainees.

1) In the section "Description of experiments" Verkhovskiy, in addition to describing the manufactur-



Figure 4. Diagrams of devices from (29).

Device or experiment name	Device number in Figure 4		
Beaker (making from a test tube or lamp glass and fixing it)	1 а-д, 2		
Simplified beaker for determining the volume of solids	2		
Communicating vessels, fountain	3		
Elongation of the wire when heated	4 a and б		
Elongation of various bodies when heated	5		
The heated object expands in all directions	6		
Liquid expansion when heated	7 a and б		
Expansion of water upon freezing	8 а, б, в, г		
Thermal conductivity	9 a and б		
Air takes up space	10		
Air displacement with water	11 a and б		
Stirrer	12		
Pump	13 а, б, в		
Compressed air pressure	14 a and б		
Dependence of air elasticity on temperature	15 а, б, в, г		
Air mass	16		
Atmospheric pressure	17 а, б, в		
Sand filter	18		
Water distillation apparatus	19		
Device for producing carbon dioxide and hydrogen	20 а, б, в, г		
Pneumatic bath	21 a and б		
Device for obtaining and collecting oxygen	22		
Homemade oxygen burning spoon	23 a and б		
Air composition	24		
Rusting iron consumes air	25		
Dry distillation of wood	26		

Table 2. The names of the experiments and their numbers on the diagram (Figure 4)

ing of devices (Figure 4), provided a list of experimental procedures, and also gave a description of the auxiliary aids necessary for the devices and demonstration of experiments (Table 2).

Table 3. The names of the experiments and their numbers on the diagram (Figure 4 or 5)

Name of auxiliary aid	Device number in Figures 4 and 5
Heating sources	27 - Fig. 4
Tripods and trivets	28, 29 - Fig. 5
Scales, weights, tweezers	30 - Fig. 5
Clamp for rubber tubes	31 - Fig. 5
Blowpipe	32 - Fig. 5

2) The names of auxiliary aids are presented in the Table 3.

3) This section provides descriptions of both the work and the tools and devices necessary for their implementation:

•Glass work (cutting thin glass tubes, bending, pulling, and cutting thick tubes and bottles) (33, 34 - Figure 5);

•Work with corks (crimping with a board and on a cork mill, burning holes, drilling and waxing). Handling rubber tubing. Handling chemical glassware (35, 36, 37 - Figure 5);

Wood processing;

•Metal processing (38 - Figure 5);

•Handling tools.



Figure 5. Diagrams of auxiliary aids from (29).

Without fail, course participants prepared solutions, glue, labels, washed dishes, collected and tested devices, demonstrated experiments (as they would later after the lessons). Verkhovsky was a chemist who was interested in many branches of chemistry. His scientific achievements in the study and teaching of chemistry are briefly described below.

Verkhovskiy invented, developed, perfected and tested a set of experiments and instruments during the decades of his work. Some of them have kept his name in their titles: V. Verkhovskiy's ozonator, the test-tube of Verkhovskiy-Sozonov, Verkhovskiy's Tripod, and Verkhovskiy's eudiometer (30, 31). Later, Verkhovskiy developed the technique and methodology of chemical experiments and published textbooks of experimental chemistry (32, 33). These books were famous also abroad. In 1957 they were translated to Polish, and in 1962–1963 they were published in Japanese.

It is important to note that in 1910-1930 Verkhovskiy established the direction for many other methodologies for 40-50 years within the Russian pedagogy of chemistry (33). Note that the knowledge of foreign languages (Russian, German, English etc.) substantially widens the pedagogy of chemistry and allows the teachers to work significantly more productively on the issues of improvement of teaching their subject.

At the beginning of 20th century Verkhovskiy worked at the scientific-technical laboratory of the Russian Navy Office. He was also involved in scientific research together with future academician V. N. Ipatieff (34). Verkhovskiy had been working in Tenishev commercial (private) college for 25 years since 1906. There he created the chemical laboratory according to the highest standards of the second half of the 20th century: the laboratory was equipped with cold and hot water, gas supplies and working ventilation chambers. On the college grounds he undertook the course preparations for the teachers and lessons for the students of the Pedagogical Academy.

Verkhovskiy was an assistant at the Women's Pedagogical Institute together with Ipatieff. In 1918, Verkhovskiy was invited to take a position of a head of the Department of Inorganic Chemistry at the newly organized Pedagogical Institute in Petrograd, which was transformed from the Women's Pedagogical Institute. In 1922 he was approved as a professor, and in 1938 he was awarded, based on a set of works without defending a thesis, the scientific degree of Doctor of Pedagogical Sciences. He became the first doctor of pedagogical sciences in the history of Russia in pedagogy of chemistry. Under the leadership of Verkhovskiy, the first Soviet curriculum for a systematic course in chemistry was developed. He wrote the first Soviet textbooks on inorganic and organic chemistry (35-37) and wrote guidelines for teaching chemistry (38-43). In 1927, the first two editions of Chemical Alphabet (44), based solely on his experience as a secondary school teacher were published. Chemical Alphabet included a set of cards, as well as guidelines, not only for teachers, but also for school students. In

1930s Prof. P. Lebedev (45) perfected Verkhovskiy's cards, which enabled a better understanding in writing the graphical formulas. The improved cards were used in the modern Russian school textbook (46).

Verkhovskiy designed and developed a new type of training manual, which were named "model-chart" of chemical plants. Model schemes allowed students to understand more easily the principles of a production device (better than the drawings). The following modelschemes were issued and applied in schools: production of sulphuric acid (47), production of hydrochloric acid (48), gas plant and an open-hearth furnace (49). In 1935, with his student A. N. Kokovin, he created the following training educational films: "Steam-iron Production of Hydrogen," "The Use of Hydrogen," "Liquid Air and Oxygen: Production and Use," "The Nitrogen Cycle in Nature," and "The Production of Hydrochloric Acid and Sodium Sulfate" (50).

Conclusions

Recently universities have begun offering a variety of chemistry outreach programs to increase interest in science. Knowingly or not, they echo some of Verkhovskiy's practices. For example:

Teachers' workshops. During summer workshops, teachers are trained in chemistry theory, chemistry pedagogy and laboratory experiments. The evaluation of the seminars showed that teachers' knowledge in chemistry and chemistry pedagogy increased and students in schools were better prepared for standardized state chemistry exams (16). In Lithuania in the period of 2000-2017, during the school year teachers were able to share their experience and improve their pedagogical qualification at the international teachers' conference "Chemistry at School" (organized by Prof. A. Šulčius) at Kaunas University of Technology. These conferences were attended by teachers and lecturers from Lithuania, Latvia, Poland, Russia, and Belarus. During the teachers' conference, a chemistry competition of academician J. Janickis was organized for students of grades 8-12. During the pandemic outbreak of COVID-19 disease in 2020, a distance competition was organized in which 440 students from 84 schools participated.

Sets of simple chemistry laboratory kits and experiments. Lack of laboratory equipment for the school chemistry program motivated universities to prepare sets for simple chemistry laboratory experiments, e.g., the ChemKits program. ChemKits was prepared by Virginia Tech University and students in 33 high schools performed 23,450 experiments in the period of 2002-2004, whereas in 2004-2005 ChemKits were conducted at 17 high schools (16). As an alternative approach, another path was chosen in Lithuania: 8th-12th grade students from schools all over the country can arrive to Kaunas University of Technology during the school year and perform three selected laboratory experiments out of 50 offered. In 2019-2020, this program included visits of 2,050 students from 105 schools.

In 1921, Verkhovskiy was able to organize several rail courses in the mobile carriage-laboratory, which were accompanied by tremendous success and showed that the idea of the carriage-laboratory was quite effective. Nevertheless, for reasons beyond the control of the organizers, further courses were stopped, and the full potential of this undertaking was not realized.

Despite the poverty of the experimental base compared to the modern mobile chemistry laboratory and the simplicity of the goals set, the Verkhovskiy carriage-laboratory (wagon-laboratory) is considered to be a prototype of mobile chemistry laboratories. The authors claim that these rail courses were the prototype of the mobile chemistry laboratory that turns one hundred years old in 2021.

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2021 Citation for Chemical Breakthrough Awards

Three papers were selected for Citation for Chemical Breakthrough awards in 2021. HIST has made these awards since 2006 under the direction of Jeffrey I. Seeman, the program's founder and non-voting committee secretary. The term "breakthrough" in the award title refers to advances that have been revolutionary in concept, broad in scope, and long-term in impact. Plaques are presented to the departments and institutions at which these breakthroughs occurred for display in their classrooms or corridors. The purpose of the plaques, according to Seeman, is 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 2021 awardees span a century:

- * J. Willard Gibbs, "On the Equilibrium of Heterogeneous Substances," *Trans. Connecticut. Acad. Arts Sci.* **1878**, *3*, 108-248; 343-524.
- * Kenichi Fukui, Teijiro Yonezawa, and Haruo Shingu, "A Molecular Orbital Theory of Reactivity in Aromatic Hydrocarbons," J. Chem. Phys. 1952, 20, 722-725.
- * R. Noyori, T. Ohkuma, M. Kitamura, H. Takaya, N. Sayo, H. Kumobayashi, and S. Akutagawa, "Asymmetric Hydrogenation of β-Keto Carboxylic Esters. A Practical, Purely Chemical Access to β-Hydroxy Esters in High Enantiomeric Purity," J. Am. Chem. Soc. 1987, 109, 5856-5858.

The treatise-length paper by Gibbs is a landmark in chemical thermodynamics, defining and analyzing the quantities known today as chemical potential and free energy.

The paper by Fukui and coworkers recognized the relevance for chemical reactivity of a molecule's highest occupied and lowest unoccupied molecular orbitals. Frontier Molecular Orbital Theory was later successfully applied by Robert Burns Woodward and Roald Hoffmann in determining the stereochemistry of electrocyclic reactions. Fukui and Hoffmann shared the 1981 Nobel Prize in Chemistry.

Ryoji Noyori was also recognized with a Nobel Prize in Chemistry—shared with William Knowles and Barry Sharpless in 2001. The Citation award paper by Noyori and coworkers represents a very early example of catalytic asymmetric synthesis. Catalysis in asymmetric synthesis has continued to be at the forefront of synthetic organic chemistry, as was recognized by the 2021 Nobel Prize in Chemistry as well.

PIONEERING MOLECULAR MODELS FOR CYCLOALKANES BY DERX IN BÖESEKEN'S LABORATORY AT DELFT, A CENTURY AGO

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Abstract

Spatial insight is essential in many fields of chemistry. Therefore, three-dimensional models are indispensable tools both in chemical education and research. Already in the early days of spatial thinking in organic chemistry, Henri Derx constructed such models, which were important in the pioneering research that was carried out on the conformational analysis of cyclic compounds in the group of Jacob Böeseken at Delft. In this paper, this work of Derx and his doctoral advisor Böeseken is put in a historical perspective. Furthermore, the careers of these two chemists is followed after their joint research on conformational analysis.

Introduction

Models of molecular structures have long been important in chemistry. Until the second half of the nineteenth century, structures were pictured two-dimensionally in a shorthand manner: atoms were represented by their symbols and bonds by dots or lines between them. In 1874, van 't Hoff was the first to point out that this two-dimensional approach was inadequate to explain, for example, the occurrence of the two forms of lactic acid with opposite optical rotations. In his famous publication "La chimie dans l'espace," he proposed that the carbon atoms in saturated hydrocarbons are surrounded by four monovalent groups located at the four vertex corners of a tetrahedron (2).

Van 't Hoff used tetrahedra made of cardboard to illustrate his stereochemical theory. These van 't Hoff models (see Figure 1) allowed one to assemble, for example, the two isomeric forms of lactic acid and the three isomeric forms of tartaric acid. At that time, most organic chemists used commercially available molecular models designed by the Ghent professor Kekulé, in which the tetrahedral atoms were represented by spheres, which in the case of carbon were provided with four tetrahedral rods. The spheres were connected by a flexible coupling of the rods. In 1885, probably based on such a model, Baeyer came up with the, as we now know, erroneous hypothesis that the carbon atoms of cyclic hydrocarbons always are co-planar (3, 4). For cyclohexane, for example, this is only possible in a highly strained system with kinked C-C bonds (see Figure 2). In 1890, Sachse proved mathematically that, with tetrahedral carbon atoms, two forms of cyclohexane can be constructed free from angle strain, which both are non-planar: the rigid chair conformation with D_{3d}-symmetry and a set with an infinite number of flexible boat conformations having lower symmetry. He assumed that the chair conformation was the most stable one (5-7). In his publication, Sachse recommended his readers to construct cardboard models analogous to Van 't Hoff's to visualize this (see Figure 3). Sachse's theory was supported by Mohr (8), who demonstrated in 1918, on the basis of X-ray data reported by Bragg and Bragg (9), that the cyclohexane chair is the main structural motif in diamond. Moreover, Mohr proposed that the chair and boat forms interconvert in cyclohexane (8). However,

little attention was paid to Sachse-Mohr's theory until about 1950. Usually, Baeyer's planar conformation was considered to be the effective structure as the result of averaging of conformations, because at that time, it was not understood that the preference for a particular conformation would have any chemical consequences (10, 11).



Figure 1. Tetrahedral elements used by J. H. van 't Hoff to construct molecular models. Preserved in the Boerhaave Museum, Leiden, The Netherlands.



Figure 2. Kekulé model of the structure of flat cyclohexane as proposed by Baeyer. Note the kinks in the middle of the C–C bonds. Reproduced with permission from Ref. 4.



Figure 3. Cardboard models according to Sachse of cyclohexane chair (left) and boat (right) conformations. From J. M. McBride (12).

The Delft School of Böeseken

Jacob Böeseken (1868-1949) was born in Rotterdam (the Netherlands) as a son of a well-known portrait photographer. Through his father's profession, he became acquainted with chemistry early on. He had his secondary education in Rotterdam at the "Hoogere Burgerschool," a practically oriented education for higher functions in industry and trade, and after that, he studied chemical technology at the Polytechnische School Delft under the supervision of Prof. S. Hoogewerff. At that time, access to a Ph.D. degree at a Dutch university required knowledge of the classical languages Greek and Latin, which were not taught at the schools that Böeseken had attended. Prof. Holleman of the University of Groningen (The Netherlands) helped him out by appointing him as his assistant. Through this detour, Böeseken received his Ph.D. (with the qualification magna cum laude) in 1897 at the University of Basel (Switzerland) on organic chemical research that he had conducted in Groningen with Holleman as Ph.D. supervisor. His thesis was entitled: "Über die Einwirkungsprodukte der primären Amine auf die Dinitrosacyle." After obtaining his Ph.D., Böeseken wanted to start a family, but that was financially not feasible with the low salary that Holleman was able to pay him. Therefore, he accepted a better-paid job as a chemistry teacher at the "Hoogere Burgerschool" at Assen (the Netherlands) in 1898. In the little spare time he had there, he was amazingly able to conduct pioneering research into Friedel-Crafts acylation of aromatics, an early example of catalysis in organic chemistry (13). In 1905, he returned to Groningen to become a reader (associate professor) in charge of the education of freshmen. Teaching left him not much time for research, a situation that worsened by a fire that destroyed the chemical laboratories in Groningen completely.

In the meantime, in Delft, his former mentor Hoogewerff and Jacob Kraus, a professor in hydraulics, managed to get the Polytechnische School Delft upgraded to a technical university (at that time named Technische Hoogeschool Delft) with a strong chemistry faculty. In 1907, Hoogewerff, who was rector of the young university, retired and Böeseken was appointed as his successor as a full professor in organic chemistry. At Delft, Böeseken developed into a versatile research leader. He was unique for his time in making stereochemistry the basis of his research as well as his teaching. In 1915 in the preface to the syllabus of one of the organic chemistry courses that he taught (14), he wrote "First of all I have selected stereo-chemical subjects, where stereochemistry means the relationship between materials and our understanding of the geometry of the molecules and the atoms.... Some of these relations, such as catalysis, unsaturation, and ring strain are treated in the various chapters." Catalysis, especially with AlCl₃, remained an important research item. He continued his research on catalytic acylation, which resulted in a series of 20 publications. The gifted Ph.D. candidate H.J. Prins discovered in 1912 the catalytic addition of small polyhalogen compounds,

such as chloroform, to polyhalogen systems such as tetrachlorethylene. Serendipity played a role here. The conversion was called the Prins reaction. A second Prins reaction was found a few years later: the catalytic addition of carbonyl compounds such as formaldehyde to olefins, such as isobutene. This reaction has industrial relevance. Prins is one of the few people with two name-reactions. A second topic of Böeseken's research was oxidation with peroxy compounds such as peracetic acid with the oxidation of 1,2-dihydroxybenzene by peracetic acid to muconic acid as a highlight. (See Figure 4, the structural formulas on the blackboard.)



Figure 4. Böeseken lecturing on the oxidation of phenols to muconic acid by peracetic acid (1932).

Another important research area of Böeseken and his-coworkers was the systematic study of interactions between polyhydroxy compounds (e.g., sugars) and boric acid by conductivity measurements. The aim was to assign the spatial structure of sugars. They found that the acid strength of boric acid and thus conductivity increases, when oxygen atoms of neighboring hydroxyl groups of a polyhydroxy compound can bind to the boron atom of borate. It appeared that this effect only occurs if the conformation of the polyhydroxy compound is such that two neighboring hydroxyl groups can bind to borate without too much reorganization, in other words, if the hydroxyl groups are pre-organized for binding the boron atom. In the period 1920-1924, Böeseken guided several brilliant Ph.D. students (also known as the Delft School) with ideas that were far ahead of their time. They investigated, amongst others, the interaction of boric acid with dihydroxy derivatives of cyclic hydrocarbons as model substances for sugars.

Aside from the conformational research, they worked on synthesis of derivatives of polysaccharides, including cellulose and starch.

The Molecular Models of Derx

With conductivity measurements on boric acid and diol systems of saturated 5- and 6-membered rings, Ph.D. candidate Henri Derx (1894-1953) was the first to provide experimental evidence for the correctness of the then forgotten Sachse hypothesis (15, 16). He used molecular models manufactured by an instrument maker of the faculty. One of these models (a cyclohexane chair) has been preserved and has been on display in the corridor of the Organic Chemistry Laboratory at Delft for many years (Figure 5) (17). Derx's models consisted of wooden tetrahedra, representing the carbon atoms, with brass bars pointing from the corners. Hydrogen atoms were assumed to be located at the free ends of carbon-bonded brass rods, while oxygen atoms were represented by spheres. It is important to note that the C-C bonds, unlike those in Kekulé models, could not kink and were also freely rotatable. By manipulation of these models, Derx was the first to experience the sensational feeling that the chair conformation is rigid, but that, after overcoming some resistance, it loses its rigidity and flips into the very flexible boat conformation. Somewhat later, in collaboration with the Delft professor of thermodynamics F. E. C. Scheffer, Ph.D. student P. H. Hermans demonstrated from equilibrium reactions of the respective diols with acetone (a reaction somewhat analogous to the boric acid interaction) and with force field calculations avant la lettre that the chair is indeed the most stable conformation. In a lecture, Böeseken summarized these findings as follows: "In the saturated ring-shaped molecules with six and seven carbon atoms the ring-forming atoms are not fixed in one plane, but they lie tension-less in a curved surface, which travels through space in undulatory movements" (18).



Figure 5. Derx's models of cyclohexane chair (left) and boat (right) (16).

The Later Development of the Conformational Analysis of Cyclohexane

The work of the Delft school had the same fate as that of Sachse: it hardly received any response from organic chemists and disappeared into oblivion. Although the experimental support of the hypothesis of Sachse provided by Mohr and Derx were very convincing, most organic chemists stuck to the theory of Baever that all cycloalkane rings are planar. Around 1950, when much more had become known about chemical bonding and after Hassel had proven the cyclohexane chair conformation by electron diffraction (19), the interest in conformational analysis increased sharply, especially in the then-popular steroid research field. In 1950, Barton published an article about steroid conformations in the fairly obscure journal Experientia (20), in which he drew many conclusions regarding cyclohexane derivatives, which had been suggested by the Delft school almost 30 years earlier. It is noteworthy that Barton had models made for his research by a watchmaker (21) which surprisingly

resembled very much those of Derx (see Figure 6). Barton and Hassel received the Nobel Prize in 1969 for their work in developing conformation analysis. Barton later wrote to Derx's friend Hermans: "The question why the work of this school [the Delft school] was not well appreciated is an interesting one. I think myself, that theoretical treatment only becomes well accepted if there is a real need for a large body of chemists to use it" (22). Based on Barton's molecular models, the Dreiding models were developed, which were commercially available until about 2015. Nowadays generally computer models are used, for which reasonably good freeware can be found on the internet.

At present, it is generally accepted, on the basis of experimental results, that the stabilities of cyclohexane conformations are determined not only by angle strain but also by other effects. The chair and boat are equally angle-strain free, but particularly their non-bonded steric interactions differ significantly (10). Actually, the perfect boat (C_{2v} symmetry) appears to be a transition state between two twist-boat conformations (D_2 symmetry, see Figure 7). The energy difference between chair and twist form is about 21 kJ/mole and that the energy of the true boat is about 4 kJ/mole higher than that of the twisted form.



Figure 7. Schematic representation of the cyclohexane conformations and their energies. The hydrogens have been omitted for clarity.

Böeseken's Boric Acid Method

With the boric acid method that he developed, Böeseken determined the position of hydroxyl groups in a large number of sugars. He clarified, for example, the configurations of α - and β -D-glucose (23, 24). This is probably the first research on conformational analysis and of molecular recognition of sugars. He also gained a great deal of insight into the mechanism of the mutarotation of these sugars. In the year of his death, he summarized his extensive oeuvre in this field in a much-cited review article (24). The work forms the basis of boric acid chemistry, which has found a wide variety of applications, including catalysis, petroleum exploration, glucose sensors (for diabetics), and anti-cancer agents such as the boric acid derivative bortezomib (25).



of his molecular models, constructed

around 1950. The photograph

originates from Cushing Memorial

Library and Archives, Texas A&M University.

The Scientific Heritage of Böeseken

Böeseken supervised 47 doctoral candidates and thus occupies a top position in the list of Delft Ph.D. supervisors. Many of his students found jobs in industry, where they played a major role in the development of the emerging Dutch chemical industry. For example, P. H. Hermans, who was involved in the research on the interaction between polyhydroxy compounds and borate, was appointed at the just founded "Algemene Kunstzijde Unie" (at present AkzoNobel), where he conducted fundamental research on cellulose and finally became director of the research laboratory.

The influence of Böeseken on the Delft research is still noticeable to this day. Spatial aspects were and are always important issues in the research. For example, Prof. Wepster conducted thorough studies of steric influences on mesomerism (26). The conformations of cyclohexanes and bicyclo[3.3.1]nonanes were extensively investigated by NMR in the 1960s and 1970s in the groups of profs Wepster and van Bekkum (27, 28). Steric factors also played a major role in the later research on zeolites in the van Bekkum group, again supported by "home-made" models (29). The research on boric acid and derivatives was picked up in the 1980s by the van Bekkum group. A recent highlight is the design of a tumor-selective phenyl boronate-based MRI contrast agent (30).

Henri Derx, a Multidisciplinary Scientist in a Turbulent Era

The Delft University of Technology emerged from the "Royal Academy for the education of civilian engineers," which was founded in 1842 by King William II of the Netherlands. This academy was intended to stimulate the industrial revolution, both in the home country and in the colonies. Böeseken was the first professor of organic chemistry after it received its academic status and was renamed as Technische Hoogeschool Delft. Around 1900, many children of colonists in the Dutch East Indies enrolled and about a third of all graduates found employment over there. This is exemplified by the two brothers of Jacob Böeseken, who also graduated from Delft: one became director of a quinine factory in Bandung (in what is now Indonesia) and the other played an important role in the sugar industry of Java. Remarkably all Ph.D. students of the Böeseken group that were involved in the research on the borate-diol interactions originated from the Dutch East Indies. Typically, Henri Derx was born from a line of colonial servants (31);

his grandfather was one of the founders of the railway network in Java. He was an exceptionally bright Ph.D. student, who was able to complete his Ph.D. research in only one year with a thesis that was published in full in an issue of the Recueil des Travaux Chimiques des Pays-Bas (15). After that, he did not return to the East Indies but he accepted a job at Calvé, a food industry based in Delft, which obtained its raw materials mainly from the East Indies. During that time, he became an expert in food chemistry and biochemistry and performed research often in collaboration with Prof. A. J. Kluyver of his alma mater. In 1928, Calvé was taken over by Unilever, which resulted in fewer research opportunities for Derx. To compensate for that, he started to grow and study orchids, which made him a worldwide recognized authority in that field. In the period 1939-1940, he served as an officer in the Dutch army (Corps Grenadiers), and during the German occupation, he performed biochemical work on food processing, on oxidative enzymes, on the production of Provitamin A and the nutritive value of palmitates and stearates. He was imprisoned for a short time in a German concentration camp at Vught (the Netherlands). After the war, he was sent to Java as a head of a nutrition team of the Netherlands Red Cross, where he developed various biochemical procedures and produced baby food from milk powder. Somewhat later, he was appointed as a professor and head of the Treub Institute at the famous botanical gardens in Bogor (Java), which was left in chaos by the Japanese occupiers. There he performed microbiological research. In those years, an independence struggle was going on in Indonesia, which ended with its recognition as an independent state in 1949. A year later, Derx repatriated and became an advisor of the Shell Research Laboratory in Amsterdam, where he was involved in the start-up of a microbiology department.

Conclusions

The development of stereochemistry in the period 1870-1960 parallels the evolution of physical molecular models as tools. Van 't Hoff applied simple cardboard models (Figure 1) to illustrate his ideas about the three-dimensional structures of molecules. Sachse demonstrated with similar models that cyclohexane is not flat, although these cardboard models actually are rather inconvenient for that purpose. He needed further support from rather complex mathematical calculations. The generally used alternative ball and stick molecular models of Kekulé (Figure 2) had a flexible connector in the middle of the bonds that allowed kinking and consequently also led to the easy construction of flat cycloalkane rings supporting the incorrect hypothesis of Baeyer.

Derx and later Barton constructed models that had stiff C–C bonds that allowed rotation around those bonds. These models convinced Derx that the Sachse hypothesis is correct and maybe, more importantly, led him to the conclusion that "with such a model one can clearly demonstrate the phenomena of rigidity or flexibility of such a ring, while it is almost impossible to describe them" (15). It helped him also to prove the correctness of the Sachse-Mohr hypothesis with the use of borate-diol interactions. This work was published in a 31-page article in French (15). Its rather difficult accessibility may have contributed to the lack of response by the organic chemistry community. The insights of Sachse and Mohr were neglected as well for the most part. A possible reason for this may be that organic chemists in the first half of the twentieth century were reluctant to think and communicate in three dimensions. This is illustrated, for example, by the popularity of Haworth projections that reduced the three-dimensional 5- and 6-membered rings to flat planes. This is remarkable because Haworth discussed the conformations of sugars already in 1929 in terms of the ideas of Sachse and Mohr (7). Even Böeseken used this two-dimensional representation of pyranose and furanose rings in his review article in 1949 (24).

A second reason for the very low impact of the publications of Sachse, Mohr, and Derx may be the point raised by Barton (see above) that the results of organic chemistry research up to about 1950 could generally be rationalized by two-dimensional models. This only changed with his seminal research on steroids (10, 20), which was a breakthrough that resulted in a huge boom in conformational analysis and would have been impossible without three-dimensional thinking.

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About the Authors

Herman van Bekkum was born in Rotterdam in 1932 and was emeritus professor in organic chemistry at the Delft University of Technology. He obtained his Ph.D. with Prof. B. M. Wepster on a thesis entitled "Studies on Cyclohexane Derivatives." After some years at the Shell laboratory, he was appointed at Delft. In the tradition of Böeseken, he was active in the fields of sugars and catalysis, the latter particularly with the use of zeolites and ordered mesoporous materials. In 1975 and 1976, he served as rector of the Delft University of Technology. He supervised 77 Ph.D. students and was a member of the Dutch Academy of Sciences. Prof. van Bekkum died from COVID-19 just after finishing the work on this manuscript on November 30, 2020.

Joop Peters was born in The Hague in 1944. He obtained his Ph.D. with Prof. H. van Bekkum on a thesis entitled "Synthesis, Configurational and Conformational Analysis of Some Types of Cyclohexane and Bicyclo[3.3.1]nonane Derivatives." He remained at the Delft University, where he performed research on catalysis, non-food applications of sugars (among others: sugar-borate interactions), and lanthanide-based MRI contrast agents. He has been involved in several European research networks, two of which as chairman.

Davy Notebooks Project

Researchers at Lancaster University and the Royal Institution of Great Britain are operating a crowdsourced project to transcribe and digitally preserve seventy-five of the notebooks kept by Sir Humphry Davy (1778-1829), one of the most significant figures in science and literature in early 19th-century Europe. To view and help transcribe, see www.zooniverse.org/projects/humphrydavy/davy-notebooks-project and for more information about the project, see wp.lancs.ac.uk/davynotebooks/.

GEORGE BERNARD KAUFFMAN (1930-2020): A UNIQUE CHEMIST, EDUCATOR, CRITIC, AND HISTORIAN. AN OBITUARY-TRIBUTE (1, 2)

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Supplemental Material

Abstract

An obituary-tribute is presented for George B. Kauffman, noted chemist-historian, memoirist, critic, educator, and social activist. The centerpiece of this paper is an interview I conducted with Kauffman and his wife Laurie Kauffman in 2004.

Introduction

When George B. Kauffman died on May 2, 2020, at the age of 89, he was 50 years past being Chair of the Division of the History of Chemistry (HIST) of the American Chemical Society (ACS) and 42 years past his receipt of HIST's Dexter Award. The Dexter Award, now morphed into the HIST Award, is the oldest and most prestigious lifetime achievement award in the history of chemistry. Kauffman did not rest on those laurels. He continued publishing and even in the year before his death, he published 13 papers.

In addition to HIST's Dexter Award, Kauffman received five ACS national awards: the George C. Pimentel Award in Chemical Education (1993); the ACS Award for Research at an Undergraduate Institution (2000); the Helen M. Free Award for Public Outreach (2002); American Chemical Society Legislative Action Honor Roll (2003); and Fellow of the American Chemical Society (2011). Along the way, Kauffman published some 2500 papers. He authored or co-authored four books; and he edited 12 books, many of which he translated as well. Although many of Kauffman's publications appeared in the popular press, e.g., *The Fresno Bee*, still, the list of publications includes 357 papers in the *Journal of Chemical Education*, 335 in *The Chemical Educator*, 58 in *Angewandte Chemie*, 23 in *Isis*, and eight in the *Bulletin for the History of Chemistry*, though *SciFinder* lists fewer than his listing indicates. I have not endeavored to reconcile the count.

If Kauffman really did publish some 2500 papers, and it does appear that he did (see his list of publications in the Supplemental Material), that would imply three papers each and every month, over his 70-year career. About 170 of those papers were co-authored by his (second) wife of 50 years, Laurie. And sprinkled throughout the list are other co-authors, but most of Kauffman's papers were single-authored. He was particularly fond of writing obituaries and book reviews. Kauffman always seemed to have many good things to say about the books he reviewed. I know that characteristic of Kauffman quite well: He reviewed 13 of the autobiographies in the *Profiles, Pathways and Dreams* series that I originated and edited. He was always complimentary.

With at least one exception. In his 1986 review of the book *History of Polyolefins* based on a symposium hosted by HIST, Kauffman wrote (3), *Table 1.* Notable dates and awards and achievement highlights of George Kauffman. The six American Chemical Society awards are highlighted in gray.

Year	Notable dates	
1930	Born on September 4, 1930, Philadelphia, PA	
1948	Science Talent Search, second place, Philadelphia	
1951	B.A. with honors in chemistry, University of Pennsylvania	
1952	Married Inge Solomon. Two daughters: Ruth (1958) and Judith (1961)	
1956	Ph.D., University of Florida	
1955-1956	Instructor, University of Texas	
1955	Research chemist, Humble Oil and Refining Company	
1957, 1959	Research chemist, General Electric Company	
1956	Assistant professor, California State, Fresno	
1968	Divorced	
1969	Married Laurie Papazian	
2002	Emeritus professor, California State University at Fresno	
2020	Died (age 89) on May 2, 2020, Fresno, CA	
Awards and Achievements		
1970	Chair, Division of History of Chemistry of the American Chemical Society	
1973	Outstanding Professor Award, California State University System	
1976	Manufacturing Chemists Association Catalyst Award for Excellence in College Chemistry Teaching	
1976	Chugaev Medal of the N.S. Kurnakov Institute of General & Inorganic Chemistry, USSR Academy of Sciences	
1978	Dexter Award of the Division of History of Chemistry of the American Chemical Society	
1990	Kurnakov Medal of the N.S. Kurnakov Institute of General & Inorganic Chemistry, USSR Academy of Sciences	
1991	Chernvaev Medal of the N.S. Kurnakov Institute of General & Inorganic Chemistry, USSR Academy of Sciences	
1992	Marc-Auguste Pictet Medal of the Société de Physique et d'Histoire Naturelle de Genève	
1993	George C. Pimentel Award in Chemical Education of the American Chemical Society	
1994	President's Medal of Distinction of the California State University at Fresno, inaugural presentation	
2000	ACS Award for Research at an Undergraduate Institution of the American Chemical Society	
2002	Fellow of the American Association for the Advancement of Science	
2002	Helen M. Free Award for Public Outreach of the American Chemical Society	
2003	American Chemical Society Legislative Action Honor Roll	
2011	Fellow of the American Chemical Society	

Unfortunately, in addition to the unattractiveness of the combination of various types and formats of the various papers, some of which contain free hand notations, the book is marred by other signs of hasty publication. For example, [Herman] Mark's preface contains no fewer than ten errors, and M. E. P. Friedrich is spelled four different ways on four different pages (two ways in each of two chapters) with only one page cited in the index.

I have been fascinated for several decades by the "George B. Kauffman" whom I had known only by his hundreds of publications and by his legend. So in mid-2004, I contacted George and asked if I could visit Fresno

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Figure 1. Kauffman discussing chirality and the crystal structure of one of the diastereomers of tartaric acid. At the top of the blackboard, Kauffman wrote "Pasteur 1848." Courtesy Kauffman family.

and interview him. That interview took place in his home on November 5, 2004. My vision was to publish the interview in the ACS journal *Chemtech*. But one thing led to another, and before I knew it, *Chemtech* had ceased publication. (A warning to all, especially young authors: delays can be fatal.) That interview rested quietly on my hard drive until I read of George's death. With the compelling awareness of George's attraction to writing obituaries-tributes, a vision immediately came to me. This publication is the consequence of that vision. And this paper is now a debt repaid.

Kauffman was also a *bona fide* chemist, with almost 80 papers in *Inorganic Chemistry*. He was a *bona fide* historian of chemistry. He was a *bona fide* chemical educator (Figure 1). He was also a book critic and an obituarist. His productivity did not diminish, even in his late 80s. Ten of his last 13 papers, all published in 2019, were, in Kauffman's own words, *Obituary-Tributes*. It is thus fitting that this paper borrows from Kauffman's own terminology. It is my honor to write George Kauffman's obituary-tribute.

Kauffman's Chronology

Table 1 lists notable dates and awards in Kauffman's life. Highlighted in gray are the six American Chemical Society awards that he received. These awards are quite substantial.

Kauffman's First and Last Publications and Some In Between

Table 2 lists Kauffman's first and last few publications as well as a somewhat random selection of nonscientific publications during the entire course of his professional career. Some observations are immediately apparent:

• Even during his graduate school years, Kauffman was involved in publishing biographical memoirs

Table 2. Representative publications of George B. Kauffman

Kauffman's First Ten Publications^a

Year	Journal	Title
1955	J. Chem. Educ.	Frédéric Swarts: pioneer in organic fluorine chemistry (4)
1957	Chem. Eng. News	Explosion of nitrosyl chloride and acetone in the presence of platinum (5)
1958	J. Chem. Educ.	Stability of solutions for the iodine clock reaction (6)
1959	J. Chem. Educ.	Sophus Mads Jørgensen (1837-1914)—a chapter in coordination chemistry history (7)
1960	Chymia	Sophus Mads Jørgensen and the Werner Jørgensen controversy (8)
1960	Inorg. Syn.	Copper(I) iodide (9)
1960	Inorg. Syn.	Dipyridinesilver(I) perchlorate (10)
1960	Inorg. Syn.	<i>Tri-n</i> -butylphosphine (11)
1960	Inorg. Syn.	Tris[tetrammine-µ-dihydroxocobalt(III)] cobalt(III) sulfate 4-hydrate (12)
1960	Inorg. Syn.	cis- and trans-Dichlorobis(diethyl sulfide)platinum(II) (13)
^a From J	SciFinder.	

Kauffman's Last Fourteen Publications^a

2019	Chem. Educ.	Aaron Klug (1926-2018), whose 3-D images of biological molecules won him the 1982 Nobel chemistry prize, dies at 92, an obituary-tribute (14)
2019	Chem. Educ.	Alfred Bader (1924–2018), Chemist, Philanthropist, and Art Collector, An Obituary- Tribute (15)
2019	Chem. Educ.	Sydney Brenner (1927-2019), Decipherer of the Genetic Code, an Obituary-Tribute (16)
2019	Chem. Educ.	Paul Greengard (1925-2019), an Obituary-tribute (17)
2019	Chem. Educ.	Manfred Eigen (1927-2019), an obituary-tribute (18)
2019	Chem. Educ.	Thomas A. Steitz (1940-2018), an obituary-tribute (19)
2019	Chem. Educ.	Murray Gell-Mann (1929-2019), an obituary-tribute (20)
2019	Chem. Educ.	Less Is More: Samuel Hahnemann, Physician, Chemist, Translator, and the Founder of Homeopathy (21)
2019	Chem. Educ.	Products of Chemistry: the Other Wyeth: Nathaniel Convers Wyeth (1912-1990) and the Poly(ethylene terephthalate) Bottle (22)
2019	Chem. Educ.	Marcel Delépine (1871-1965): A Versatile, Long-lived French Chemist (23)
2019	Chem. Educ.	Dr. Boom: Hurbert Newcombe Alyea (1903-1996), America's Master Lecture Demonstrator (24)
2019	Chem. Educ.	Leo A. Paquette, Master of Total Synthesis (1934–2019), An Obituary-Tribute (25)
2019	Chem. Educ.	Kary B. Mullis (1944-2019), an Obituary-Tribute (26)
2019	Chem. Educ.	John Robert Schrieffer (1931-2019), an Obituary-Tribute (27)

A Selection of Non-technical Publications from Kauffman's Intermediate Years^b

1975	Isis ^c	Discovery of Optically Active Coordination Compounds—A Milestone in Stereochemistry (28)
1980	1981 Yearbook of Science and the Future by Encyclopædia Britannica	The Science Year in Review: Chemistry: Applied Chemistry (29)
1985	Gold Bulletin	The Role of Gold in Alchemy, Part I (30)
1990	The Fresno Bee	Discovery Rich with Drama: Politics, Persistence in Saga of Carbon-14 (31)
1995	<i>The World & I: A Chronicle of</i> <i>Our Changing Era</i>	A Giant among Chemists, a Giant among Men: The Only Person to Have Won Two Unshared Nobel Prizes, Controversial Chemist, Humanitarian, Educator, and Pacifist Linus Pauling Is Considered One of the Greatest Scientists of All Time (32)
2000	The Fresno Bee	Valley Voices: Former Fresnan [George C. Pimentel] Plays Huge Role in Mapping Mars (33)
2005	The Fresno Bee	Valley Voices: Goodyear Patently Improved our Lives (34)
2010	Book: Great Lives from His- tory: Inventors & Inventions	Carl Djerassi, Austrian American chemist (35)
2015	Community Alliance	IPCC Issues "Final Word" on Climate Warming (36)
2018	Community Alliance	Book Review: <i>Candidate Without a Prayer: An Autobiography of a Jewish</i> <i>Atheist in the Bible Belt</i> by Herb Silverman (37)

Annetsi in the Bible Bett by Herb Silverman (37) ^bFrom Kauffman's own list of publications as updated by myself. See the Supplemental Material. The first citation from a non-science community publication was chosen for each time period for this table.

^cA history journal.

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of eminent chemists in the chemical literature, notably in the chemical education literature. Especially in his latter decades, he used the deaths of eminent chemists as the motivation to write necrologies and publish these in chemical education journals.

- In his initial years as an independent scholar, Kauffman continued to publish biographical memoirs as well as short pieces on methods of preparation of important inorganic compounds.
- Kauffman reported on chemists in all subdisciplines of chemistry.
- Kauffman published many news and feature articles and opinion-pieces in the non-technical literature, especially in *The Fresno Bee* and in the *Fresno Community Alliance*. Kauffman's career blossomed as he brought the history of chemistry and chemistry itself to both students and chemistry professionals and to the non-chemist as well.
- With time, Kauffman's interests and thus his publications transmuted from experimental inorganic chemistry to history and education of chemistry and to his political and social activism which was manifested in the popular press.

Kauffman also had a tendency to optimize his outreach and increase his efficiency, which added numbers to his list of publications. He often wrote more than one paper on the same individual or theme. The first instance of this appeared in his fourth and fifth publications (Table 2) on Sophus Mads Jørgensen, one in the *Journal of Chemical Education* (7) and the second in *Chymia* (8). Comparison of these two papers easily reveals significant duplication of text, an example of what is called today "self-plagiarism." Now considered a "questionable research practice" (38-42), self-plagiarism was not judged as negatively in the 1960s as it is today. But in doing so, Kauffman increased the outreach value of his writings.

Interview with George and Laurie Kauffman

Preface to the Interview

On November 5, 2004, I visited Fresno, California, and spent two days with George and his wife Laurie. What follows is a transcription of my notes from an afternoon interview with them.

George is speaking and responding to my questions (which generally do not appear in the interview). When Laurie speaks, her comments are indented and italicized for ease in identification as to who is speaking.

The interview was edited for cohesion.

Kauffman's Youth

I was born on Labor Day, September 4, 1930, in Philadelphia. My parents, ever intelligent, soon were divorced. That was very unusual for that time. I lived with Mom. She was typist with the government. My father was in politics, ran a dry-cleaning store, was into various things. I was an only child. On my father's side, no one had gone to college. On my mother's side, I had three uncles all of whom went to college.

The Kauffmans were of peasant stock, from Poland. The Fishers, my mother's side—not their real names, we have no idea of what their real name was—were from Russia. I am Jewish. Any minority feels different. I grew up in a Jewish neighborhood. Everyone was Jewish. The teachers were Jewish too. I felt different, it was paradoxical, everyone was Jewish. One day, I felt that I was going to do something different, so I went to school on a Jewish holiday. The entire school was bunched in one room.

Laurie: George was very precocious, that got him into trouble a lot.

As a youth, I was very studious. The *Studs Lonigan* books where you find dirty words ... Paul de Kruif's *Microbe Hunters* ... I read *Arrowsmith* as a teenager. On page 144, this book discussed reproduction, *The Science of Life*. Making explosions, the usual pyrotechnics. I often cut school. When I was 10, I was placed in a foster home, as my mother could not control me. After a year, I was back with my mother (Figure 2).



Figure 2. Kauffman as a young teenager and his mother, ca. 1945. Courtesy Kauffman family.

In the 11th grade, I discovered Wagner. My grades were going down. I was called down to the counselor's office and was told, "You will never get into college." That frightened me. I studied continually, I was overdone, I worried about entrance exams. I was afraid I would not get into college. I studied instead of doing everything else including girls. "Schmuck!" I used 3×5 cards to memorize. I was 16^{th} in the class, not that good, considering how hard I was working. Laurie says I am brilliant, I could question that. I work hard, which I did, which I do. Nothing came easy.

I've repressed many things. I felt so horrible, rejected ... I was thinking about Tyrone Power [the American actor who was typecast in swashbuckler roles and romantic leads] and Jessie James. There were a bunch of us in the foster home. I had siblings for one year. I was a gang leader. I did questionable things, things that today, I would characterize myself as a juvenile delinquent. The foster parents would beat us. It was the only way to have discipline, even if it was being beaten to be controlled.

I found that being contrary is a way of getting attention, acting up, acting out all those years.

Laurie: No one paid attention to him, everyone just ignored him. He always had this brilliant mind. He was in a special school in Philadelphia but was expelled for acting up.

I was setting up fireworks in the boys' bathroom. I was antisocial. I still am antisocial. Still am.

Laurie: Most of George's writings are about dead people. It's easier for George, because there is no interaction. He gets his information from the written word.

College and Graduate School

I wanted to go to the University of Pennsylvania, an old and prestigious place. I always knew I wanted to be a chemist, from the time at age of 7 when I got the Gilbert Chemistry set.

I earned a B.A. with honors, not a B.S., in 1951 from the University of Pennsylvania. I got a classical education and three years of German and a year of Italian. I was getting 100s in freshman chemistry, so I went to Lou Baker where I made coordination compounds with lots of colors. I can get them for you. I never liked organic chemistry. I memorized to get through. Inorganic chemistry is where it is at, all these elements and colors, they have unique personalities. I applied to Indiana University and Purdue University for graduate school, but I went to the University of Florida (Figure 3) and worked with Joe Simons, the eminent fluorine chemist. It was my first time away from home, and I was feeling lonely. I was interested in the guy behind the reactions. His name was Frédéric Swarts, a Belgian chemist, who was the first to prepare a chlorofluorocarbon $[CF_2Cl_2]$. I studied his reaction. I wrote to Belgium; things were primitive then. I wrote a paper that was published in the *Journal of Chemical Education* (4, 43). It was my initial article, nothing to be really proud of.



Figure 3. The youthful George Kauffman. Courtesy Kauffman family.

I married in 1952 in Florida. Inge Solomon was the UF librarian. She was born in Germany, arrived just at the last time, in 1939 at the age of 11. We had two daughters, Ruth in 1958 and Judith in 1961, on Einstein's birthday, March 14th. In 1968, we separated.

I switched advisors to John Baxter, and I've written his obituary (44). Baxter was an educator, and I followed in his footsteps. I had heard he was a real taskmaster, and that's what I needed to get my degree. Neither of us knew much about research. My research data was scanty, and thank God for the literature that my thesis research wasn't published. *Anion-Exchange Studies of Fluoride Complexes* (45).

I was primarily interested in education (Figure 4). After receiving my Ph.D., I first went to the University of Texas as an instructor from 1955-1956. Norm Hackerman was chairman. He wanted just research. Texas was a big university on the way up, and I wanted to do education. I saw in *Chemical & Engineering News* that Fresno State was looking for a professor interested in education. So I came here in 1956. Everyone was saying that I was going to God's country. I did little travelling. I had no expectation other than teaching inorganic chemistry. There was no interview. I came as an assistant professor. My salary rose from \$4500 to \$5400, percentage-wise that was a lot.



Figure 4. Kauffman enjoying one of his lectures, ca. 1980. Courtesy Kauffman family.

Kauffman's Professional Life

The experimental research I did was inorganic syntheses and separations of isomers. All with undergraduates, two M.S. students. Almost all students published a paper. They worked during the school year and during the summer. We were funded by the Petroleum Research Fund and by the National Science Foundation. I did most of the history of chemistry by myself. I had no grand plan, one thing led to another.

Constantly I did research through my students. I received an undergraduate research award in 2002 from the ACS. I had about 58 research grants at Cal State.

I was a scientific dilettante. I was interested in teaching, not so much in research. I did not have any research pressure, in fact, it was the other way. Everyone was jealous, I was the only one doing any research, I was contrary to the system. I was doing whatever I am interested in, flitting from one topic to another, you name it, I've published on it, many of my publications I've totally forgotten.

When I first came here, it was Fresno State. Now it is CSF, California State University Fresno. The first day

of every class, I tell the students: I need your help. You perform the lecture demonstration. I give the freshman chemistry course students instructions, whatever they need, and some encouragement and advice. And they follow through and prepare the demonstrations. Sometimes the students provide a draft, and I rewrite it and submit it for publication. These freshmen are co-authors and have a publication before they are even sophomores. This has happened dozens of times.

Laurie: The satisfaction that George has gotten comes from getting the grants and the accolades. He also found a big kick when his students can perform and get accolades and awards, which they do. He's had great admiration between his students and himself over many years. He feels proud like a parent or a father.

Writing book reviews keeps me up with all kinds of things, mostly historical (Figure 5). Pick a name or a topic, and I'll have written or reviewed something about it. People think that I know far more about topics than I do. The secret of my success: paper clips. I have an upside-down Mexican hat full of paper clips. I read and write notes, even when walking the dog. There's a belt around Lucky's leash, as I must be careful about falling. Once I bumped into a parked Winnebago. I underline. Once something is read, then I use paper clips to mark papers I want to deal with. When all the paper clips are gone, I am finished. If Beethoven wrote symphonies that way ... it works for me.



Figure 5. Kauffman with two of his heroes, Harry Gray and Linus Pauling (middle), April 12, 1993. Kauffman has written about both Gray (once) and Pauling (over 40 times). Courtesy Kauffman family.

It's been years since I've been chair of HIST [in 1970]. I'm too busy writing. When you go to a meeting, you kill a week. Laurie likes the socializing, I can take it or leave it. I am not a social animal. Laurie talks with everyone, for example, even when we are shopping. I talk

to no one. We did a lot of things when we were younger. Motivation is practically everything. At one time, travelling was exciting, having symposia was exciting. We are at a different point in our lives, the last 10 years.

When you are too busy, as I am, I frequently wake up with ideas that I have had during my sleep. And I immediately come out to the study and write these ideas down. I have no goal with regard to numbers of papers. Most of the papers just evolved, no grand plan. By being a scientific dilettante, I can drop this and go to that.

Yes, most of my book reviews have been "positive"? Why? Because I realize how much work has gone into them, and I am not trying to catch them [the authors]. If the book is loaded with errors, those I mention. I try to find the positive in everything. I wish it were true in everything else in my life.

What motivates me, personally and professionally? Eighteen hundred, almost nineteen hundred papers. Who's counting? Writing is as natural as breathing. I don't analyze it, I just follow it.

Kauffman and the History of Chemistry

History of chemistry vs. chemistry: I am not an experimentalist, not good with my hands. I became interested in the humanistic aspects rather than the detailed mathematics or underlying chemistry.

Why HIST? I was interested in the history of chemistry and that was the place to go. Still is.

What is the role of history of science in the chemical profession? To add a humanistic dimension to what might be the stereotypical cold, hard science. Most chemists are interested in the history of their subject, but they don't have the time or inclination to put history at a higher priority.

Satisfaction

I do what I want, I enjoyed research. I just like writing about history. Everyone wants to be creative. What are we put on earth for other than to make something that wasn't there before? My students are my legacy. My personal satisfaction ... it is like the meaning of life ..., having fun. I do not question any further, that's it, that's the meaning of life.

Am I happy, yes. But I don't know why. I don't question things very much. This is not of concern to me because I am living happily. When you are young and have questions about the meaning of life, you are lacking something, I feel that I have it all.

We are very lucky, have all we need. We are having our best years now, we're happy.

Two years ago, I started on the treadmill: 40 minutes every day. My weight was ballooning. So I lost 25 pounds, cut down on food. Laurie works out three times a week at the fitness center. She doesn't like the treadmill.

All I do now is work, write. I have all sorts of compulsive obsessive things. I have a stop clock when I work. I found useful a constant background of TV or music. Lately, with commercials with live TV, I set it for 6 minutes and off it goes, I go back to my work.

When I am not writing, Laurie and I are together. Laurie and I are together talking about ideas and things. All this is documented. I publish everything.

Kauffman's Wife, Laurie

Laurie was born and raised in Fresno. She graduated from CSF magna cum laude in 1971 and has a teaching degree specializing in elementary school education. She was married for 18 years to her first husband, by whom she has three children (one son and two daughters). She was separated in 1961, divorced in 1968, met me in 1968 and married me in 1969. It was just really chemistry. It was just electrical, wonderful. (See Figure 6.)

Laurie: I did not take a single chemistry course. George tried to get me to sit in on a class he was teaching, but I found out I had to go back and take remedial math. I just did not want to do it.

I am always interested in the person behind what he is writing about. I wonder if he was married, had children, why was he interested in this particular thing ... I love to know why they got into this or that ... I started to ask George these questions. George found out that he could use all that information. That is how it began.

I read all the books that George is going to review. Usually I read it first, write up a blurb, mention the pages that I am interested in. George writes the only substantive draft.

George would say, "Why don't you read this and tell me what you think of it?" So, that's how it began. This is the way that George and I deal with our lives. We discuss everything. Our working together is a natural extension of our life together.

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For me, my greatest reward has been being a mother of three children. When pregnant, I felt that I was full of miracles. I've been married to George for 35 years, going to bed happy at night.

I converted from Lutheran to Judaism because I felt at the time that he and I should be one religion.



Figure 6. George and Laurie Kauffman, ca. 1980. Quoting George: "We are completely absorbed in each other." Courtesy Kauffman family.

I usually give in. Laurie's got better common sense than I do. She keeps me out of trouble. Laurie thinks of things on a different level. She is a much deeper thinker than I am. Laurie will gaze into space and comes up with all sorts of ideas. The human side.

I am more dependent on Laurie than vice versa.

Kauffman's Greatest Rewards

Feeling good about myself. Having joy in my life.

What were my most embarrassing moments? I remember several.

- One, when I wrote about Vladimir Prelog, a legend in his own time, and I call him dead -- rather prematurely.
- Another: At the first symposium I chaired, the opening speaker on the program kept on talking and talking. I failed to stop him. I was inept and knew it. The audience finally clapped to stop his talk.
- A third: At a meeting in Davis [California], my slides were not in the right orientation. After 10

minutes, it was clear that I made a poor impression. I didn't have enough time to finish.

• Fourth: I minored in bacteriology in graduate school at the University of Florida. I intended to take a course in pathogenic bacteriology. I saw three people in a room and asked, "I hear that this Emerson is a real bastard." One said, "He's not so bad." On the first day of class, there he was, the professor.

I've interacted with a lot of scientists, so even though I'm not great, I've been close to and interacted with many great minds. Most of these interactions have been positive. I've gotten to know them as three-dimensional human beings. I've been able to see the differences: some were and are warm, open feeling; others maybe more standoffish.

I am always delighted to get feedback. It is the process rather than the product. If I do get feedback, I am always surprised. Usually the feedback is positive. Years ago, I reviewed a book and said good things and the authors still found some fault with my review. I felt they had a lot of nerve, most of it was positive.

Laurie: George will say, about a new idea, "I can really dash this off." I always ask him, "Do you really want to do this?" Because we both feel like there is a limited number of years left, we have to be selective as to what we do.

I ask, 'Would I enjoy doing this task, in preference to others?'

Whenever I encountered a new name, I looked for biographical material and this led to articles.

Usually when I start something, I finish.

My advice to young scientists? Motivation is as important as knowledge. Make sure you do a good job on everything.

Laurie: Take your education seriously but be sure you enjoy yourself on the way.

Kauffman's Most Important Lessons and His Legacies

Laurie: I learned to be patient.

I could use some of that. I interrupt people, before they finish their sentences.

Laurie: To realize that life is short, so use it wisely.

I say: Stay away from toxic people ... someone like a vampire, someone who takes your energy or someone who doesn't like you.

Inspiring students. Turning-on students, especially to history through my writings.

Laurie: The best thing I've done with my life is to be a helpmate: to my children, my husband, makes me feel good to feel useful.

We like to leave something behind, hey out there, we were here. To leave this world different, a better place, because we were here.

Perhaps we are trying to show our parents. Neither George nor I was paid much attention by our parents. Get of age, make a statement, "Look what we've done."

[Interview ends.]

Conclusions

Kauffman's early years were not easy. But if we slice away perhaps the first 20 of his years and a divorce a few years later, then George Kauffman lived a life as best as he, himself, could have hoped: A soul-mate marriage of 50 years; close relationships with his two children (Figure 7) and with Laurie's three children; a professional career incorporating his loves—education and pedagogy *plus* history of chemistry—as designed by himself. Reading and writing. Spontaneity with freedom. And awards and recognition, to certify his accomplishments.

Kauffman's mode of operation was unusual, to say the least. He hardly ever published a comprehensive



Figure 7. Kauffman at his 80th birthday celebration with his two daughters, Judith (left) and Ruth, Fresno, 2010. Courtesy Kauffman family.

research publication, that is, a full paper! According to Laurie,

George was always interested in something new and found it more satisfying to have something completed. This allowed him to move on to whatever his next project would be.

George entered academia at a time where there was a lot of support for science education. His move from the University of Texas, a major academic institution in a state that was and is proud of its institutional heritages, to Fresno is an example of great foresight. Not that Fresno State was going to be a national academic force. Rather, George realized that his own passions and professional needs would mesh perfectly with Fresno State's vision and mission; that this new institution was growing, and that he would be unique and a highly valued commodity. He projected that he would have great flexibility and opportunity to teach, and to do so with his particular style that included the history of chemistry. He anticipated that living in Fresno-170 miles from Sacramento, 190 miles from San Francisco, and 220 miles from Los Angeles-would have no negative effect on his ability to make a real contribution his way. And he was right in his assessment.

It is a shame that George disengaged from the social aspects of the history of chemistry. In the midst of his career as a chemist-educator and chemist-historian, he seemed to isolate himself from face-to-face contact with the community of other chemists and chemist-historians. For example, he was Chair of HIST in 1970 and received HIST's highest award, the Dexter Award, in 1978. Yet from roughly the 1990s, he was inactive in HIST and the American Chemical Society. Hardly ever did he attend ACS meetings. His lecture entitled "History of Chemistry: A Dexter Awardee's Reminiscences on the 50th Anniversary of the Dexter and Edelstein Awards" (46) was scheduled for September 11, 2006, at the symposium Fifty Years of the Dexter and Edelstein Awards. Sadly, the lecture was withdrawn at the last moment due to health complications. And I invited George to participate in another celebratory symposium, this being HIST's 85th birthday at the 233rd ACS National meeting on March 27, 2007, in Chicago (47); he did not accept.

I guess it could be said, truthfully enough, that George's contacts were though correspondence, eventually email, and his reading and writing. Of that, there was much. I even wonder whether his move to Fresno—a rather isolated island in California's central valley—foreshadowed the nature of his future connectivity with the chemistry community. Was it the location that resulted
in that privacy? Or was it the desire for privacy and a measure of peacefulness that led George to Fresno? I believe it was the latter. Nonetheless, George and Laurie did enjoy travelling. But perhaps like so many others, they especially valued their return to home and a quiet daily life in Fresno. They both certainly welcomed me to their home with gusto and warm hospitality. I remember that clearly.

George wrote hundreds of articles published in *The Fresno Bee* and the Fresno *Community Alliance*, often dealing with his concerns about the environment, public policy and health. Nestled among his book reviews was one on Luis Granados's *Twenty Rebels Who Bucked the God Experts* (2018) and another on Herb Silverman's *An Autobiography of a Jewish Atheist in the Bible Belt*, both published in the *Community Alliance* (2018). But also appearing in the *Community Alliance* were articles on Earth Day in Fresno.

As Laurie said recently,

He never lost his excitement and interest in chemistry, but as he got older he looked at things more globally and saw what was happening to the environment and this concerned him. I know he always wrote a piece for Earth Day every year for the paper. He often wrote letters to the editor about his concerns.

George's essays were always short enough to be tempting to read. They always met his promise to be informative and entertaining. I was never surprised to see his name pop up on a paper, new or old. We now can only rely on his past, but what a past!

Coda

The most vivid memory of my visit with the Kauffman's at their home in 2004 is the stacks of books in their home and especially in their garage. I don't know how many books one can pile up, before this unstable equilibrium causes a disastrous domino effect. But surely George and Laurie were tempting the gods of calamities. I admit that I looked enviously at those hundreds of new books, knowing that I'd love to have more than several of them. Today, I wish I had taken a photograph of that ensemble. Those were pre-smart phone days, and I did not have my camera with me. So I ask you, dear readers, to imagine with me those enticing academic stalagmites.

Kauffman was a hungry professional, as all successful professionals must be in their very own ways. As a capstone to this obituary-tribute to Kauffman, the following excerpt from his review of Alan Mackay and Maurice Ebison's book *The Harvest of a Quest Eye* is presented (48).

For more decades than I care to admit I have been an avid collector of quotations and aphorisms-scientific and otherwise. And semester after semester, whenever publishers visited my office in search of salable manuscripts, my persistent inquiries about the marketability of a book of quotations-a sort of scientific Bartlett's Familiar Quotations always met with a negative reply. Now I am able to report, with an ambivalent mixture of admiration and envy, that not only is such a venture financially feasible but it has actually been done-with considerable success, in my opinion. My professional jealousy of Dr. Mackay for beating me to it is mitigated by the fact that his collection, although duplicating a number of items in my own, differs considerably from mine, thus clearly demonstrating the possibility for additional books of this type ...'

-George Kauffman, 1978

Supplemental Material

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

George Kauffman's list of publications, a working document obtained in 2020 from his grandson Nick Baron who downloaded it from Kauffman's computer. I have updated and organized this list and deleted duplications and never-published manuscripts.

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When in a reminiscent mood, Frédéric Swarts loved to tell his colleagues how he had swallowed a few cubic centimeters of difluoroethyl alcohol in order to prove the physiological inertness of this compound. This substance was only one of scores of organic fluorine compounds which Swarts was first to prepare and study with his characteristic thoroughness—compounds through which he became internationally recognized as a pioneer in this field of research.

• • •

In reviewing the life and work of Frederic Swarts, one is tempted to draw an analogy between him and his fellow countryman, the composer César Franck. Each devoted himself wholeheartedly to his art; each was a bold innovator and an original thinker; and although each did his life's work in a narrowly circumscribed physical environment, Franck in the organ loft at St. Clothilde, Swarts at the University of Ghent, each is numbered among Belgium's outstanding creative minds.

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About the Author

Jeffrey I. Seeman received his B.S. in chemistry from Stevens Institute of Technology, Hoboken, New Jersey, and his Ph.D. in chemistry from the University of California, Berkeley. He was a research chemist for over 30 years in industry and a fulltime consultant in the field of chemistry for another 10 years. His first career highlight in history of chemistry was the creation and editing of a 20-volume set of autobiographies of eminent organic chemists entitled Profiles, Pathways and Dreams which was published by the ACS from 1990 to 1997. In 2007, Seeman accepted a courtesy appointment in the Department of Chemistry at the University of Richmond in his hometown in Virginia. As his work in chemical research decreased in magnitude in the early 2000s, his research in the history of chemistry correspondingly increased to the extent that today it consumes most of his professional time.

BOOK REVIEW

African American Chemists: Academia, Industry, and Social Entrepreneurship. Sibrina N. Collins, PhD, Ed. ACS Symposium Series 1381. Ebook American Chemical Society: Washington, DC, 2021; to be distributed in print by Oxford University Press. ISBN13: 9780841298385, eISBN: 9780841298378.

This book chronicles the lives of eleven chemists who represent eleven different perspectives and eleven different sets of experiences along their journey. Yet, in the differences, lies a unifying thread stitched throughout each of their stories. The strong impact of parental influence and mentoring is a common theme that can be drawn in each chapter. Though most of their parents were not formally educated as scientists, their support, sacrifices and encouragement were instrumental in the successes achieved by each of the chemists.

The dedication to the memory of Dr. William Moore is befitting on multiple levels. As so many can attest, Dr. Moore was a teacher. Yes, he taught chemistry to numerous students over the years, but Dr. Moore is widely known and admired for being a teacher of life. Regardless of their chosen career path, he encouraged his students and protegees to do their best in all things. His influence and encouragement were invaluable to countless African American students and professionals. Just like the parental influences of the chemists featured in this book, Dr. Moore was a father figure to many in the sciences and is likened in the parents of the eleven scientists in this book. (On a personal note, Dr. Moore was the first African American to earn a PhD in Chemistry from Purdue in 1967. I was the fourth African American woman to obtain a PhD in Chemistry from Purdue and the first to do so in the Organic division in 2001. In this span of 34 years, there are only thirteen (13) people that separate us.)

The editor, Dr. Sibrina Collins, sets the tone and expectation for reader by explaining the importance of these biographical narratives given the current climate in the United States caused by decades of institutional racism and societal unrest. The expressed desire of organizations to become not only more diverse, but also inclusive and equitable rings especially true for those in the field of chemistry. Whether in the K-12 classroom, lecturing in a university, or holding senior level management positions at top industry and governmental agencies, the dearth of representation of African American chemists holding these positions continues to remain significantly disproportionate to the US population of African Americans.

While social media has allowed more exposure to budding and active practicing chemists, there remain countless others who have made significant impact in advancing inclusion in chemistry for African Americans. This book documents the journey and career path of eleven (to leverage the phrase) hidden chemists who are in plain sight. To further ensure that these scientists are introduced to all students, each chapter ends with an assignment that can be included into the curricula of STEM educators. This serves as a practical approach to expose students of all genders and races to the lives and scientific contributions of African American chemists.

Dr. Collins provides an excellent comprehensive summary of lessons learned from each of the scientists' stories in Chapter 12. The stories are a short and quick read, yet each chapter is packed with its wisdom, knowledge, and inspiration. Therefore, in my review, I have chosen to highlight key points that stood out to me as I reflected on their narratives.

Each of the scientists featured experienced some level of challenge during their formative years, yet because of the support and encouragement of their family and support systems, they rose to that challenge and thrived. It is an important reminder that even if a student does not understand the subject matter, positive affirmation, praise, and support will help them get through the rigor and demands of STEM undergraduate and graduate degrees.

The essays represent a cross section of industry, academia, governmental labs, and entrepreneurship. The narratives address all career levels and includes a mix of both gender and generations. The stories provide just the right balance of the human aspect to their careers and the technical prowess that got them there. This is by far one of the strengths to the book. These authors allow the reader to see the humanness of their journey. It is relatable and real.

The first scientist featured is **Dr. Bettye Washington Greene**, a graduate of a Historically Black College or University (HBCU) who received her chemistry degree in the mid 1950s. Like many in that era, she found the love of her life during her college years, married shortly after graduation, and began a family. Her drive and desire to pursue a doctorate degree and enjoy a successful career as a chemist in corporate America is a testament to the power of role models for young girls to pursue STEM degrees. Her achievement was evidence and encouragement that led to her daughter, Dr. Willetta Greene-Johnson, not only having a love for science, but ultimately earning her PhD in theoretical physics. No truer example of the saying "like mother, like daughter."

Dr. Nodie Monroe Washington, also attended an HBCU in the segregated South and had the unvielding support of her parents. Her parents instilled in each of their children the need to continue their education and ensured that she participated in science fairs and NSFsponsored summer science programs during her high school years. She continued her scientific journey all the way to Ohio State University where she earned a PhD in Chemistry. After a brief time teaching at a local college while completing her doctoral studies, she decided to pursue a corporate industrial career as a research chemist. The highlight of Dr. Washington's chapter lies in the tips she shares for those considering a career in industry as a chemist. It is a blueprint that will guarantee a productive and rewarding career, filled with opportunities and advancement. This guidance and advice is only a snapshot of how she used her position and voice throughout her career to mentor and help others realize their full potential.

When you think of someone being the first at something, you tend to think it may have occurred hundreds or even thousands of years ago. So, imagine learning that the first African American to earn a PhD in Chemistry would serve as your advisor during your undergraduate studies. This was the experience of Dr. Richard A. Evans at Tougaloo College, an HBCU in Jackson, Mississippi, during the mid-1950s under the tutelage of **Dr. Saint Elmo Brady**. This chapter provides an insider's view of the commitment and mentorship of Dr. Brady's that has influenced the education of Black chemists for decades.

Physicist turned filmmaker **Dagmawi Abebe** was reading an article on the role of African Americans in the Westward expansion when he noted a minor mention of a photographer's granddaughter's groundbreaking scientific discovery. This chance finding eventually led to funding from the Alfred P. Sloan Foundation to write, direct and produce a short film about the scientific contributions of the woman responsible for the first effective treatment of Hansen's disease, better known as leprosy. *The Ball Method* is a historical account celebrating the life and achievements of Alice Augusta Ball, the first woman and African American to earn a master's degree in chemistry from the College of Hawaii.

Parental influences fueled the chemistry journey of **Dr. Darryl Boyd.** They instilled a continuous thirst for knowledge and ensured that he received exposure to science programs at an early age. Furthermore, the community service that he witnessed his father perform and the sheer strength and perseverance of his mother to then provide for the family after the untimely death of his father shaped not only his pursuit of a doctorate in chemistry but also his becoming more attuned to the importance of women mentors. Through his company, Science Made Simple LLC, Dr. Boyd pursues entrepreneurial interests while living out his passion for science communication and outreach.

A challenging life experience as an undergraduate student at an R1 institution is the impetus for the STEM advocacy work of **Dr. Pamela Leggett Robinson.** She is a technically trained PhD chemist who has a passion for educating students who look like her in STEM. At each step along her journey from an undergraduate chemistry degree at Georgia State University to the professoriate at HBCU Tuskegee University, she acknowledges challenges and exemplifies the importance of shifting from a deficit mindset to a growth mindset to strategically grow...and address equity in STEM. Dr. Robinson's chapter includes a chart in which she creatively likens her career journey from organic chemist to consultant to that of the lifecycle of a butterfly.

Not all roads will lead to a PhD in chemistry, but the 20-year career of LaVetta Appleby as a chemistry educator has been filled with unexpected adventures and celebrity. Though she pursued and obtained a master's degree in chemistry, she realized that her preference for teaching far outweighed her interest in research and decided to join the faculty at Lawrence Technological University. As a science teacher, Ms. Appleby understands the value of experiential learning and meeting students where they are. As an educator, she has learned that pedagogy has significant impact on learning outcomes. She, along with colleagues at LTU have used Vibranium, the most recognizable element to hit the big screen in Marvel Studios' Black Panther, to spark a newfound interest in the periodic table of elements in science classrooms ranging from kindergarten to college.

Dr. Angela Peters comes from a family of educators who lived by the principle that "education is the vaccine for poverty." Even though she experienced early challenges in chemistry, it was a teacher/tutor who had a true love for the sciences that poured into her and helped Angela turn an F grade into a B by the end of the semester. This was an early example of mentoring in her career, but not the last. At each stage of her industry and academic career, she has relied on mentors to guide and develop her management and leadership skills. In this chapter, Dr. Peters allows the reader to listen in to informal conversations held with three women chemists who have been influential in her career. Now, the product of an HBCU serves as the Provost and Vice President of Academic Affairs at Albany State University, an HBCU in Georgia. Dr. Peters has expanded her visibility and serves as a role model to women in STEM in academic leadership positions.

When your first experience with the concept of mentoring is within your immediate family, it is likely to have a lasting impression. For **Dr. Renã A. S. Robinson** the early positive affirmations that she was smart and praise for doing well is a reminder that this is an important part of mentoring for all students, and especially for underrepresented students in STEM. An accomplished scientist whose research was born out of personal interests and experiences, Dr. Robinson is also a leader in STEM advocacy. As the 2021-2023 national president of NOBCChE, she will have an even greater voice and platform to mentor students of color who are interested in STEM. There are several examples and nuggets of wisdom on mentoring shared in this chapter. One of the simplest yet profound statements surrounding mentoring is that the role of a mentor is not to create carbon copies, but instead meet the student where they are and help them thrive.

Dr. Leyte Winfield's narrative sheds light on what it means to "see the invisible scientist." Her penchant for STEM can possibly be traced to her mother teaching her multiplication facts at the age of four years old. From there, her scientific curiosity propelled a desire to pursue a chemistry degree at Dillard University, an HBCU in New Orleans, Louisiana, followed by a PhD in organic chemistry from the University of New Orleans. Dr. Winfield learned to master the art of work-life integration early in her graduate career as the mom of a young child and a productive researcher. This may be one of the main reasons that she emphasizes cultivating one's STEM identity through role modeling and mentoring.

As the final scientist featured in this book, her closing thoughts on broadening participation are perfectly situated and summarize the importance of highlighting the stories and raising the visibility of academically mobile African American and other women of color in STEM. She has a particularly unique vantage point, as a professor and researcher at Spelman College, an allwomen's HBCU in Atlanta, Georgia. She closes out her chapter by sharing online and web-enhanced pedagogies that have been used to influence the learning and behaviors of women of color at a small liberal arts college.

I have had the pleasure of meeting or interacting with several of the scientists featured in this book. I have walked the campuses of each institution where they were trained. Yet reading each of their stories in this book has given a new perspective on their journeys. I have learned something new about each of them and gained a greater sense of respect for their accomplishments. They are truly inspirational and trailblazing African American Chemists.

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