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# JEAN-BAPTISTE AND ANSELME PAYEN, CHEMICAL MANUFACTURERS IN GRENELLE NEAR PARIS (1791-1838)

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### Introduction

French scientist Anselme Payen discovered cellulose in 1838 after having been a manufacturer of chemical products for more than twenty years. His memory is honored annually by an award of the American Chemical Society's Cellulose and Renewable Materials Division (1).

The study of Payen's family and professional notarial acts (2) gives a new vision of their industrial activities, how they were developed through partnerships with other manufacturers, and how and why they ended. The present paper is based on the analysis of close to thirty acts from 1791 to 1863 coming from seven Parisian notarial offices. These notarial acts about Anselme Payen and his family members and industrial partners report births, marriages, deaths, inheritances, sales of properties and factories, and creations, mergers and dissolutions of companies. By focusing on how these chemical product companies were organized and run, this work complements two papers dealing mainly with the scientific and technical activities of Anselme Payen (3).

### The Payen Family

Although not a proper biography of Anselme Payen, several hagiographic papers written a few months after his death inform us about his family and his youth (4). Jean-Baptiste, the father of Anselme, was a magistrate who studied law but also science and founded a chemical manufacture in 1791. It was located in the Grenelle plain in the town of Vaugirard, currently in southwest Paris. The same year, he married Marie-Françoise Janson or Jeanson depending of the notarial acts. Anselme, born in 1795, was educated at home by his father. During his youth, Anselme met famous scientists who were friends of his father, among them, Claude-Louis Berthollet, Jean-Antoine Chaptal and Louis-Nicolas Vauquelin. Anselme was invited to visit their laboratories and spent time daily in the factories of his father where he started to work at the age of nineteen. The factory was managed by Anselme Payen after the death of his father in 1820 until 1838 and became one of the main manufactures of chemical products of its time (5).

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# Constitution of Land and Industrial Properties by Jean-Baptiste Payen

In 1791, Jean-Baptiste Payen bought a mansion, called *la Maison Blanche*, and the surrounding land in the Grenelle plain on the Seine river's left bank (6). When married, he lived there and started a chemical factory in those buildings (7). During the next twenty years, he continued to buy land properties in the same area, mainly former *biens nationaux*, which were properties confiscated during the French Revolution. In 1820, at the end of his life, Jean-Baptiste Payen owned 7 hectares of land in Grenelle, extending about 500 meters along the

Seine river left bank and mainly dedicated to chemical industry (8).

Two days after his marriage, Jean-Baptiste joined his brother Pierre and Jean Carny to form a company called Payen frères et compagnie to produce soda in Grenelle (9). Carny was a chemist involved in gunpowder manufacturing who held a patent on obtaining soda (10). The patented process was based on a reaction between iron sulfate and sea salt to obtain crystallized sodium sulfate which was then reduced with coal powder to produce sodium sulfide. The next step was to make sodium sulfide react with sodium plumbate after the dissolution of both products in water, and then to finally obtain soda after separation from solid lead sulfide. The company was dissolved before two years of existence probably due to poor economic results (11), because Carny's process to manufacture soda was far less effective and profitable than the Leblanc process which prevailed from this time for close to the next century (12).

This industrial failure did not stop Jean-Baptiste from investing in chemical industry. Following unsuccessful attempts by Antoine Baumé to produce sal ammoniac (13), both Jean-Baptiste in Grenelle and the Pluvinet brothers in Clichy (a town touching Paris at the northwest) restarted its manufacturing process from 1797 (14). Their process was based on distillation of animal waste. Sal ammoniac manufactured in both plants was sold by a joint company between Payen and the Pluvinet brothers. Total quantities between 25 and 80 tons were manufactured annually in both plants, occupying between 50 and 120 workers (15). In 1820, the inventory at the death of Jean-Baptiste indicated that 14 tons of sal ammoniac were stored by this joint company for a value of 40,000 francs (16). The same notarial act assessed the quantity of chemical products stored by Jean-Baptiste in his own factory at 107 tons, among them 78 tons of crystalized sodium sulfate valued 9,400 francs and 26 tons of ammonium sulfate valued 14,000 francs.

# Manufacture Management by Anselme Payen and his Mother

After the death of Jean-Baptiste Payen on February 20, 1820, his widow inherited all properties located in Grenelle. They included the sal ammoniac factory and a strong glue factory which were both evaluated at 110,000 francs. Anselme, his brothers and sisters inherited other properties. Anselme received shares of two houses in Paris for a value of about 65,000 francs.

Anselme who wished to become a manufacturer, had for the time being to share the factory management with his mother. Together they created a company called Veuve Payen et fils in which they each invested 80,000 francs. This investment was done in cash by the son and mainly in raw materials, products and equipment by the mother. Anselme was in charge of manufacturing and his mother dealt with accounting. Pursuant to article 9 of the company statutes, in case of death of one of the associates, the other one became owner of the company and had only to pay cash to the heirs of the deceased associate for the shares to which they were entitled (17). After his mother's death, Anselme Payen paid to her heirs a total amount of 1,999 francs and became in April 1823 the only owner of the chemical products manufacture located in Grenelle (18).

# Manufacture Development by Anselme Payen and his Associates

The first partnership of Anselme Payen was dedicated to producing and marketing noirs which were black powders, generally of organic materials, mostly bones, but sometimes of vegetable matter, which all were first carbonized and then ground. These noirs were initially used as coloring agents, the highest quality being made from ivory. A new application of these powders was developed by Pierre Figuier in the first years of the 19th century for the discoloration of beet juice and then sugar cane juice in the sugar industry (19). These new markets drastically increased the demand, pushing Julien Lecerf and Antoine Didier, both already associated with each other as manufacturers of noirs, to join Anselme Payen and create the Paven, Lecerf et Didier company on January 28, 1824. Both moved their factories from Paris to Grenelle to merge them with Payen's. The merger enabled the company to invest in a steam machine to replace horse power for grinding carbonized bones (20). At that time, it was a rare piece of equipment, the number of steam machines being estimated at only 625 in all France in 1830 (21). The use of this steam machine enabled them to complete the entire process in Grenelle, eliminating the need to transport carbonized bones to a grinding mill located on the Bièvre river, a few miles from Grenelle.

The next steps of partnership were mergers concluded with *Salmon, Lupé et compagnie*. This company was founded by Louis-Joseph Salmon and the Lupé family (Pierre-Augustin the father, Charles-Auguste the son and Pauline the daughter), to produce *noirs*, sal ammoniac and fertilizers in a factory also located in Grenelle. The company's foundation and both the following mergers occurred in September 1832.

The first merger was made between *Salmon, Lupé* et compagnie and *Payen, Lecerf et Didier* to give birth to *Payen, Salmon et compagnie*. This company rented the factory belonging to Payen, Lecerf and Didier for an annual fee of 5,400 francs and manufactured the following there: *noirs*, Glauber salt (22), Epsom salt (23), *eau de Javel* (24) and volatile alkali.

The second merger was made between *Salmon*, *Lupé et compagnie* and Anselme Payen himself to create the *Salmon*, *Payen et Lupé* company. Manufacturing was done in the Salmon and Lupé factories and in one of the Payen factories. The products were mainly *noirs* and sal ammoniac.

Borax manufacturing in Grenelle by Payen was kept outside of these joint ventures and operated directly by him.

The management of both joint ventures was similar. All manufacturing was under the management of Louis-Joseph Salmon, also including the responsibility of purchasing, logistics, maintenance and human resources. Both Lupé father and son were in charge of payments and accounting. All associates including Payen, Lecerf and Didier were in charge of sales. Two new functions appeared which are now common in most industrial companies. Antoine Didier was in charge of product applications including testing in the factory and customer assistance for *Payen, Salmon et compagnie*. Anselme Payen was responsible for external communications with the mission of promoting success of the *Salmon, Payen et Lupé* company by demonstrating products' utility and environmental safety of the factories (25).

On November 6, 1833, Anselme Payen and his wife Zélie, borrowed 100,000 francs at 5% interest. This loan was secured by a mortgage on fifteen properties, in fact all land and factories belonging to them on the Grenelle plain. A part of this loan was to be invested in the Payen companies: 25,000 francs in the merged company *Payen*, *Lecerf et Didier* to develop *noirs* manufacturing, and 15,000 francs in *Salmon*, *Payen et Lupé* company to develop fertilizer manufacturing (26). A few months later, both companies were in trouble. Following unknown disagreements between associates, the Lupé family left both companies on January 25, 1834. The choice of a new partner to replace them caused a conflict between the remaining associates leading Lecerf to also quit both companies on March 14, 1834. Finally, on March 31, 1834, both companies were dissolved (27).

On that same day, Anselme Payen shared his borax activity with Guillaume Buran by creating a new company with him. As mentioned above, Paven had always kept the borax factory located in Grenelle separate from other manufacturers. This partnership may be seen as a need for cash by Payen who brought his factory and equipment to the company when Buran brought 15,000 francs in cash. At the beginning of the 19<sup>th</sup> century, sodium borate known as borax was used for its melting properties in welding products and in enamel compositions (28). Both associates brought to the company the market shares of borax they had in France, mainly in Lyon and Marseille, and equally shared profits and losses (29).

Another thing occurred on that fateful day of March 31, 1834: Payen and Salmon associated with Buran (we think he was the partner Lecerf refused to work with) to create a new company called *Salmon, Payen et Buran*. This company, whose starting date was January 1, 1834, was organized in three branches: patent management, manufacturing, and sales.

The first mission of this new company was to exploit, sell or grant patents, mainly on *noirs* and fertilizers, which were previously the property of *Salmon, Payen et Lupé* and of *Payen, Salmon et compagnie* and were taken by the new company. The job definition of the clerk in charge of patents' management included to conclude agreements, to sell or grant patents and to monitor their application in factories, to pursue counterfeiters for damages and for destruction of counterfeited products (30).

The second mission under the supervision of Salmon was to run the factories which the company rented to their owners Payen, Lecerf, Didier and Salmon. For example, the plant owned by Payen which produced sal ammoniac and bitumen was rented annually for 600 francs, and the plant owned by Payen and Salmon which produced fertilizers was rented annually for 2,000 francs.

The third mission ensured by Payen and Buran was to sell products manufactured by Salmon according to a contract among all of them which defined the annual quantities to be sold. These forecasted quantities, which had to be updated every year, are listed in table 1 for the whole year 1834. Payen and Buran being responsible for increasing sales, Salmon engaged by contract to produce up to three times the above quantities if he was alerted three months in advance and if Payen and Buran were reliable for three years on the new filed on December 19, 1831 intended to replace those waters by human fecal matter through a process which was claimed to be odorless (32). This process had two main advantages. First, the use of human fecal matter as a

quantities.

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Selling prices and net profits were given in this contract for some products. Let's take the example of ammonium sulfate which was the product with the highest annual profits according to the forecast in the contract. The selling price was 1 francs/kg with a usual discount of 3% giving a real selling price of 0.97 francs/kg. The net profit was estimated at 0.27 francs/kg giving a margin of 28%. Calculations for 60 tons of ammonium sulfate manufactured and sold according to year 1834 forecast indicate 58,200 francs in receipts and 16,200 francs of net profit. These forecasted profits for one product were significantly higher than the rent of the factories where several other products were also manufactured

Product	Quantity (ton)
Sal ammoniac (grey)	31
Sal ammoniac (white)	5
Ammonium sulfate	60
Bone tallow	36
Muscle flesh	24
Desiccated blood	4
Liquid ammonia	18
Sodium sulfate (raw)	36
Sulfates (crystallized, half Epsom salt, half Glauber salt)	18
<i>Noirs</i> from bones (granulated and ground, for the 3 first months of the year)	60
<i>Noirs</i> from bones (granulated and ground, for the 9 last months of the year)	315
Fertilizers	24
Ivory noirs	24
Vegetal noirs	24
Coal (ground)	60

 Table 1. Amounts of products to be manufactured by Salmon and sold by Payen and Buran for year 1834.

to its treatment which was a huge problem for large cities such as Paris (33). Secondly, carbonization of sludge used the same process and equipment as the noirs manufacturing: vertical iron cylinders with a small hole on the top which were placed in a furnace and heated. When the cylinders were incandescent a small flame appeared at the hole and the treatment was finished when the flame disappeared. The fertilizers obtained by these processes had the same attractive appearance of the recycled noirs which facilitated their sales.

raw material was a solution

To manufacture these fertilizers Payen and Salmon wanted to create two new factories in Grenelle, a rendering one, and another one for the heat treatment of sludge and the mixing of the fertilizers' components. According to the decree from

## **Environmental Conflict**

In addition to the products above mentioned, Payen and Salmon planned to start production of a new fertilizer. *Noirs* after being used to discolor syrups in the sugar industry were mostly recycled as fertilizers first in England and then in France. The quantities of this fertilizer were limited by the sugar industry needs of discoloration products, but the market demand for such fertilizers was growing. To answer this high demand, Salmon filed two patents on new fertilizers. The first one filed on May 14, 1829, was dedicated to a fertilizer made from a mixture of carbonized sludge and waters with organic residues, for example from tallow plants (31). The second patent October 15, 1810, on uncomfortable and unhealthy odors, factories which were listed in the first category needed to be authorized by the *Conseil d'État* before starting (34). Payen and Salmon finalized their authorization request in 1833.

The mayors of Auteuil and Passy (two towns close to Grenelle but on the other side of the Seine river) and most of the neighbors of the projected factories living in Grenelle and Vaugirard opposed the project. They all feared pestilential odors coming first from transportation and storage of dead animals and fecal matters, but also from preparation and use of these materials. One additional fear of the opponents was that if such a polluting industry was authorized on the Grenelle plain, it would open the doors to the installation of other polluting factories in the same area. Indeed, manufacturers favored this kind of grouping because it enabled them to hide the origin of one nuisance behind another one when they addressed complaints from the surrounding neighborhood.

Technical experts were opposed to the way both patents would be applied practically at large scale to guarantee that the process of mixing carbonized sludge and organic residues would be really odorless. Payen and Salmon demonstrated it on small amounts of products by having respected the ratio of sludge versus organic matter which was explained in the patents. Some opponents argued that for larger quantities of organic matters to be treated, the respect of this ratio would be too costly and would impact too negatively the whole economic balance of the process to be maintained (35).

The Conseil consultatif des arts et métiers which had the official mission of counselling the Conseil d'État concluded that its six members who were consulted on this topic disagreed on the authorization of both factories. Half of its members were in favor of authorizing the factories if the organic matters were covered during their transport and storage and if the ratio of carbonized sludge versus organic matters was strictly respected. The other half of the members opposed the authorization of the factories with the arguments that manufacturers never respect recommendations because of economic interest or negligence by the factory workers (36).

Finally, in 1837, the *Conseil d'État* did not authorize the rendering factory and the other one for the heat treatment of sludge and the mixing of the fertilizer components, depriving Payen and Salmon of a new source of income (37).

# Guillaume Buran and the *Manufacture de* produits chimiques de Grenelle

Salmon left the *Salmon, Payen et Buran* company, which was renamed as *Payen et Buran*, in July 1834, to focus on manufacturing fertilizer in several regions of France (38). On May 3, 1838, the *Payen et Buran* company went bankrupt and was dissolved, showing that the forecasted turnover and profits (shown above for year 1834) were highly too optimistic. Both associates agreed that Buran had to cover the company losses with 40,000 francs in cash and that in exchange Payen had to abandon all his patents, equipment, raw materials and finished products. On the same day Payen and his wife had also to sell to Buran 2.5 hectares of their land in Grenelle for 70,000 francs (39).

To host all the factories he possessed himself and that he recovered from Anselme Payen, Buran immediately founded *Buran et compagnie*, one of the first French private limited companies. This kind of company had the advantage of opening the capital to an extended number of shareholders with a responsibility limited to the shares amount and was one of the first of the large industrial companies (40). The company's capital was fixed at 1,000,000 francs and divided in 1,000 shares of 1,000 francs each. Buran who possessed 550 shares of the company had the whole responsibility of the operation for it and was entitled to receive 30% of its profits.

The commercial brand of the company was *Manufacture de produits chimiques de Grenelle*. It manufactured and sold numerous chemical products: borax, enamels, *noirs*, ammonium sulfate, ammonium chloride, volatile alkali, quicksilver salts, refined camphor and sulfur. It also prepared and used animal flesh and blood for the manufacturing of fertilizers and prussiates.

Buran kept Payen in the company as manufacturing expert, giving him 25 shares with 5% of the company's profits and the use of a house and a laboratory located in the plant.

### **Indebted Anselme Payen**

After May 1838, Anselme Payen was no longer a manufacturer but became an employee of his former associate Guillaume Buran. In addition to having lost all his factories, he and his wife had accumulated significant debt.

They both had difficulties repaying the mortgage loan of 100,000 francs contracted in November 1833. This loan had to be repaid in November 1837 but was rescheduled at least until 1851 (26). In March 1842 they were obliged to again borrow 40,000 francs, through a new mortgage loan. As all their properties were already mortgaged Anselme Payen had to ask his sister Amélie and her husband who was a forge master to grant them an absolute guarantee (41). In January 1843 Anselme Payen and his wife had to borrow again 55,000 francs (42).

In addition to borrowing money, Anselme Payen sold most of his remaining land properties in Grenelle. These properties were mostly sold to craftsmen who already rented them. Between 1839 and 1863 Payen sold properties for an amount of at least 240,000 francs (43).

### Conclusion

Although Anselme Payen's life as a manufacturer ended in a bankruptcy and in a failure which forced him to sell all his factories and land properties, this rich experience of manufacturing gave him an advantage over most of the scientists of its time: "M. Payen had had this singular fortune of being a learned industrialist before being an industrial scientist (44)." That manufacturing experience enabled him to develop industrial skills which, combined with his scientific knowledge, allowed him to create the first industrial chemistry teaching chair in France in 1839 at the *Conservatoire des arts et métiers de Paris*, and finally enter the *Académie des sciences* in 1842.

### **References and Notes**

- 1. The Anselme Payen Award is presented by the American Chemical Society to honor and encourage outstanding professional contributions to the science and chemical technology of cellulose and its allied products.
- 2. Almost all Parisian notarial acts, regardless of the political regime changes, since the end of the 15<sup>th</sup> century up to the beginning of the 20<sup>th</sup> century, are kept at the Archives Nationales in Paris which is abbreviated as AN in the references.
- (a) J. Mertens, "Anselme Payen (1795-1871), Learned Manufacturer of Chemical Products," *Ambix*, 2003, 50, 182-207. (b) J. Wisniak, "Anselme Payen," *Educación Química*, 2005, 16(4), 568-580.
- (a) J.-A. Barral, "Éloge biographique de M. Anselme Payen," Mémoires publiés par la Société centrale d'agriculture de France, 1873, 67-87. (b) A. Girard "Éloge de M. Payen," Annales du Conservatoire des Arts et Métiers, 1871, 9, 317-331. (c) "Nécrologie de M. Payen avec discours funèbre de M. Chevreul," Bulletin de la Société d'Encouragement pour l'Industrie Nationale, 1871, 18[ser. 2], 246-251.
- F. Jarrige and T. Le Roux, *La contamination du Monde,* une histoire des pollutions à l'âge industriel, Seuil, Paris, 2017, p 71.
- 6. AN, MC/ET/LXXXIV/643.
- 7. AN, MC/ET/LXXV/879.
- 8. AN, (a) MC/ET/LXXV/926. (b) MC/ET/LXXV/1035.
- 9. AN, MC/ET/LXXV/879.
- French Patent Nr 1BA1373, Fabrication de la soude et du sulfate de soude, extrait du sel marin, filed Jan. 31, 1792, granted Feb. 12, 1792.
- 11. AN, MC/ET/LXXV/896.

- 12. J. G. Smith, *The Origin and Early Development of the Heavy Chemical Industry in France*, Clarendon Press, Oxford, 1979, p 209.
- 13. T. Le Roux, *Le laboratoire des pollutions industrielles: Paris 1770-1830*, Albin Michel, Paris, 2011, p 139.
- 14. Ref. 5, p 250.
- 15. Ref. 12, p 311.
- 16. AN, MC/ET/LXXV/1035.
- 17. AN, (a) MC/ET/CIII/243. (b) AN, MC/ET/LXVII/958.
- 18. AN, MC/ET/LXVII/947.
- L. Figuier, "Pierre Figuier et la découverte des propriétés décolorantes du noir animal," *Moniteur scientifique -Quesneville*, 1895, 9[ser. 4], 5-14.
- 20. AN, MC/ET/LXVII/950.
- 21. Ref. 5, p 65.
- 22. Glauber salt: sodium sulfate.
- 23. Epsom salt: magnesium sulfate.
- 24. Eau de Javel: aqueous solution of sodium hypochlorite.
- 25. AN, MC/ET/CIII/289.
- 26. AN, MC/ET/LXVII/990.
- 27. AN, MC/ET/LXVII/991.
- A. Payen, Précis de chimie industrielle: à l'usage des écoles préparatoires aux professions industrielles et des fabricants, 1<sup>st</sup> ed., L. Hachette, Paris, 1849, pp 228-229.
- 29. AN, MC/ET/LXVII/992.
- 30. AN, MC/ET/LXVII/996.
- 31. French patent Nr 1BA3208, *Nouvel engrais*, filed May 14, 1829, granted June 13, 1829.
- 32. French patent Nr 1BA3845, *Composition d'un nouvel engrais*, filed Dec. 19, 1831, granted Jan. 27, 1832.
- L. Roux, De Montfaucon, de l'insalubrité de ses établissements et de la nécessité de leur suppression immédiate, Delaunay, Paris, 1841, p 3.
- 34. The decree from October 15, 1810, on uncomfortable and unhealthy odors defined three categories of activities producing industrial nuisances. Industrial sites of the first category had to be away from homes and needed to be authorized by the *Conseil d'État*, the highest French administrative authority, after a *commodo* and *incommodo* investigation. Second-category industrial sites could be authorized close to homes by regional administrative authorities after a *commodo* and *incommodo* investigation. Third-category industrial sites could be authorized close to homes by regional administrative authorities after the mayor's opinion. For more information on this decree see G. Massard-Guilbaud, *Histoire de la pollution industrielle: France 1789-1914*, EHESS, Paris, 2010, pp 43-46.

- 35. Bessas-Lamegie, Breschet et Legrand, Commission de salubrité du 10<sup>e</sup> arrondissement, rapport à monsieur le Conseiller d'état Préfet de police, sur l'établissement de MM. Salmon, Payen et Lupé, à Javelle, commune de Grenelle, banlieue de Paris, pour fabrication de noir animalisé, etc., E. Duverger, Paris, 1834.
- 36. AN, F/12/4797, Avis du Conseil Consultatif des Arts et Manufactures, 18 octobre 1835.
- J.-B. Dumas, L.-J. Gay-Lussac, P.-L. Dulong, E. Chevreul, F. Savart, "Prix relatifs aux moyens de rendre un art ou un métier moins insalubres," *C. R. Séances Acad. Sci.*, 1837, 5, 216-226 at 218.
- 38. AN, MC/ET/LXVII/993.
- 39. AN, MC/ET/XXI/938.
- F. Braudel and E. Labrousse, Eds., *Histoire économique* et sociale de la France, PUF, Paris, 1976, vol. 3, p 528.

- 41. AN, MC/ET/LXVII/1032.
- 42. AN, MC/ET/LXVII/1036.
- 43. AN, (a) MC/ET/X/1189. (b) MC/ET/X/1219. (c) MC/ ET/XXVIII/1109. (d) MC/ET/LXVII/1135. (e) MC/ ET/LXVII/1143. (f) MC/ET/LXVII/1148. (g) MC/ET/ LXVII/1149.
- 44. Ref. 4(b), p 318.

### About the Author

Paul Netter was educated as a chemical engineer. After working 35 years in industry, he gained a Master of History degree at EHESS in Paris (France) writing his thesis on the subject of Payen's factories.

# 2020 Partington Prize to Mike A. Zuber

The Society for the History of Alchemy and Chemistry (SHAC) is delighted to announce that the winner of the 2020 Partington Prize is Dr Mike A. Zuber of the University of Queensland for his article "Alchemical Promise, the Fraud Narrative, and the History of Science from Below: A German Adept's Encounter with Robert Boyle and Ambrose Godfrey."

Dr Mike A. Zuber is a Postdoctoral Research Fellow at the Institute for Advanced Studies at the University of Queensland. He obtained his doctorate with distinction at the University of Amsterdam in 2017 and subsequently received grant funding from the Swiss National Science Foundation for a postdoc project based at the University of Oxford. He has published on the scientific, religious, and intellectual history of the seventeenth century, with particular expertise in German-speaking contexts.

SHAC established the Partington Prize in memory of Professor James Riddick Partington, the Society's first Chairman. It is awarded every three years for an original and unpublished essay on any aspect of the history of alchemy or chemistry. The prize-winning article will appear in the Society's journal, *Ambix*, in due course.

# DIE CHEMIE IST SCHWIERIG: WINKLER AND THE DISCOVERY OF GERMANIUM

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### Introduction

The classification of the elements had long been a subject of interest before Mendeleev's monumental achievement of composing his periodic system of the elements. The first seeds of this endeavor were planted by Antoine-Laurent de Lavoisier in his textbook Traité Élémentaire de Chimie (Elementary Treatise of Chemistry) published in 1789, which was the first chemistry textbook to contain a listing of the known elements at the time. By elements, Lavoisier referred to materials that could no longer be broken down into simpler substances, and this list included 17 metals (1). The binary compounds of oxygen with various metals and non-metals, as well as numerous other binary compounds, were also compiled (1). Then, in 1829 Johann Wolfgang Döbereiner first reported the organization of certain elements into groups of three that he called "triads." These triads were based on the trends in the atomic weights of the elements, and in each of the four triads he proposed the atomic mass of the second heaviest element was very close to the average mass of the lightest and heaviest element (2).

Dumas carried out more precise measurements of the atomic weights between 1858 and 1860, and he reported the atomic weights of a number of elements in 1859 with hydrogen being assigned an atomic mass of one, therefore establishing a system of equivalents or relative atomic weights (3). Building upon this, another more detailed attempt to classify the elements into groups came in the form of the "Law of Octaves" proposed by John Alexander Reina Newlands in 1865 (4). In his method that was based on atomic weights, every eighth element ended up being placed in the first group, such that every eighth element showed a repetition of properties. In contrast to the modern periodic table, the groups of elements were arranged from left to right while the periods of elements were arranged from top to bottom. There were numerous errors, however. For example, lithium was listed as element 2 since it was the second lightest element known at the time, followed by glucinium (beryllium) as element 3, boron as element 4, etc. In his system, cerium and lanthanum shared the same element number. From most accounts, his proposed ordering of the elements was not taken seriously and the Chemical Society of London would not publish it. Newlands is generally credited for the general idea of a periodic system, despite the fact that his system appears to be quite unsystematic.

The major breakthrough in organizing the elements in a systematic way came shortly thereafter by Lothar Meyer and Dmitri Mendeleev. In his textbook, *Die Modernen Theorien der Chemie* (Modern Theories of Chemistry) published in 1864, Meyer included an early version of the periodic table consisting of 28 elements (5). The elements were arranged in a series of six columns and in this case the elements were grouped for the first time

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according to their valence and their equivalent atomic weight. When this was done, it was shown that when the elements were arranged in order of their atomic weight they also lined up in groups by their valence. Each row or period of Meyer's table ended with a divalent alkaline earth metal and the columns, which would later become groups in the modern periodic table, were essentially correct except that thallium was grouped with the alkali metals. It is easy to see why this was done, however, as thallium prefers the +1 oxidation state. Moving away from the relative atomic weights and using a system of valence resulted in Meyer's 1864 periodic table strongly resembling the modern one. However, although Meyer had spaces in his table for elements that were unknown at the time, he did not offer any predictions of the properties of the new elements that had yet to be discovered.

In 1869, Mendeleev published a periodic table containing all known elements at the time, including a few that were not completely characterized, first in Russian (6) with a short summary appearing in German (7). The system he proposed was based both on valence and atomic weight, and he recognized that there were unknown elements that would be analogous to existing elements next to them in their respective groups. For example. Mendeleev indicated that there were missing elements beyond both aluminum and silicon that he later called eka-aluminum and eka-silicon, respectively. In 1871, he published an account with an updated periodic table that contained extensive details on the properties of the predicted elements (8,9). This version of the periodic table is typically regarded as the basis for the one that is used today (Figure 1). Lothar Meyer also published an updated version of his periodic table in 1870 (10).

Ekasilicon, with an atomic mass of 72 as predicted by Mendeleev, would of course turn out to be the element germanium. It would be about fifteen years after the appearance of Mendeleev's 1871 periodic table before this element was actually discovered. This discovery took place in 1886 in Freiberg, Saxony, by Clemens Alexander Winkler, and the story of this discovery is the focus of this paper.

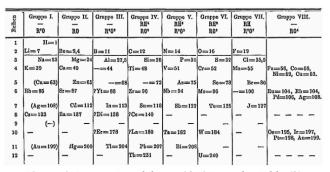


Figure 1. Dimitri Mendeleev's 1871 Periodic Table (9).

### **Clemens Winkler**

Freiberg, which is located in present-day Saxony near Dresden, is known as "die Silberstadt" or The Silver City, due to its proximity to the Himmelsfürst mine that has produced vast amounts of silver-containing ores. Freiberg is also home to the Technische Universität Bergakademie Freiberg, which is the oldest mining and metallurgy university in the world, established by Prince Franz Xavier in 1765.

Clemens Winkler was born in Freiberg, Kingdom of Saxony, on December 26, 1838, to Kurt Alexander, a chemist and metallurgist who had studied under Berzelius, and Antonie Elmonde Winkler. He was the third oldest of seven children. He first attended a private school and then secondary school in both Freiberg and Dresden. He then attended the Royal Trade School in Chemnitz (now Technische Universität Chemnitz) from 1855 to 1856, where he acquired his knowledge base in chemistry. He then attended the Bergakademie Freiberg from 1857 to 1859.

Following the work of his father, grandfather, and great-grandfather, Winkler then began his professional career at the Niederpfannenstiel Blue Dye plant. In 1864 he received his doctorate from the University of Leipzig, where his thesis focused on the alloys of silicon and silicon/arsenic metal compounds (11). He was promoted to head smelter at the plant in 1864 as well. During his time there, Winkler developed a pioneering method of technical gas analysis, and eventually published a book on the subject entitled *Handbook of Technical Gas Analysis* in 1885 (12). In this work, Winkler described his invention of the three-way stopcock (Figure 2). Also, he was successful in producing the first large castings of nickel and cobalt (Figure 3) that he presented at the 1867 World's Fair in Paris.



Figure 2. Winkler's three-way stopcock (12).



Figure 3. Winkler's castings of nickel and cobalt, presented at the 1867 World's Fair in Paris. Photo courtesy of Prof. Mike Haustein (Nickelhütte Aue GmbH and TU Bergakademie Freiberg).

In 1873, at the age of 34, Winkler (Figure 4) was appointed Professor of Inorganic Chemistry at his alma mater, the Bergakademie Freiberg. He succeeded his former teacher Theodor Scheerer, who passed away in 1875. He would remain at Bergakademie Freiberg for the rest of his scientific career.

Winkler was known to be very personable and had an excellent sense of humor. He was a very popular instructor due to the inspiring lectures that he continuously delivered. Winkler also wrote poetry and played several musical instruments (13). He married Minna Laura Pohl in January 1863, and they had six children together.

### The Discovery of Germanium

In September 1885, a previously unknown mineral was discovered in the Himmelsfürst mine outside Frei-

berg during the excavation of a cross passage in the mine. It was gray, silver-rich, and also had a coating of iron and pyrites on the outside. A sample of this was given to Albin Weisbach and he determined that the silver content was 73.5 percent, and also that the mineral contained sulfur and mercury. The ore was named argyrodite (Figures 5 and 6), which comes from the Greek meaning "rich in silver." The formula of this mineral, which of course was unknown in 1885, is  $Ag_8GeS_6$ . This was an unusual composition for the ores normally obtained from this particular mine, and Weisbach asked his cousin and good friend Clemens Winkler to handle the mineral analysis, as he had done several times previously.



Figure 4. Clemens Winkler as a young professor.

When Winkler carried out his analysis of the ore, he found that the silver content was 74 percent and that the sulfur content was 17 percent. He also found trace amounts of mercury, iron, and zinc in the ore but all together these made up less than one percent of the composition. So, Winkler determined that there was an additional seven percent or so of the ore that was not accounted for. Winkler repeated his analysis several times, thinking that he might have overlooked something. But, each subsequent analysis gave the same result in that seven percent of the ore was some unknown species. Winkler speculated that this might be one of the new elements that Mendeleev had predicted.



Figure 5. A sample of argyrodite from the Himmelsfürst mine in Freiberg.



Figure 6. Sample of argyrodite analyzed by Winkler.

The fact that he was faced with an unknown component in argyrodite that could potentially be a new element was bothersome to Winkler, and he was determined to ascertain the identity of this unknown species. He worked day and night to attempt to identify this mysterious substance, but the typical analyses he used to determine the composition of other minerals were unsuccessful. To further complicate matters, only a small amount of argyrodite was available and samples were also significantly contaminated with antimony and arsenic.

Winkler refused to give up and spent four months of solid work to identify the unknown component present in the argyrodite ore. Finally, on the morning of February 6, 1886, his efforts came to fruition. Winkler had been using the "Freiberger digestion" to analyze the argyrodite. This involved mixing the ore with sodium carbonate and elemental sulfur and heating the mixture until it was red hot. This method had been widely used for the analysis of sulfur salts, which were very common in the ores obtained from the Himmelsfürst mine.

Using this method with argyrodite, the same process occurs as for mixed silver/arsenic and silver/antimony sulfides as shown in Equation 1. Upon digestion, a soluble sodium thiogermanate is formed that dissolves when water is added after the heating process, and the silver sulfide does not dissolve.

 $[1] 2 \operatorname{Ag}_8 \operatorname{GeS}_6(s) + 2 \operatorname{Na}_2 \operatorname{CO}_3(s) + 3 \operatorname{S}(s) \rightarrow 2 \operatorname{Na}_2 \operatorname{GeS}_3(s) + 8 \operatorname{Ag}_2 \operatorname{S}(s) + 2 \operatorname{CO}_2(g) + \operatorname{SO}_2(g)$ 

Since the argyrodite ore was contaminated with both arsenic and antimony the aqueous extract also contained the thiosalts  $Na_3AsS_4$  and  $Na_3SbS_4$ . The key to isolating the germanium salt was to separate it from the arsenic and antimony contaminants. Winkler ultimately achieved this by weakly acidifying the aqueous solution with hydrochloric acid and allowing the solution to sit overnight in order for precipitates to form.

On the morning of February 6, 1886, Winkler filtered off the precipitates that had formed, which from experience he expected were sulfide salts of antimony and arsenic. To the resulting clear filtrate he added a large quantity of hydrochloric acid, and this resulted in the formation of a spongy white precipitate. Winkler strongly suspected that this was the sulfide salt of the new unknown element. The fact that this material was insoluble in only strongly acidic solutions was what had prevented its discovery and accounted for Winkler's previous failures to isolate the sulfide salt of the new element. The Na<sub>3</sub>SbS<sub>4</sub> and Na<sub>3</sub>AsS<sub>4</sub> are also highly colored, such that the white Na<sub>2</sub>GeS<sub>3</sub> salt was easily hidden in the precipitates of these two salts.

The final isolation of germanium was achieved by slow acidification of the material obtained by the Freiberg digestion. In solution are the anions  $AsS_4^{3-}$ ,  $SbS_4^{3-}$ , and  $GeS_3^{2-}$ , and slow acidification results in the precipitation of the arsenic and antimony sulfides  $As_2S_5$  and  $Sb_2S_5$ , respectively, while the  $GeS_3^{2-}$  ion remains in solution. Hydrogen sulfide gas is also formed as a byproduct in this reaction.

After all of the arsenic and antimony sulfides have precipitated out of solution, the mixture was filtered to provide a clear filtrate. The difficulty in isolating the new element experienced by Winkler, and presumably others who missed its presence entirely, stems from the unusual fact that the sulfide is *soluble* in dilute acids and water but *insoluble* in concentrated acids. Addition of excess hydrochloric or sulfuric acid then leads to the precipitation of germanium(IV) sulfide (Equation 2).

 $\begin{array}{ll} \mbox{[2]} & \mbox{GeS}_3^{2-}(aq) + 2 \ \mbox{HCl}(aq) \rightarrow \\ & \mbox{GeS}_2(s) + \mbox{H}_2 \mbox{S}(g) + 2 \ \mbox{Cl}^-(aq) \end{array}$ 

The sample of  $\text{GeS}_2$  initially obtained by Winkler was sealed in a glass tube and is currently located at the Bergakademie in Freiberg, and that tube is shown in Figure 7. It was later determined that washing the solid  $\text{GeS}_2$  with sulfuric acid and then alcohol would prevent it from re-dissolving in water. The element itself could be isolated from the sulfide by roasting in oxygen (Equation 3) followed by reduction of the resulting oxide by hydrogen gas (Equation 4).

 $[3] \operatorname{GeS}_2(s) + 3 \operatorname{O}_2(g) \rightarrow \operatorname{GeO}_2(s) + 2 \operatorname{SO}_2(g)$ 

 $[4] \operatorname{GeO}_2(s) + 2\operatorname{H}_2(g) \rightarrow \operatorname{Ge}(s) + 2\operatorname{H}_2\operatorname{O}(g)$ 



**Figure 7**. Winkler's sample of GeS<sub>2</sub> from February 6, 1886. Photo courtesy of Prof. Mike Haustein (Nickelhütte Aue GmbH and TU Bergakademie Freiberg).

On the same day of his discovery, Winkler wrote a short communication entitled "Germanium, a New Nonmetallic Element" about the discovery of the new element that he sent to the *Berichte der Deutschen chemischen Gesellschaft* (14). The famous quote contained therein reads (translated from German to English by this author):

After several weeks of painstaking searching, I can state with certainty that argyrodite contains a new element that is similar to antimony, but sharply distinguished from antimony, to which the name "germanium" may be given. This discovery brought great difficulties and distressing doubts, since the minerals accompanying the argyrodite contained arsenic and antimony, which closely resembled germanium and resulted in a lack of sharp methods for their separation.

Also included in his communication was a brief description of germanium and its oxide, sulfide, and chloride. In this initial report, Winkler stated that germanium was the element eka-antimony that was predicted by Mendeleev (14) although later it would be realized that this new element was actually eka-silicon.

On February 12, 1886, Winkler received a note from Viktor von Richter, who was at Breslau in Silesia (then part of Germany, now Wrocław, Poland), describing the publications of Mendeleev and Meyer detailing their laws of periodicity. It was von Richter who correctly identified that the new element germanium was *not* eka-antimony as Winkler had proposed, but rather eka-silicon. In a letter dated February 25, 1886, von Richter wrote to Winkler to inform him of this. He stated that based on the properties of the oxide, sulfide, and chloride of the new element, it must lie in between gallium and arsenic, and that the properties of eka-antimony would be much different than those exhibited by germanium.

Next to step in to comment on the discovery of the new element was Lothar Meyer, who agreed with von Richter that the new element was indeed identical to eka-silicon rather than eka-antimony. Finally, a letter dated February 26, 1886, arrived for Winkler from St. Petersburg from Dmitri Mendeleev. This was the first interaction between Mendeleev and Winkler, but certainly not the last. In fact, the two scientists forged a friendly relationship and exchanged many personal messages over the subsequent years. This is interesting, since Mendeleev spoke little German and Winkler's knowledge of Russian was also guite limited. Mendeleev used a translator to compose the letters he sent to Winkler, and his letter of February 26 offered a different assessment as to where germanium should lie in the periodic system. Mendeleev suggested that germanium could not lie between antimony and bismuth as eka-antimony because its atomic weight would have to be between 160 and 165 g/mol. Mendeleev suggested that germanium should fit between cadmium and mercury in the periodic system, such that it would have an atomic mass of approximately 155 g/mol, and he maintained that the new element could not be eka-silicon.

Winkler himself was by now confident that the identity of germanium was indeed that of eka-silicon, and it would be the determination of the actual atomic mass that would finally confirm this. Winkler was eager to carry out a full characterization of germanium, but there was the complication that he needed more argyrodite to provide more material in order to carry out a detailed characterization.

Fortunately, the managing director of the Himmelsfürst mine, Eduard Wilhelm Neubert, was generous and provided Winkler with a total of 5.34 kg of argyrodite, with the stipulation that the silver obtained from this material would be returned. This ore ended up yielding about 100 g of germanium. In five months of intense research, Winkler was able to obtain the majority of the compounds of the element for which Mendeleev had made predictions. The properties of both elemental germanium and those of its compounds agreed very well with those predicted by Mendeleev.

This confirmed the power of the periodic system of the elements proposed by Mendeleev, which at this time still had a great many doubters (15). Winkler published a second, longer and more detailed account of his findings in July 1886 (16). In this, he detailed the properties of germanium including the determination of its atomic weight of 72.32 g/mol from  $\text{GeCl}_4$ , as well as the oxide  $\text{GeO}_2$ , the sulfides GeS and  $\text{GeS}_2$ , and the iodide  $\text{GeI}_4$ . In this publication, Winkler also stated (again translated from German to English by this author):

There cannot be more convincing proof of the principle of the periodicity of the elements than that implied by the previously hypothetical eka-silicon. It serves as an important advance in chemistry and is a mighty step into the realm of knowledge.

### What's In a Name?

Interestingly, naming the new element germanium caused a bit of a stir of controversy. Winkler had at one point considered naming his new discovery neptunium, but decided against it. It was Albin Weisbach who suggested that Winkler name the element after the land in which it was first discovered, and so Winkler followed the example of Paul-Émile Lecoq de Boisbaudaran and L. F. Nilson, who named their newly discovered elements Gallium in 1875 and Scandium in 1879 after their home countries.

In June 1886, Dr. G. Quesneville, the editor of the French journal Moniteur Scientifique, accused Winkler of bringing nationalism into science, and insisted that Winkler give up the name germanium and that the new element keep the name eka-silicon, since that was Mendeleev's name for the predicted element and the naming of it should be up to him (17). However, plenty of researchers supported Winkler's naming of the new element, including Lothar Meyer. Meyer joked that Quesneville didn't realize that the name gallium had been derived from Gaul, but rather assumed it was based on the name of its discoverer Lecoq, as this word means "rooster" in French and Gallus is the Latin word for rooster. Further, Meyer jested that Winkler should change the name of germanium to Angularium, since the Latin word Angulus translates to Winkel in German or angle in English (18).

The same journal reiterated its challenge to change the name of germanium in March 1887 (19). In response, Winkler asked Mendeleev to comment on the matter, which he immediately did. Mendeleev indicated that the name eka-silicon, as well as eka-aluminum and ekaboron, were suggested only as temporary names and that he was delighted that they had been replaced by names that paid tribute to the nations in which the elements themselves had been discovered. He further stated that the use of provisional names was in itself rather foolish, since nature isn't based on provisional thoughts but rather through the expression of knowledge. This ended the dispute over the name of the element (20). Of course, this trend also continued as Marie Curie named one of her newly discovered elements polonium in 1898 after her home country (which did not exist on the map of Europe at the time), and Marguerite Perey named her newly discovered element francium in 1939 after her homeland as well.

### **Too Quick (Silver) with Envy?**

If the dispute over the name of the new element wasn't enough, some individuals attempted to pull the rug from under Winkler's feet after realizing they had passed over the discovery of germanium. Winkler's careful and meticulous mind and hands in the lab resulted in the identification of the new element, and others were quick and/or eager to discredit him for his discovery. Theodor Richter, who passed away in Freiberg on September 25, 1898, was the recipient of an obituary in an Austrian Magazine that claimed that Richter was the true discoverer of germanium (20). The ore argyrodite had been in Richter's possession at one point and he had examined it in his laboratory, but he had not the slightest idea that he had before him a new element. He clearly mistook germanium for mercury.

Winkler was swift to reply to this claim, but the editor of the Austrian journal refused to print his retort (20). The whole point was disproven of course by both Albin Weisbach and Friedrich Kohlbeck. The latter was a long-time an assistant to Richter, and clearly knew that Richter had mis-analyzed the new element. Of course, Weisbach had originally asked Winkler for an elemental analysis of argyrodite and also knew the truth. All of these false claims ultimately garnered support for Winkler and furthered his reputation as the discoverer of the new element.

Curiously enough, a mineral in the Freiberger collection from 1820 named Plusinglanz by Johann Friedrich August Breithaupt (Winkler's uncle), was also ignored. It was not until 1900, when the mineral collection was reorganized, that this sample was identified as argyrodite. Opportunity and a meticulous set of hands and eyes, as well as an intense passion for chemical analysis, paid off for Clemens Winkler and he remains the undisputed discoverer of the element germanium.

Clemens Winkler and Dmitri Mendeleev met in 1900 in Berlin, on the occasion of the 200<sup>th</sup> anniversary of the Prussian Academy of Sciences, and this is likely to be the most well-known portrait of the two scientists (Figure 8). It hangs in the conference room of the Clemens Winkler building at the Technische Universität Bergakademie Freiberg. It is truly an amazing capture of a predictor of a new element and the discoverer of said element. To be able to listen to what these two brilliant researchers talked about would be an amazing experience!



*Figure 8. Winkler and Mendeleev in Berlin in 1900. Courtesy of Technische Universität Bergakademie Freiberg.* 

Clemens Winkler remained on the faculty of the Technische Universität Bergakademie Freiberg until 1902, at which point he resigned his professorship. He passed away on October 8, 1904, in Dresden due to complications from carcinoma. His legacy remains one of an intense passion for science and discovery, and he is highly revered in Freiberg to this day as well as in the chemistry community. Several monuments in Freiberg exist to celebrate his legacy (Figure 9).

## **Further Reading**

Several additional accounts of the life and achievements of Clemens Winkler are available in the literature (13, 18, 21, 22), as well as an in-depth biography written by Mike Haustein (20).



Figure 9. Monument in honor of Clemens Winkler in Freiberg.

### **References and Notes**

- 1. A.-L. de Lavoisier, *Traité Élémentaire de Chimie*, Cuchet, Paris, France, 1789.
- J. W. Döbereiner, "Versuch zu einer Gruppirung der elementaren Stoffe nach ihrer Analogie," *Ann. Phys. Chem.*, 1829, 15, 301-307.
- J. Dumas, "Mémoire sur les équivalents des corps simples," Ann. Chim. Phys., 1859, 55, 129-210.
- 4. J. A. R. Newlands, "On Relations among the Equivalents," *Chem. News*, **1865**, 83.
- 5. J. L. Meyer, *Die Modernen Theorien der Chemie*, Maruschke & Berendt, Breslau, Germany, 1864, p 137.
- 6. D. Mendeleev, "On the Relationship of the Properties of the Elements to their Atomic Weights," *Zhurnal Russkoe Fiziko-Khimicheskoe Obshchestvo*, **1869**, *1*, 60-77.
- D. Mendeleev, "Ueber die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente," Z. Chem., 1869, 12, 405-406.
- 8. D. Mendeleev, "The Periodic Regularity of the Chemical Elements," *Zhurnal Russkoe Fiziko-Khimicheskoe Obshchestvo*, **1871**, *3*, 25-56.

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- 9. D. Mendeleev, "Die periodische Gesetzmässigkeit der chemischen Elemente," *Ann. Chem. Pharm. Suppl.*, **1872**, *8*, 133-229.
- J. L. Meyer, "Die Natur der chemischen Elemente als Function ihrer Atomgewichte," Ann. Chem. Pharm. Suppl., 1870, 7, 354-364.
- 11. C. Winkler, "Über Siliciumlegirungen und Siliciumarsenmetalle," J. Prakt. Chem., **1864**, 91, 193-208.
- C. Winkler, Lehrbuch der technischen Gasanalyse [Handbook of Technical Gas-Analysis], J. G. Engelhardt'sche Sortimentsbuchhandlung, Freiberg, 1885.
- 13. L. W. McCay, "My Student Days in Germany," J. Chem. Educ., **1930**, 7, 1081-1099.
- 14. C. Winkler, "Germanium, Ge, ein neues, nichtmetallisches Element," *Ber. Dtsch. Chem. Ges.*, **1886**, *19*, 210-211.
- 15. E. Scerri, *The Periodic Table: Its Story and Its Significance*, Oxford University Press, Oxford, 2007.
- 16. C. Winkler, "Mittheilungen über das Germanium," J. Prakt. Chem., **1886**, 34, 177-229.
- 17. Dr. Q [G. Quesneville], "Le Germanium," *Moniteur Scientifique*, **1886**, *16*, 691.
- O. Brunck, "Clemens Winkler," *Ber. Dtsch. Chem. Ges.*, 1906, *39*, 4491-4548.
- "Sur un nouvel élément chimique," *Moniteur Scientifique*, 1887, 1[4], 331

- 20. M. Haustein, *Clemens Winkler, Chemie war sein Leben*, Verlag Harri Deutsch, Frankfurt, 2004.
- 21. K. Volke, "Clemens Winkler—zum 100. Todestag," *Chem. Unserer Zeit.*, **2004**, *38*, 360-361.
- 22. M. Haustein, "Germanium. Die Lücke im Periodensystem," Chem. Unserer Zeit., 2011, 45, 398-405.

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# EuChemS at 50

EuChemS, the European Chemical Society, celebrates its 50<sup>th</sup> anniversary in 2020. A brochure describing highlights from its first 50 years can be seen here: https://www.euchems.eu/euchems-publishes-a-brochure-for-its-50th-anniversary/

It will hold an online celebration on July 3. Its 8<sup>th</sup> Chemistry Congress was to have been held in Lisbon, Portugal, later this year; that conference has been postponed to 2022, in late August and early September, still in Lisbon.

# **AN OLD ENGLISH PHARMACY**

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A feature article titled "About an Old English Pharmacy" appeared in an 1895 issue of *The Chemist and Druggist* (1). By that time, Randall & Son Chemist and Druggist, 146 High Street, Southampton, England, had been a well-respected establishment for over a century. Forty-five years later, a Luftwaffe raid totally destroyed the premises and ended this business after over 150 years of continuous operation.

Randall & Son participated in the vast changes in the profession and its business model during the late eighteenth and especially during the first half of the nineteenth century. In the seventeenth century, a "tripartite system" of medicine was comprised of apothecary-surgeon-physician-in increasing order of status (2). While surgeons and physicians focused on diagnosis and treatment, apothecaries formulated and sold medicines to the public and medical practitioners. To control unauthorized entrants to the field and to better assure quality, The Worshipful Society of Apothecaries was founded in 1617 and received the Royal Charter. It exists and remains active today (3). In 1671 the Society established a major facility for manufacturing drugs that functioned for two and one-half centuries until it closed in 1922 (3). Although there was widespread quackery in the medical professions during the seventeenth century (4), this facility helped the populace gain a degree of confidence in the drugs it was purchasing. Apothecaries also began dispensing medical advice as well as drugs, especially for those who could not afford to visit surgeons

and physicians. A lawsuit filed by the Society against the Royal College of Physicians (the Rose Case) established that "... from 1704 apothecaries enjoyed the legal right to give medical advice... so long as they charged only for the medicines" (5). Gradually many apothecaries evolved to diagnose and provide drugs to patients-precursors to the modern general practitioner. The Apothecaries Act of 1815, which did not include druggists and chemists, and the Medical Act of 1858 introduced rules relating to training, licensing and practice (6). In 1841, the founding of the Pharmaceutical Society established schools of pharmacy and the Pharmacy Acts of 1852 and 1858 established standards for training and testing of new apothecaries (6). By mid-nineteenth century, organic chemistry had begun to emerge as a precise science and this led to isolation of natural drugs such as morphine and quinine and synthetic drugs such as diethyl ether and chloroform. The contemporary chemists and druggists needed to become familiar with the principles and methods of organic chemistry.

The 1895 article describes the establishment of this pharmacy, by William Randall, an apothecary, and assigns an approximate start date of 1795 (1) although 1793 appears more likely (7, 8). The founder, son of John Randall, an organist and Cambridge professor of music (8), "broke family tradition by going into trade" (9). He started in London as a druggist, was cheated by his business partner and relocated to Southampton in 1792 with his wife Sandra Mayor and two small children—John who eventually became a surgeon, while the younger

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son died in infancy (8). The article includes contemporary illustrations of the storefront (Randall & Son Pharmaceutical Chemists, Figure 1) as well as William Brodribb Randall, grandson of the founder. There is also a portrait of the founder in an 1900 issue commemorating the pharmaceutical business at the end of the nineteenth century (10). In 1795, Randall published a pamphlet: *Medical Observations Adapted to the Medicine-Chests, Fitted Out by William Randall, Chemist* (11). This retail pharmacy was "...the haunt of the 'nobility and gentry' of the neighborhood since George the Fourth was King, and here are any day to be met with members of the best county families and heads of great mercantile houses, who resort thither for that which will make them well"

(1). George IV and his brother Frederick, the Duke of York, were regular customers and consumers of Randall's "anodyne opodeldoc" (more on that later) (1, 9). William Randall's daybook (10) of 1799-1800 lists items sold during the period. Powdered rhubarb sold for 6 shillings/ oz. "Hyrudines," a polite term for leeches (subclass Hirudinea in the phylum Annelida), sold for 6 pence each. The daybook confirmed to the



Figure 1. Illustration of the storefront of Randall & Son Pharmaceutical Chemists, 146 High Street, Southampton around 1895. (See Ref. 1.)

journal that "apothecaries trespassed on the province of the vintner by selling wines, on the ground that they were used for medicinal purposes" (10).

William Randall's first wife died, he married again, moved to Fareham, died in 1838 and was buried in Southampton (8). His third son Edward Mayor Randall (born 1794) took over the business (1). Randall the younger was one of the founders of the aforementioned Pharmaceutical Society in 1841. William Randall's grandson, William Brodribb Randall (born 1821), was sixteen when he began an apprenticeship with his father. He enjoyed close contact with Michael Faraday and William Thomas Brande, attended Thomas Graham's chemistry lectures at University College in London in 1843 (1, 9), and gained Graham's first silver medal for chemistry (12). He joined the business in May 1845 and took it over following the death of his father in 1867 (8). William Brodribb was the person primarily interviewed for the 1895 article.

By 1895, a large basement area as well as a top floor served as storage. The back shop had become a saloon added on to the pharmacy. A "very complete manufacturing laboratory" still existed in the back area of the shop reflecting wholesale trade with druggists, and sales to medical practitioners and regular customers. Until the 1860s the shop had typically trained apprentices for fiveyear periods, taking on one new apprentice each year and thus maintaining five at any one time. However, William Brodribb noted that the growing need to train extensively in both the increasingly sophisticated chemistry and

> business conflicted with his own time pressures and he had to cease this source of income for the business. Also interviewed was an employee, a fortyfive-year veteran of the Randall pharmacy, engaged in the process of making black-currant lozenges (1):

Yes sir; I learnt off an old hand who got it off Grandfather Randall when he was a boy. 'Twas Grandfather Randall first made the black currants.

But they made 'em different when I came in. They rolled out the lozenge-paste and hung it up to dry, then cut it out in squares with scissors like. I have to make 'em yet, y'see, for some old customers.

Sadly, none of William Brodribb's four sons had any interest in joining the family business. They pursued careers as a doctor, a solicitor, an electrical engineer, and purveyor of aerated waters on the Isle of Wight. Thus, in 1894 he took on Harry Wilson, F.I.C., F.C.S., as a partner (1), and retired on December 31, 1898. The March 22, 1902 issue of *The Chemist and Druggist* (7) reports the death of William Brodribb Randall (age 81).

Harry Wilson brought new energy and entrepreneurial zeal to the venerable Randall establishment. The 1895 visit by *The Chemist and Druggist* may well have been arranged by the publicity-conscious junior partner shortly

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after joining Randall. Having passed the Major examination of the Pharmaceutical Society in 1885, Wilson had been employed in the laboratory of James Woolley, Sons & Co. in Manchester and rose to manager. Woolley had earlier been an associate of John Dalton. Upon the passing of Randall, Wilson formed a limited liability company, Randall & Wilson, Ltd. The seven signatories were the preparations to be made from them and the recommended dosages. Although Randall & Sons had a wellheeled clientele including King George IV, Randall took pride in the broader societal mission for his pharmacy: "To relieve the wants of the industrious poor." He advises in his Introduction: "When medical assistance can be had, it should be preferred; but disorders attack suddenly, and

all pharmaceutical chemists and Wilson assumed the position of Managing Director, holding the majority of ordinary shares. A year earlier, Wilson introduced the pharmacy into a new venture "... practically the only firm of whole sale druggists in England who manufacture methylated spirit" (13, 14). Methylated spirit is alcohol denatured with wood naphtha (toxic methyl alcohol). In order to add space for the manufacture of methylated spirit, the pharmacy purchased the Zion Chapel, constructed of Portland stone, on Lansdowne Hill, itself the site of the former

	ns in the Randall & Son medicine nest (11).
1. Calcined Magnesia	17. Goulard's Extract
2. Turky Rhubarb	18. Essence of Peppermint
3. Powder of Bark	19. Nitre
4. Tincture of Bark	20. Jalap
5. Essence of Rhubarb	21. Dr. James's Powders
6. Spirits of Sal Volatile	22. Sweet Spirits of Nitre
7. Nervous Drops	23. Ipecacuanha Powder
8. Aether	24. Cream Tartar
9. Opodeldoc	25. Ginger
10. Fryar's Balsam	26. Gum Arabic
11. Antimony Wine	27. Senna Leaves
12. Tincture of Guiacum	28. Blister Plaister
13. Salt of Wormwood	29. Liniment to Dress Blisters
14. Asthmatic Elixir	30. Yellow Basilicon
15. Elixir of Vitriol	31. Turner's Cerate
16. Liquid Laudanum	32. Ointment of Elder

keep (fortified tower) within a castle erected after the Norman invasion (8, 15). In order to store numerous barrels of alcohol, the new owner converted the galleries and rebuilt the floors to hold enormous weight, equipping the storage space with a huge hoist (15). During his career, Wilson achieved numerous appointments and honors in the professional and business communities. Upon his retirement in 1927 his memberships in the British Association for the Advancement of Science and the Royal Southampton Yacht Club were duly noted (9). Randall & Wilson, Ltd later purchased Rayson & Co., Chemists in Ringwood with records dating from 1935 through 1972 (8, 16). A Herbert Richard Hussey, living in Southampton, was next associated with the firm during the 1930s (8). Harry Wilson, F.I.C., Ph.C., died in 1941 (17). Before returning to 146 High Street, let us revisit William Randall's late-eighteenth-century pharmacy.

William Randall's 1795 pamphlet (11) lists the 32 medications included in his commercial medicine-chest, it frequently happens that neither advice or medicines can be procured." Table 1 shows the complete list of medications in the Randall & Son medicine-chest.

> This list is then followed by a directory of 59 "disorders" each accompanied by numbers corresponding to the above medications. For Apoplexy, Fainting Fits, Head-ach, Hysteric Fits, Lethargy, and Nervous Tremors, No. 6 (Spirits of Sal Volatile, *i.e.*, ammonia smelling salts) is recommended. For "Anodynes" (i.e., condition of lacking vigor or zest), Convulsions, Diarrhoea, Looseness, and Spasms, No. 16 (Liquid Laudanum, i.e.,

tincture of opium) is recommended although caution is advised. And what of the "Anodyne Opodeldoc" (No. 9) regularly procured by King George IV? George IV lived an exorbitant lifestyle, including heavy drinking, over-eating, mistresses and staggering debt. He suffered painful gout as well as "dropsy" (peripheral edema) which can also be painful. Opodeldoc is an external treatment for various discomforts including gout, rheumatic pains and sprains. The U.S. Pharmacopeia describes it as consisting of powdered soap, camphor, oils, alcohol and water (18), although in earlier periods small amounts of laudanum were often added. "Anodyne" in this context means painless or pain-relieving.

Randall & Son also sold to customers a simple set of scales and weights (Figures 2 and 3). The Randall & Son business card found with the set (Figure 4) has a handwritten table of apothecaries' weight measures on the back of the card. This table is identical to the one printed in the 1795 pamphlet (11). It is not unreasonable to assume that these were handwritten by William Randall on the business cards also provided to customers. The apothecaries' weight measures (employed in England and the United States until 1858) included: the grain (1 grain = 0.065 gram), the scruple = 20 grains (1.296 gram); the dram = 3 scruples (60 grains; 3.89 gram). As noted in the pamphlet, the impressions in the thin weights make so many grains, the smallest being half a grain. Undoubtedly, the balance and weights employed in the apothecary shop itself were much more sophisticated.



Figure 2. Simple scales for weighing drugs supplied in the Randall & Son medicine chest along with the wooden box which held them along with weights and a business card. Photograph by Richard Johnson.



Figure 3. Weights supplied with the scales in Figure 2. Top row (left to right): 1 Scruple, ½ Dram, 2 Scruples, 1 Dram, 2 Drams; Bottom row (left to right): 4 grains, 5 grains, 7 grains; a 20 pfennig 1875 silver coin (1.00 gram) added perhaps 80 years after the set was originally sold. A ½ scruple weight may well be missing. See the text for definitions of these weights. Photograph by Richard Johnson.

What became of the Randall pharmacy? The 1940-41 *Kelly's Directory* (Southampton, UK) has a listing for Randall & Wilson, Chemist & Druggist, 146 High Street, but the establishment is not listed in the 1948-49 *Kelly's Directory* (8, 19). Sadly, an entry in the War Damage Index dated November 30, 1940 (Figure 5), indicates total loss of the building in a Luftwaffe bombing raid. Southampton, a port city, was frequently attacked during



Figure 4. Both sides of the Randall & Son business card. It is likely that the weights were handwritten by William Randall since they exactly match those in his 1795 pamphlet. Photograph by Richard Johnson.

the war and was heavily bombed on November 30 with loss of a large portion of High Street (8). William Randall was buried over a century earlier at St. Mary's Church in Southampton, which was also harmed by bombing. The church was rebuilt but the badly damaged headstones were removed and there is no marker to visit (8). Edward Mayor and William Brodribb and some members of their families are buried in Southampton Old Cemetery. Presently, High Street is a modern commercial thoroughfare with no trace of the famous pharmacy that served royalty, the wealthy and "the industrious poor" through parts of three centuries.

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*Figure 5.* War Damage Index sheet for 146 High Street, Southampton. Courtesy Southampton, UK, City Archives.

The total destruction of the 150-year-old Randall & Wilson pharmacy would be a somber ending to this essay. Why not end humorously with a satire on a satire: "The Pharmaceutical Major-General," published in the same 1895 issue of *The Chemist and Druggist* that featured the Randall & Son pharmacy (20)? It is a play

on the popular song from the comic opera *The Pirates* of *Penzance*, written by Gilbert and Sullivan and first performed in 1879. Atrocious puns and all, it does hint at the scope of the knowledge and duties of a turn-of-the-century pharmacist.

### The Pharmaceutical Major-General

(A Reminiscence of Mr. W.S. Gilbert)

I am the very pattern of a modern Major-Pharmacist In training theoretical there's really nothing that I've missed; I know the nice distinctions 'tween the orders in my botany, Can analyze a triple salt and quote with ease a lot o' the Jaw-breaking polysyllabics that please our wise societies, Which breathless hang upon the words of learned notorieties. I'll give you points in knowledge of the laws of diathermancy, I weekly catch the latest craze that blows across the German sea. I know the therapeutic use of hexa-hydro-pyridine And just how much red iodide will salivate a horse-marine; But in practical dispensing and the knowledge of the patent-list I am the very model of a modern Major-pharmacist.

Why malva has been added to the order of Malvaceae, Why orchids are not scheduled with the Amaryllidaceae, Why the analytic principles of chemical philosophy Have failed to find the alcohol in spirits of theosophy; Why bandages are made with lint that's first been highly sterilized,

Why kittens now are reared on milken diet that's been felinised;Why logic's been replaced by an induction that's magnetical,And organized productions made by processes syntheticalI know; and why it's hard to find fit uses therapeuticalFor novel and for elegant productions pharmaceutical:But in counter work and knowledge of the contents of the market-list,

I am the very model of a modern Major-pharmacist.

I know by heart each separate fact in tables posological, I estimate specific heat in contests theological; I qualitate the gold from mines that always will be minerless, And quantitate the butter in the milk of human kindliness; I estimate the casein in the Kurds that are Armenian, And soon rejuvenate a face that trouble's made a seamy 'un; I can theorize for ages on an isomorph that's tertiary, Can sterilize the pap that's served to infants in the nursery; Can fix a worm condenser to retorts that are satirical, And with a scientific law explain away a miracle: But in practical dispensing and in knowledge of the patent-list, I fear I am the model of a modern Major-pharmacist.

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### **References and Notes**

- "About An Old English Pharmacy," *Chemist and Druggist*, **1895**, *47(Aug. 31)*, 346-348. For the illustration of the pharmacy storefront see https://archive.org/details/ b19974760M0861/page/346 (accessed Feb. 26, 2020).
- Center for the History of Medicine at Countway Library of Medicine, Who Were the Apothecaries? http://collections.countway.harvard.edu/onview/exhibits/show/ apothecary-jars/sequence/ (accessed Feb. 26, 2020).
- See the website of the Worshipful Society of Apothecaries, http://www.apothecaries.org/history/origins/ (accessed Feb. 26, 2020).
- P. J. Corfield, "From Poison Peddlers to Civic Worthies: The Reputation of the Apothecaries in Georgian England," *Social History of Medicine*, 2009, 22(1), 1-21.
- H. J. Cook, "The Rose Case Reconsidered: Physicians, Apothecaries, and the Law in Augustan England," *Journal* of the History of Medicine and Allied Sciences, 1990, 45, 527-555.
- Center for the History of Medicine at Countway Library of Medicine, Apothecaries from the Eighteenth Century Onward: England, http://collections.countway.harvard. edu/onview/exhibits/show/apothecary-jars/eighteenthcentury-england (accessed Feb. 26, 2020).
- "DEATHS. Randall," Chemist and Druggist, 1902, 60(Mar. 22), 459. The 1783 date cited in this obituary appears to be unlikely given Mr. Randall's move to Southampton in 1792 (Ref. 12 below). The 1795 date provided in Ref. 1 above is likely to be more authoritative since it is an extended discussion of the history of this pharmacy.
- Correspondence with Lisa Moore, Archivist, Joanne Smith, Archivist, and Jean Watts, Archive Volunteer, City Archives, Southampton City Council, Southampton (UK).
- "Retirement of Mr. H. Wilson," *Chemist and Druggist*, 1927, 10(July 23), 114-115.
- "The Closing Century: English Pharmacy when George III was King," *Chemist and Druggist*, **1900**, *56(Mar. 31)*, 540-543.
- Medical Observations Adapted to the Medicine-Chests, Fitted Out by William Randall, Chemist, Southampton, Printed in the year MDCCXCV, by T. Baker. Gale ECCO Eighteenth Century Collections Online Print Editions. Reproduction from British Library. Also available online

at https://books.google.com/books?id=hIDHEuqtx90C (accessed Feb. 26, 2020).

- 12. "Obituary. RANDALL," *Pharmaceutical Journal*, **1902**, *68(Mar. 22)* [Fourth Series Vol. 14], 252.
- 13. "No. 30 in S.V.M.," *Chemist and Druggist*, **1901**, *58(Apr. 27)*, 703.
- 14. "Pharmacists as Methylators," *Pharmaceutical Journal*, **1901**, *66(Apr. 27)* [Fourth Series Vol. 12], d.
- 15. "From the Days of Good Queen Bess," Chemist and Druggist, 1907, 71(July 27), 160-161.
- Roundabout Ringwood and Fordingbridge Now and Then, Rayson & Co Chemists at Fridays Cross, http:// www.roundaboutmags.co.uk/wp-content/uploads/2010/ 09/Now-Then-August-2010-low-res.pdf (accessed Feb. 26, 2020).
- 17. "DEATHS. Wilson," Chemist and Druggist, 1941, 136(Oct. 25), 111.
- Pharmacopoeia of the United States of America, 9<sup>th</sup> ed., P. Blakiston's Sons & Company, Philadelphia, 1916, p 234.
- 19. Directory of Southampton and Neighbourhood 1948-9, Kelly's Directories Ltd, London, 1949.
- 20. "The Pharmaceutical Major-General," *Chemist and Druggist*, **1895**, *47(Aug. 31)*, 349.

#### About the Author

Arthur Greenberg was born in Brooklyn in 1946. He graduated with a B.S. in Chemistry from Fairleigh Dickinson University (1967) where he met Susan Covici, another chemistry major; they are celebrating 51 years of marriage. He obtained his Ph.D. from Princeton University (1971) studying dynamic stereochemistry with Pierre Laszlo. Following a U.S. Army commitment, he taught at Frostburg State College (1972-1977), New Jersey Institute of Technology (1977-1989), Cook College of Rutgers University (1989-1994), and was Chemistry Department Chair at University of North Carolina at Charlotte (1994-2000). He joined the University of New Hampshire as Dean, College of Engineering and Physical Sciences (2000-2005) and Professor of Chemistry (currently). Research interests include strained organic molecules (notably distorted amide linkages), polycyclic aromatic hydrocarbons on airborne particulates and metabolic ring opening of benzene. His antiquarian book collection stimulated long-standing interest in history of chemistry (authored From Alchemy to Chemistry in Picture and Story). He has sung with Portsmouth Pro Musica for the past fifteen years, roots for the Red Sox but still mourns the loss of the Brooklyn Dodgers.

# Erratum

In the review of *The Posthumous Nobel Prize in Chemistry. Volume 2. Ladies in Waiting for the Nobel Prize* (this Journal, **2019**, *44(2)*, 139-147), the order of the editors was mistakenly inverted. The volume was edited by Vera V. Mainz and E. Thomas Strom.

# TRIPLY FORMULATED NITROCELLULOSE: CELLULOID, VISCOSE AND CELLOPHANE

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### Introduction

Is it perhaps too early in this century to single out a material, or a class of materials, as the most popular. During the twentieth century, nylon and plastics were contenders. In the nineteenth century, nitrocellulose had such a role, at first as an explosive, often termed guncotton or, in French, *fulmicoton*; and as collodion, a nitrocellulose gel used to dress wounds.

In 1845, the German chemist Christian-Friedrich Schönbein (1799-1868) had inadvertently nitrated cellulose. He found the ensuing product to be highly explosive. In 1846, he supplied Michael Faraday with a sample (1).

Nitrocellulose, under these two formulations, became much written about. The novels by Jules Verne featured it prominently. In *From the Earth to the Moon* (1865), guncotton is the explosive used to hurl the explorers. In the same novel, an American named Maynard is credited tongue-in-cheek with the devising of collodion—when in fact the French Louis Ménard had devised it in 1846 (2). Jules Verne was deriding what his French readership perceived as American one-upmanship. In *Journey to the Center of the Earth* (1864), the heroes blow up with guncotton a mountain of granite blocking their progress (3).

These examples show that nitrocellulose, in either formulation, was very much part of the popular culture—

to such an extent that it spawned other inventions, which I shall now chronicle.

#### Antecedents

During much of the nineteenth century, American billiard balls were made of ivory, a precious material that was already becoming rare (4). It became so ruinously expensive that a company manufacturing these balls, Phelan & Collander, in 1860 launched a competition for a substitute product (5). The selected inventor would win a \$10,000 prize, hefty at that time (6).

Alexander Parkes (1813-1890), an Englishman, son of a locksmith, was a prolific inventor (7). He worked for the Elkington's Company in Birmingham, where he developed a technique of fine electroplating. In 1856, he came up with a replacement material for ivory, which he named parkesine (8, 9). It consisted in cellulose treated by nitric acid—such an ester was then named a collodion (10)—which the incorporation of ethanol rendered plastic (11). This artificial ivory rewarded Parkes with a bronze medal at the Universal Exhibition in London in 1862, in addition to a flattering reputation (12).

Daniel Spill (1832-1887), an Englishman who made raincoats in his brother George's company, became interested in the waterproofing properties of parkesine. The George Spill & Co., in Stepney Green near London, thus started manufacturing it. However, it was an expensive material, on account of the ethanol component. Moreover, it tended to lose its shape and to show cracks after a relatively short time.

The American John Wesley Hyatt (1837-1920) then entered the scene. Born in Starkey, in the state of New York, he had become apprenticed in a printing shop in Illinois aged only 16, and found a similar job subsequently in Albany, New York. When Phelan & Collander made their prize public, he sought also to make an artificial ivory. Like his predecessors Spill and Parkes, Hyatt modified collodion; Hyatt's modification was to add camphor to it (13, 14). He had the astute idea, in order to obviate the need for ethanol, to do this under heating and pressure. As a consequence, his product did not suffer, as parkesine did, from premature ageing (15). He patented the new material, a cellulose derivative that he named celluloid, in 1863. Hyatt convinced his brother Isaiah Smith Hyatt to join him, and they started a company. Hyatt was gifted not only in chemistry, but also in mechanics and industrialization. He built machines for molding celluloid pieces by injection. The first artificial plastic material in the modern era was born (16). It was the scion of two natural products, wood pulp and camphor. Parkesine failed to sustain the competition with the newer material. Its manufacture stopped in 1868; later on, during the 1880s, the British Company Xylonite of Daniel Spill would merge with Hyatt's Celluloid Manufacturing Company, as it was named by then.

By 1870, the Hyatt brothers had their own business, the Albany Dental Plate Company. Indeed, their main production was not billiard balls but dental plates (17, 18). These prosthetic devices made out of celluloid had some problems, however: they were poorly compatible with hot drinks, for heat made them soft, and one's tea left a taste of camphor in the mouth. As early as 1871, the Hyatts' company moved to Newark, New Jersey, close to New York City, and took a new name, the Celluloid Manufacturing Company. It would remain active there until 1949, for a total of 77 years. The Hyatt brothers diversified their production into haberdashery items such as buttons, detachable collars and stays for shirt collars and for corsets. These stays superseded the earlier metallic battens, that rusted on contact with sweat and thus stained clothing.

Celluloid was also turned into large combs for elegant ladies to plant in their hair. The Celluloid Manufacturing Company also produced shirtfronts, referred to under the affectionate and rather vulgar name, dickies. Compared to shirts, they had the advantages not to shrink upon washing and to be cleaned easily, with just the brush of a sponge. They met therefore with huge commercial success.

What are the factors in the adoption of a new material such as celluloid? Its already mentioned low production cost. The three inventors referred to above, Parkes, Spill and Hyatt, did not attempt a frontal attack on the problem posed—to come up with a substitute material for ivory with the assets of whiteness, hardness, mechanical resistance, and ability at undergoing elastic collisions (billiard balls). Nurtured in the Industrial Revolution, they knew to start their research by choosing their raw material. They all opted for cellulose, i.e., wood pulp. This answer surely was assisted by the great contemporary vogue of cotton powder, aka fulmicoton. It was made initially from cotton dipped into a nitric acid bath, which after drying yielded an explosive.

The next question these inventors faced was how to render plastic the derivatized celluloses. How, once they had been functionalized by nitric or sulfuric acids, to have them be shaped or molded? The rather obvious answer was by adding a solvent. Indeed, mankind has for millennia known how to evolve a malleable, plastic material such as playdough or its predecessor, fuller's earth, from the parent dry powder, simply by adding water. Parkes and Spill did not go beyond this second step. Hyatt conversely did. He was inventive enough to conceive of the operational procedure of camphor incorporation. In addition, he was able to mechanize the molding step, thus gaining access to reproduction of the identical object in as many copies as necessary.

As early as the 1870s, in the US, at the instigation of Leland Stanford—the founder of the university bearing his name—Eadweard Muybridge was photographing at regular intervals running horses. This technique enabled him to analyze the detailed motions of their various strides, the step, the amble, trot and gallop.

Independently from Muybridge, the Frenchman Etienne-Jules Marey invented in 1892 what he named chronophotography, an identical photographic technique for decomposing movements. Marcel Duchamp became interested in the chronophotographs by both Muybridge and Marey, to such an extent that he labeled "chronophotograph" his great 1912 canvas, *Nu descendant un escalier*. Thus, things were ripe in the 1890s for the appearance of cinematography. Persistence of images on the retina was a well-known phenomenon, due in part to stroboscopy.

It only remained to find a suitable support. Celluloid answered that need: it had the hoped-for characteristics, which were rather numerous. One had to scroll photographic images in sequence, in linear temporal sequence. The support thus had to be linear, enabling each image in turn to have the light of a projector shine on it. A projector was also needed. To evoke motion for the viewers, many images were required. This called for their miniaturization, and thus for enlargement as they were displayed. Even if each image had dimensions of the order of a centimeter, a projection time of only five minutes translated into a ribbon several meters long. Hence, a reel. Moreover, there was a need for that support to be transparent.

Indeed, yet another criterion was the recording of this cinematographic sequence. A possibility, by analogy with the stacking of the pieces of perforated cardboard used in a mechanical organ or pianola, would have been to use equal length strips, vertically superimposed on one another. In that case, the chosen support would have needed to be rather rigid. However, as you know, the prevailing solution was winding the strip of images cylindrically, in the manner of Edison's original phonographic recordings, or around a pulley. Since storage was by winding, the tape had to be a pliable and flexible film.

Last but not least, the material had to be inexpensive. This was all the more important because the fast, exponential growth of the Seventh Art—it becoming a novel, lucrative industry—quickly made multiple copies a necessity. In the early twentieth century the number of existing plastic materials was limited to bakelite, galalithe and celluloid. Bakelite had liabilities: it was opaque and unwieldy to condition into strips of film with a thickness of the order of a tenth of a millimeter. Moreover, it was a late invention, occurring only about 1909. As for galalithe, a polymer devised from casein in 1889, the raw material would have made it too expensive.

Vinyl might have been an option. However, it was deemed useless until the 1920s. Polyvinyl chloride (PVC) was first made by the German chemist Eugen Baumann in 1872. He never applied for a patent. PVC was patented in 1913 only when another German, Friedrich Klatte polymerized vinyl chloride using sunlight. Klatte was the first inventor to obtain a patent for PVC. But no useful application of PVC existed until Waldo L. Semon made it into a better product. Semon has been quoted as saying, "People thought of PVC as worthless back then [circa 1926]. They'd throw it in the trash" (19).

All of which explains the choice of celluloid, in existence and in commercial availability since 1870-with the added asset of being made in the United States, which rapidly became the seat of the movies industry (20). As early as 1856, Parkes had proposed substituting parkesine for glass in photography. Daniel Spill followed suit and pushed his xylonite in 1870. After David and Fortier used celluloid as a support for gelatin emulsion in the 1880s, John Carbutt, of the Keystone Dry Plate Company in Philadelphia, made it commercial in 1888. He purchased the celluloid sheets from the Hyatt brothers. Celluloid had the assets of transparency, being unbreakable and light. In the West Orange laboratory of Thomas Edison, W. K. L. Dickson experimented on the Kinetoscope-a cylinder device-the following year. Magic lanterns were also experimenting with celluloid slides, less heavy to carry around than slides made of glass. An important step in the transition from photography to cinematography, was the celluloid film band proposed by Walter Poyner Adams in 1888. Another crucial step was a change in the formulation of celluloid, making it into thin and flexible films (John H. Stevens, 1882). This was the time when George Eastman stepped in, decisively. Together with William H. Walker, he marketed a roll film holder in 1885. Roll film allowed shooting photographic sequences. Production of celluloid-backed roll film began in 1889. It met with considerable commercial success. Thomas Henry Blair, who had founded a company in Boston, competed with the Eastman company, located in Rochester, NY. The Blair company proposed a full range of photographic products. The Edison-Dickson Kinetoscope was ideally suited for the Blair celluloid films. Such projections happened until nearly the end of the nineteenth century. Ousted from the American company he had started, Blair moved to England. The European Blair Camera Company supplied raw film stock for the pioneering experiments in cinematography of the Lumière brothers, in Lyon, France. All that explains the strong, durable association of celluloid and the movies (21, 22). At the turn of the twentieth century, there were simply no alternatives to celluloid in devising motion pictures. It had one major drawback, though, its flammability (23).

Even today, more than a century later, a search on the Web shows that the majority of sites elicited by the word "celluloid" relate to the movies. Production of the first cinematographic films increased even further the wealth accruing to the Newark-based Celluloid Manufacturing Company. It even indirectly increased the faraway camphor production from Taiwan. Gradually, films made from cellulose acetate started competing with those made out of celluloid, the latter having the twin drawbacks of being flammable and explosive.

### **Devising Artificial Silk**

I have sketched out briefly the history of celluloid, for its obvious parallel with the history of rayon. Ivory in the former, silk in the latter were precious, natural luxury materials for chemists to imitate and for the chemical industry to produce in large amounts. These novel artificial goods, celluloid and rayon (24), had a social impact; they—together with their retail outlets, department stores starting towards the end of the nineteenth century—were a significant factor in the rise of the middle class in Western countries.

There are enough accounts of the inventions by Chardonnet, and by Cross and Bevan, that I shall content myself by taking note of the main features; and I shall give prominence to some of the less well-known parts of the story, for the interesting questions they raise. Comte Hilaire de Chardonnet (1839-1924) was a rather idiosyncratic character, as well as an inventor of the edisonian type. He was independently wealthy and a polytechnicien. Having set-up a laboratory in his home, he devoted himself to scientific research, investigating, for instance, ultraviolet absorption by organic substances and the mechanism of vision. After long and careful observation of silkworms-Louis Pasteur was then similarly engaged-in a biomimetic spirit (25), Chardonnet threaded collodion (26) through a glass spinneret, and thus managed to mimic filaments of natural silk.

He had been at it for 30 years. He chose a derivative of cellulose, since silkworms fed on mulberry leaves, i.e., on cellulose—to gross first approximation. Little did he know that silk is another type of biopolymer, a polypeptide. After a long search, he selected, as the most promising natural form of cellulose, linters, i.e., the short hair on cotton seeds, with a maximum length of 25 mm (27). He patented his artificial silk in 1884 and proudly displayed samples at the two Paris exhibitions, in 1889 and 1900. He built and started in 1892 his first factory for producing artificial silk in Besançon, his hometown. He set up other factories outside France, in Sárvár (Hungary)—to which I shall return later—Tubize (Belgium) and Padova (Italy), among others.

The Chardonnet nitrocellulose process was rather quickly superseded. For one main reason, Chardonnet's Besançon factory did not have well-organized research (28). Also, about the time it opened, two British inventors, Charles Cross (29) and Edward Bevan, found in 1891 a significantly better procedure, the viscose process (30). They discovered that cellulose, for instance from spruce paper pulp, after treatment with strong caustic soda, can be treated by carbon disulfide and turned into a viscous, molasses-like solution. A cellulose ester—a xanthate, technically—is formed. After suitable ripening, this viscous solution is extruded through the fine holes of a spinneret, a constellation of hair-like openings in a platinum plate. The resulting fine filaments are led into an acid coagulating bath and thence wound onto reels, washed, and dried. The xanthate ester being thus decomposed, a continuous bundle of filaments of regenerated cellulose results (31).

Before continuing to spin the yarn of this story—an unavoidable metaphor, with such a subject matter—a feature of the Chardonnet episode deserves amplification. He turned to collodion, i.e., nitrocellulose, because this product had been much explored and used as a panacea by many other inventors and scientists. The chemical had been discovered by Pelouze in 1838. Under the French name *fulmicoton*, it had become an explosive, with an attractive weight-to-detonating power ratio. Fulmicoton led Alfred Nobel to the invention of dynamite. As a varnish, collodion was used to dress wounds—it was still in use during World War I.

To return to artificial silks, in 1904, Courtaulds acquired the Cross and Bevan 1892 patents to the viscose process, manufacturing artificial silks from wood pulp. They established an American subsidiary, the American Viscose Corporation (AVC) in 1909 (32). Other processes for turning cellulose into artificial fibers were devised, but the viscose process remained dominant (about 80%) throughout the first half of the twentieth century. In 1930, production of artificial silk (33)—it was named rayon in 1924, a point I shall return to—was led by the US (60 kt), followed by Italy (30 kt), Great-Britain (23 kt), Germany (20 kt), and France (18.5 kt) in fifth position only (34).

# **Devising Cellophane**

Jacques Edwin Brandenberger (1872-1954) was a Swiss engineer, employed in France in a succession of companies: in 1903, he was in charge of dyeing in a cleaning outfit. He was experimenting already with application of layers of viscose onto fabrics, to improve their aspect. In 1905, he was managing a branch of *Blanchisserie et Teinturerie de Thaon* (BTT) in Gisors (département of the Eure). He continued his experimentation with viscose cellulose silk there. In 1907, he transferred to the mother company in Thaon (Vosges), and he continued in his attempts to affix viscose artificial silk onto fabrics. Being frustrated with other techniques, he looked into the possibility of applying thin films of viscose.

This very real history has become replaced, in some quarters, by a picturesque but fallacious anecdote: "Brandenberger was seated at a restaurant when a customer spilt wine onto the tablecloth. As the waiter replaced the cloth, Brandenberger decided that he should invent a clear flexible film that could be applied to cloth, making it waterproof" (35). The truth of the anecdote is that Brandenberger was indeed trying to apply such a viscose coating to cotton fabrics.

By the end of 1908, Brandenberger had succeeded, and patented the application of cellulosic films on various supports. He mentioned explicitly in the patent applications the analogy to photographic and cinematographic film (36). The president of BTT, Paul Lederlin, granted him a subsidy and approached Société Française de la Viscose, with which a collaboration agreement was signed. By 1908 Brandenberger devised also the first machine for manufacturing transparent sheets of regenerated cellulose, at the rate of 10-15 meters per minute. The early results were rather disappointing though. Brandenberger failed to come up with films of uniform, reproducible thickness. Finally, during the spring of 1909, he was able to produce films weighing only 25 g per square meter, i.e., with a thickness of only 0.016 mm (37). By 1912, he was making a saleable thin flexible film, used in gas masks. Would they come handy just a few years hence!

The viscose films produced by Brandenberger did not fail to attract the attention of the movie-making industry, of companies such as Eastman-Kodak and Pathé, for these viscose films were much less flammable than celluloid. Brandenberger named his invention "cellophane" and trademarked it in 1912. He foresaw a possible realm of applications in the wrapping of goods (38). The same year (1912), the American Chemical Society validated cellophane for food-wrapping. The BTT company did not prove itself equal, however, to the task of marketing this new material. It sold its cellophane-producing branch to *Comptoir des textiles artificiels* (CTA), which already included *Société française de la Viscose*.

An independent company *La Cellophane* was incorporated in 1913. It started production in Bezons (Oise) during the war, in 1915. By the end of the war, in 1919, 40% of the production was already being shipped to the United States. The same percentage applied in 1923: 160 t of cellophane were produced in Bezons for the American market—which explains DuPont de Nemours becoming interested, as we shall see further on.

A vividly interesting part of the cellophane story, which we owe in part to World War I, is the feedback from technology to science. At the Rockefeller Institute, starting in 1915, Alexis Carrel and the young mathematician he had hired as an assistant, Pierre Lecomte du Nouy, measured war wounds by planimetry, after they had traced the outline of the wound onto cellophane (39). A considerably more important application to science was use of cellophane as the semi-permeable membrane in dialysis studies, it became standard just a few years later (40).

## New Words, New Brands

We live in an era of relatively new brand names, such as Apple, Amazon, Google or Yahoo. Names for their popular commercial products do not lag behind: Macintosh, iPhone, iPad, Kindle or Word. Some such names have already entered the language.

Neologisms coined by corporations have thus entered the common language. This particular development was ushered in much earlier, at the turn of the twentieth century, at least for the products I am focusing on. The names of the commercial products based on the same cellulose-derived chemical product, rayon and cellophane, for the fiber and for the transparent film respectively, have also entered the language, to such an extent as to no longer require a capital initial letter. The viscose process by which the former used to be—and continues to be, to a minor extent—manufactured has nearly achieved a similar status.

A neologism, by definition, is when a new word enters common parlance. A new brand can be deemed successful if and when its name becomes a common word and enters the dictionaries—as in the above examples. The process of generalized adoption can be likened to an epidemic. It needs a vector. There is an infection phase, when a steady state is achieved: more people per unit time—a week, say—acquire the word than forget or lose it. Infection brings about a process of collective memorization. Infection demands diffusion among a group of people, by the highly effective word of mouth. The neologism process is complete only with mutual contamination between otherwise separate social circles, when the new word, with or without a splash, enters the language. At least, this is what my intuition suggests. But words seldom exist in isolation. They belong to families. Consider as example the neologism with which this narrative began, parkesine—named after Alexander Parkes. Parkesine begot celluloid, assuredly. But not directly. There was an intermediate: the Hyatt brothers initially named their product Ivorine, since it was an imitation of ivory (41).

The name "cellophane" was coined about 1911 by its inventor, Jacques Brandenberger, as a protected brand name. This name took and held because it is transparently logical, the cellulose primary material lending it the first four letters, while the -phane suffix refers to its diaphanous aspect, *diaphane* in French. As readers will recall, French words are graced with a gender. In the case of cellophane, this gender has become ambiguous. The "e" ending suggests the feminine, "la cellophane." However, this material is shaped as a thin film. The word "film" is masculine in French. Accordingly, one also finds the form "le cellophane". According to Google, the feminine is dominant, but by a mere factor of two, 44,800 versus 23,200.

The name "viscose" for the process by which cellulose is transformed into either artificial silk or cellophane film dates to 1892, to its devising by the British chemists Cross and Bevan. It is a cognate of "viscous" and refers to the syrupy aspect of the mother liquor, after cellulose has been treated with caustic soda. The name "rayon" for the derived artificial silk, is somewhat more difficult to trace. It was coined, apparently, in 1924 at a meeting of the National Retail Dry Goods Association of America (42).

All these words share a transatlantic coloring, hybrids between French and English. There is a long list of such hybrids, going back several centuries; examples include *le weekend*, sport and tennis. In addition to naming, these words served for branding too. The technologies appeared at the time when trademarks started being legally protected as intellectual property and as a consequence of international agreements, such as the Madrid Agreement Concerning the International Registration of Marks of 1891, following upon the Berne Convention of 1886 and the Paris Convention of 1883 (43).

### The Role of Advertising

With both rayon and cellophane, it was considerable (44). There were three main features: direct advertising by chemical industry to consumers, targeting of women,

and the merging into political propaganda during the Thirties in the fascist countries, Germany and Italy.

Direct advertising from commodity producers in the chemical industry to consumers at the end of the line (45) resulted from innovation of both kinds, product innovation and process innovation, exemplified by both rayon and cellophane. Modern advertising, an industry born with the twentieth century and carried forward by visionaries such as Albert Lasker, had already shown its mettle, with its ability to create novel needs among consumers—orange juice being a prime example, introduced in the aftermath to World War I (46). Advertising could draw upon the novelty of materials such as the cellulose silks and the cellophane film. As wrote an influential designer of the times, the Thirties, primarily (47),

These new materials are expressive of our own age. They speak in the vernacular of the twentieth century. Theirs is the language of invention, of synthesis. Industrial chemistry today rivals alchemy! Base materials are transmuted into marvels of new beauty.

Inducing new tastes, new needs in customers, social trends can converge with advertising (48). John Wanamaker, a pioneer of the American department store, hired John E. Powers to write the advertising copy, on which he spent lavishly. This may have created the American model for the symbiosis of department stores and advertising agencies. The 20 largest stores in NY and Chicago in 1899 spent about \$1.775 million on advertising, an amazing amount, even in aggregate (49).

Advertising sold the new synthetic fabrics. They were applied to sportswear, a trend that originated in Southern Florida. "Beginning in the mid-1930s and culminating in the early 1950s, manmade fibers were first marketed and accepted in clothing that was to be worn for casual purposes" (50).

Some examples: in 1936 the 18th Annual Beaux-Arts Ball, appropriately named *Fête de Rayon-Fantastique*, could boast that all the costumes worn in the pageant were of fabrics made from rayon. A group of rayon manufacturers donated thousands of yards of the stuff for draperies and costumes, and in return Mrs. S. Stanwood Menken wore a rayon costume (The Spirit of Rain) and the famous stripper Gypsy Rose Lee wore a costume (The Eclipse of the Sun). It was all the idea of an advertising man named Reimars, representing the American Enka Corp., one of the main producers of synthetic fabrics at the time (51). The *Ladies' Home Journal* published an ad in 1940 featuring the Hollywood star Rita Hayworth, sponsored by the American Viscose Company, clothed in its Crown rayon brand. *Time* magazine published in 1948 for the American Viscose Corporation an advertisement entitled "Another fitting job for rayon." A lady, seen from the back, combs her hair while looking at herself in the mirror. She could be an actress putting on the finishing touches prior to stepping on the stage. The first sentences of the accompanying text are: "A fitting job vital to most women. Mysterious to most men. Challenging to the rayon engineer."

Turning to cellophane, its advertising is no less interesting. In the 1900s, celluloid still enjoyed an aura of modernity, as a brand-new plastic material, that the then nascent advertising industry embraced as a support for some of its messaging, to the extent of printing on it. In the early 1900s, celluloid thus served as support for much of the promotional items by the Hamilton watch company, of Lancaster, Pennsylvania. Retailers used them as giveaways to their customers. During the period 1917-1923, the Parisian Novelty Company, of Chicago, distributed celluloid vanity cases, serving likewise as supports for advertising. Louis L. Joseph, its founder, had a preference for novelties made of celluloid. Advantages of celluloid for such purposes were, first and foremost, its transparency. Celluloid offered also cheapness, light weight, durability, ease of molding, flexibility and ready availability in a wide range of thicknesses.

Starting in the 1930s, celluloid advertising targeted women especially, with ads in three of the most popular magazines among housewives: the Ladies' Home Journal, Good Housekeeping, and the Saturday Evening Post. Magazines were not the only media though. The Cellophane Radio Program, hosted by Emily Post, broadcast every Monday and Thursday morning in most major cities and addressed topics of interest pertaining to the home and daily social life. To give an idea of the ads, one placed by DuPont Cellophane in a 1934 issue of the Saturday Evening Post introduces housewives to the novel concept of the meat counter in supermarkets. It is entitled "New self-service meats make shopping quicker, easier." In France, the early advertising of cellophane was in the style of bandes dessinées, i.e., comic books. One issued in 1930 by the cellophane factory in Bezons is interesting in terms of gender studies: in half the frames, a handsomely dressed man uses cellophane. As for housewives, they wear an apron as their distinctive feature!

American-style advertising (52) pushing cellophane as partaking of the new shopping style (supermarkets), arrived in France rather late, only in the years following World War II. The advertising campaigns, such as the *Paris Match* weekly featured in 1954, were carbon copies of the pre-war American ones. The rhetorical question by Fohlen and Abrams (1962), "Can the French Be Americanized?" was to be answered, in the ensuing years, with a resounding YES (53).

Was the advertising effective? Enormously. In the case of cellophane (54)

A national grocery store chain reported a 2,100 percent increase in doughnut sales in two weeks after wrapping its doughnuts in cellophane. Market surveys confirmed that housewives felt no compelling urge to buy doughnuts before walking into the store but snapped them up strictly on impulse "because they looked so inviting in transparent packages."

With all the advertising pushing rayon and other cellulose-derived fabrics, cellophane as well, into the shopping bags of American ladies, was a backlash inevitable? At least one person, the great American writer E. B. White—too easily discarded as a humorist—took issue with the underlying consumerism, with the Keynesian notion—as it would become known—of jump-starting the economy by inducing people to purchase goods. In a series of three articles in *The New Yorker*, he reiterated the very American belief in the good, simple life, as had been advocated by Thoreau—a set of beliefs that periodically re-emerge, as later shown for instance in the writings by Jack Kerouac. White wrote (55):

... it is only on the surface that [nature's] variety is baffling. At the core it is a simple ideal. You feel it when lying stretched on warm rocks, letting the sun in. It is just possible that in our zeal to manufacture sunlamps at a profit, we have lost forever the privilege of sitting in the sun.

He railed against the new consumerism: "The revolution began with cellophane," people are "intrigued with its new transparencies," and driven to accumulate, egged on by advertising. White advocated instead "a society based on the assumption that nobody is going to buy anything, ever again." White even advocated an upended pay-scale, with the goal of decreasing consumption, paying the highest executives the lowest wages and the lowest-ranking employees the highest salaries.

Totalitarian states were prompt to seize upon the new synthetic materials, as both symbolical of the new man their governments purported to nurture, and making them autarchic, independent of imports from foreign countries. Fascist Italy, a major player in rayon production (SNIA Viscosa), took the lead. A rayon truck convoy took to the Italian roads in 1934, publicizing the multitudinous merits of the new fabric (56). Rayon found its bard in Marinetti, the poet who founded the Futurist movement (*Poem of Viscose Tower*, 1937-38). A whole new fascist city, Torviscosa, was built for viscose process work. The fiber itself became based on *Arunda donax* reeds from reclaimed Italian marshes, obviating a reliance for cellulose on Scandinavian firs. Nazi Germany and Stalinist USSR followed similar autarchic paths; for them too advertising artificial silks from cellulose became material for political propaganda (57, 58).

The historian faces a nagging question: did the propaganda for rayon and cellophane in totalitarian countries differ from their advertising in democracies in essence, or only in extent? I won't attempt to answer it here. To close this section on a jollier note, a hit song from those times, of the American New Deal, when the economy was starting to recover from the Depression, between the two World Wars, was Cole Porter's 1934 hit "You're the Top":

You're the purple light of a summer night in Spain You're the National Gallery You're Garbo's salary You're cellophane!

## Selling Artificial Silks: Department Stores

At the turn of the twentieth century, a retail institution already existed to sell artificial silks to customers, Chardonnet's at first, viscose silk a few years later (59). Chambers of Commerce in all big cities of the Western world prided themselves in their department stores (60). They had been in existence for a generation already. These were palaces of shopping, grandiose buildings devoted to luring the burgeoning middle class into spending money on splendidly displayed items of every description (61, 62).

They made women especially, but men also, come to visit them out of curiosity, out of idleness too—female members of the bourgeoisie as a rule stayed at home and did not work. Once they had entered a department store, they were captives. All kinds of selling tricks were used. Each client was made to feel special. The interior architecture was museum-like. It harbored luxury items that acted as motors of sales more indirectly than directly: customers who could not afford their high prices had the option of turning to less expensive substitutes, mere imitations of such luxury items—but worthwhile imitations. Artificial silks, for instance. Likewise, novelties coexisted with classics. Fashion dictated to women the purchase of dresses, and of many other pieces of clothing, which one had to be seen in, since their predecessors had been made obsolete. These temples of consumerism were made to look like aggregates of small boutiques, rather than like the huge emporiums they were. The new middle class flocked to them; all its tastes were attended to there. Department stores not only catered to the middle class, they pampered it (63).

The French novelist Emile Zola devoted his Au Bonheur des Dames (published in 1883) to one such store (64). It is a fictionalized account of how Aristide Boucicaut's Au Bon Marché worked. I quote here from that novel, because it is relevant to commercialization of artificial silks. It is a description of some of the (natural) silk fabrics, made both in the Far East and in Lyon, and sold in that Parisian department store. I beg to be forgiven for doing it in the original French, out of respect for the lyricism (65):

Au milieu du rayon, une exposition des soieries d'été éclairait le hall d'un éclat d'aurore, comme un lever d'astre dans les teintes les plus délicates de la lumière, le rose pâle, le jaune tendre, le bleu limpide, toute l'écharpe flottante d'Iris. C'étaient des foulards d'une finesse de nuée, des surahs plus légers que les duvets envolés des arbres, des pékins satinés à la peau souple de vierge chinoise. Et il y avait encore les pongées du Japon, les tussors et les corahs des Indes, sans compter nos soies légères, les mille raies, les petits damiers, les semis de fleurs, tous les dessins de la fantaisie, qui faisaient songer à des dames en falbalas, se promenant par les matinées de mai, sous les grands arbres d'un parc.

Since department stores were such a sensational innovation, monumental additions to the cityscape in France, England, the United States, and elsewhere, contemporary accounts abound. An early short essay described this novel metropolitan feature (66). Major cities all had their department stores, Paris (67), London (68). New York (63), Philadelphia, Chicago, San Francisco, (69) ... Department stores duplicated as exhibition halls for merchandise and as vehicles for its throughput—to express it crudely (70). Since they were meant and designed to manipulate the minds and the bodies of women, their main customers, department stores have become choice items in gender studies (71).

The middle class became a reality about the time (1889) when its name appeared in a dictionary, according to someone who researched the topic (72). This was the time, when Comte de Chardonnet invented his artificial silk, for the emergence indeed of the middle class. That it was contemporary with the flourishing of the first department stores is not a mere coincidence: there is a

definite correlation. One may go further, and assert a cause-effect relationship. Department stores could not have long survived, had it not been for the existence of a middle class—their prime market. This rising middle class needed to prove to itself its rising social status, which it signaled with luxury items—such as garments made of silks and, since genuine silks were extremely expensive, imitation silks would do (73).

To compare this mentality (74) with our times, nowadays the middle class shops worldwide by slavishly imitating the behavior of trendsetters—or so it is led to believe. The so-called jet set, as featured in people magazines, advertises items such as Rolex watches, Armani or Ralph Lauren clothes, Gucci shoes, Chanel perfumes, Louis Vuitton luggage, single malts, etc.—in brief the articles offered in so-called duty-free shops in airports. Members of the middle class have been brainwashed into compliance and routinely turn these into status symbols.

### **The Sprouting of Factories**

Both rayon and cellophane were commercial success stories. Customers rushed to buy them. Manufactures were built to accommodate the high demand. What did they look like? Where were they built? What kind of workforce did they host? I shall answer these questions for the rayon case, since it amounts to a lesson in economic geography.

Their aspect was both characteristic and peculiar: huge plants covering very large areas. For one thing, they associated two distinct functions, chemical production and a textile plant, in which the newly made viscose silk was turned into fabrics. These two manufacturing functions differed also in the (wo)manpower necessary. The former needed very few people, was near-automatic. The latter demanded a numerous personnel, in order to look after the individual mills which, collectively, occupied such a vast ground space. A whole article by a French geographer at the end of the Thirties expresses his admiring surprise at such industrial and architectural behemoths (75).

These viscose factories were set, typically, in areas already engaged in production of textiles. In France, production of artificial silks occupied the area of the former production of natural silk, around the city of Lyon (34, 76). In the United States (31, 77), to refer only to the plants erected by the American Viscose Company and active during the 1930s, they were located in Lewistown, Pennsylvania (PA) and Marcus Hook PA, to the northwest and southwest of Philadelphia, respectively; in Meadville PA, in the north of the state near Lake Erie; in the appropriately-named Nitro, in West Virginia (WV), near Charleston, and in Parkersburg, WV, west of Morgantown; and in Roanoke, Virginia, west of Richmond.

These implantations sought female labor both inexpensive and qualified, with prior experience in textile manufacturing. All the above locations were in the textile belt, at the boundary between the industrial North and the cotton-growing South, straddling the Mason-Dixon line. One may question also, noting such a geographic distribution of their plants, if the British corporation Courtaulds was not, deliberately or unconsciously, guilty of a neo-colonial mentality in setting-up factories in former British colonial territories, with the American Viscose Company as their subsidiary (78).

As for the workforce, it was overwhelmingly female, on account of the textile part of a viscose plant. It needed to be rather highly qualified, in addition, because the viscose process was such a complicated and capricious one. There had to be mastery, which only know-how from long habit could impart. This was required to such an extent that when a viscose plant was set up in my hometown of Grenoble, in southeastern France, a significant part of the workforce consisted of Hungarian women, transferred from a viscose plant in Hungary—as readers will recall, one of the original offshoots of Chardonnet's Besançon factory (79, 80).

### **DuPont and the French Connection**

Part of this story involves the DuPont de Nemours Corporation, as it decided during the 1920s to start producing both artificial silk and cellophane (81). In both instances, this company drew on French know-how. And those were not the only such cases. The DuPonts also exploited a license to the synthesis of ammonia using the process invented by Georges Claude and exploited by his *Société anonyme de l'Air Liquide*—a company still existing nowadays. From yet other French companies, DuPont de Nemours purchased rights for titanium pigments, for acetate flake, cellulose and the cellulose acetate yarn process (82).

To return to artificial silk and cellophane, DuPont de Nemours purchased the license for the viscose rayon technology in 1919 from *Comptoir des Textiles artificiels*, and that for the manufacture of cellophane in 1923 from *La Cellophane Société Anonyme*. The DuPont rayon plant started production in 1921. Their cellophane plant started production in 1924. Their production of rayon expanded markedly and it caught up with that of the American Viscose Company (83)—but only until the Depression hit in 1929. Just like other manufacturers exploiting the viscose process, the DuPont managers and scientists had to contend with its complications and idiosyncrasies, some of which they were able to master (28). The DuPont scientists sought other outlets than garments and hosiery for rayon. They found it, in 1936, in tire cords. This new outlet expanded greatly during World War II, for not only was rubber a strategic material, but synthetic rubber tires also came into their own during that period.

As for cellophane, DuPont remedied a major drawback by waterproofing it, as a result of the R&D by a clever young scientist, William Hale Church. Moistureproof cellophane started being produced in 1927. It proved to be not only an industrial, but also a commercial bonanza as well, contributing heavily to the benefits of the corporation until the advent of World War II.

The likely factors in the cooperation of the American with the French companies were, in the aftermath of World War I, sympathy for the French side and the will to help France regain its economic footing and reindustrialize. One might deem Francophilia natural on the part of the DuPont de Nemours family, descendants of a Frenchman who emigrated to the US at the end of the eighteenth century—and during the 1920s, this was still a company run by them. Besides, they likely appreciated the technological breakthroughs embodied in these inventions, those of artificial silk, cellophane and nitrogen fixation primarily.

There is a follow-up to this active sympathy from DuPont for French companies. In the late 1930s, prior to the onset of World War II, the French Rhône-Poulenc company and DuPont de Nemours started collaborating in the production of synthetic fibers. There was an exchange of technologies. DuPont acquired the rights to cellulose acetate from the French. They, in turn, bought a license for nylon 6,6 in 1939. During the war years, when Rhône-Poulenc was forced to collaborate with the German chemical industry and France was occupied, the collaboration with DuPont de Nemours was only put on hold, not jettisoned. Once the war was over, not only was it renewed, the DuPont de Nemours company had carefully put aside the royalties it owed the French company for exploiting the cellulose acetate license. In exchange, it gave Rhône-Poulenc the French rights to nylon production. The ensuing sudden affluence greatly assisted the rebirth of Rhône-Poulenc as a major player in French industrial chemistry during the post-war period (84).

### The Sprouting of Supermarkets

In like manner to artificial silks being sold like hot cakes by department stores in major cities, starting in the 1880s, cellophane wrappings helped in making supermarkets—also known at the time as *self-service* grocery stores—become ubiquitous, starting in the early Thirties (85). The exact date of birth is disputed. Mike Cullen, nicknamed King Kullen, opened his store in Jamaica, close to New York City, in 1930. The first prototype is said to have opened at the end of 1927 (86). This novel retail institution (73) came about as the convergence of three forces, the individual automobile, refrigeration and plastic packaging (87).

Refrigeration, viz. use of an heat-exchanging fluid freons came to be the universal vectors—and a pump, started becoming a ubiquitous feature of American life during the 1920s, at the very time when Du Pont entered the cellophane business (88). Clarence Birdseye invented the "Quick Freeze Machine" in 1926, that enabled onthe-spot food preservation. Dr. Mary Engle Pennington, refrigeration expert, private consultant to packing houses, shipping firms and warehouses, had been the first chief of the Food Research Laboratory, established in 1907 by the Department of Agriculture to help implement the Food and Drug Act. A pioneer of strict hygiene in handling food, she was instrumental during the Thirties in bringing refrigeration to American grocery stores and the newly established supermarkets (89).

Cellophane food-wrapping, as an application of the new material, was present at its birth: it was advocated in that function as early as 1912 (90). The association of cellophane packaging and refrigeration was also urged early on (91). It became the norm (92). Design was called upon to make the cellophane wraps attractive (93), and to induce impulse buying by customers (94, 95). Supermarkets sprouted everywhere in the United States during World War II when American women were needed for war production. To shop for groceries once weekly, instead of daily, freed them for the war effort (96). Supermarkets had become by 1945 as much a part of the American landscape as gasoline pumps, located likewise within easy access of highways and freeways. The Eisenhower era development of a network of interstate highways, for strategic reasons, had for its main result the spread of suburbs, made all the more widespread by cheap fuel for the cars, and by the ready availability of a nearby shopping center, with a supermarket at its core.

### Conclusions

Chameleon-like, wood pulp was turned into three different—widely different in terms of their uses—new materials. One would not construe celluloid, rayon and cellophane as identical, even though their chemical constitution is basically the same—a difference being that celluloid retains the nitrate, largely absent from the other two.

A first lesson from their story is the importance of playful pursuits to the devising of new materials. Are games and play of as much of importance to mankind as health and nutrition? One gathers so from television viewers watching nowadays professional sports, soccer in most of the world, baseball and football in the US.

What is obvious today was already the case at the turn of the twentieth century. In 1901, a decade after the British invented table tennis, an Englishman named James W. Gibb discovered celluloid during a visit to the US. As a consequence, celluloid served as the material for ping-pong balls—ping-pong is the other name of the game—until 2014, when other synthetic polymers started to replace celluloid, in the official description by the international federation running that sport (ITTF) and by the Olympics organization.

Another robust finding from the devising of novel materials from nitrocellulose is the relative insignificance of chemistry to their story. Nitrocellulose, as guncotton or collodion, was a predominant material during the second half of the nineteenth century. The inventors I have referred to selected it as their starting material for that overwhelming reason. By trial-and-error, not on the basis of chemical knowledge and reasoning, they experimented with a variety of adjuncts in order for the resulting formulations to offer satisfactory results.

What kind of results? Mechanical engineering properties predominantly, such as satisfactory plasticity for molding or extrusion (97). The visual aspect had also great importance, the artefacts made from these new materials had to look like the natural objects they were meant to substitute: billiard balls made of celluloid, aka ivorine, were imitations of the ivory-made items, garments made of rayon had to look as if they were made of silk. At no point did the inventors base themselves on the chemical make-up of the natural stuff, whether calcium and magnesium phosphate for ivory or a polypeptide for silk. Their simulacra were made from an inexpensive raw material such as cotton or wood pulp, they looked fine and were pliable enough for industrial machinery, to them inventors that was sufficient.

Rayon and cellophane were both offsprings of viscose. The writer and humorist Liebling (98) knew it, he must have been well briefed by a professional chemist (99).

Taken together, the stories of rayon and cellophane point to a gap in our view of the past. Obviously, history of science is inseparable from history of technology or corporate history. But other strands need to be woven in: social history; history of mentalities; history of games and play; literary history—exemplified here by Zola, by Marinetti and Futurism; imperial history—without which the American Viscose venture of Courtaulds loses meaning; history of language and of its nurturing of neologisms as above documented; history of advertising and of its appearance at the turn of the twentieth century in the United States; history of ideologies, such as Communism and Fascism; economic history; that of design and fashions ...

In short, a total history (100) is called for.

### Acknowledgments

I am grateful to a colleague, who wishes to remain anonymous, for extremely useful and stimulating comments.

### **References and Notes**

- 1. See, for example, C. Schönbein, "On the Discovery of Gun-Cotton," *Philos. Mag.*, **1847**, *31*, 7-12.
- 2. J. Verne, *De la Terre à la Lune*, J. Hetzel, Paris, 1865, p 97. Curiously, Maynard is absent from 19<sup>th</sup>-century English translations of *From the Earth to the Moon*.
- 3. J. Verne, *Voyage au Centre de la Terre*, J. Hetzel, Paris, 1864, pp 296ff.
- 4. It would be tedious to list all the uses ivory was put to in the 1880s, say. To mention just a few: billiard balls, buttons for clothing, combs, false teeth, jewelry, knife handles, piano keys, umbrella handles, .... No wonder if elephants were being hunted relentlessly, to the extinction we are currently witnessing.
- 5. T. Palucka, MRS Bulletin, 2005, 30, 614.
- Homo ludens—to use Huizinga's term—endures across the centuries: rubber was used originally, after the conquistadors brought back the first samples to Europe, for ball games at the Spanish court. One wishes for a history

of materials focused on their applications to *play* of all kinds.

- 7. The reason why inventors do not form social groups, differentiating them from scientists, is their restrictive means for communicating knowledge: patents are meant more for protection of ownership, of know-how and trade secrets, than for the advancement of learning. While discovery thrives on the not-for-profit competition for priority, invention is very much the province of egomaniacs engaged in the occasional wild goose chase or, more prosaically, aiming for a windfall-such as the memorable Balthazar Claës portrayed by Balzac in La Recherche de l'Absolu [Quest for the Absolute] or the many idiosyncratic inventors portrayed by Jules Verne. Inventors were very much individuals, definitely not members of a group. They resist later and thus anachronistic categorizations. They are closer to engineering than to science, to mechanical engineering more specifically. Their goals are extremely diverse: to benefit mankind; to seek fame; one-upmanship; to emulate, better to outdo nature; to reap major profit; entrepreneurship; starting a company that might outlast them ... On invention and discovery, see for instance C. Piscopo, and M. Birattari, "Invention Versus Discovery," in E. G. Carayannis, Ed., Encyclopedia of Creativity, Invention, Innovation and Entrepreneurship, Springer, 2013, pp 1139-1146; N. R. Lamoreaux and K. L. Sokoloff, "Inventors, Firms, and the Market for Technology in the Late Nineteenth and early Twentieth Centuries," in N. R. Lamoreaux, D. M. G. Raff and P. Temin, Eds., Learning by Doing in Markets, Firms, and Countries, University of Chicago Press, Chicago, 1999, pp 19-60; T. Nicholas, J. Econ. Hist., 2010, 70, 57-82.
- R. Friedel, *Hist. Technol.*, **1979**, *4*, 45-62. S. T. Mossman, "Parkesine and Celluloid," in S. T. I. Mossman and P. J. T. Morris, Eds., *The Development of Plastics*, Royal Society of Chemistry, Cambridge, UK, 1994, pp 10-25.
- 9. The natural-artificial dichotomy, much anterior to manmade plastics, goes back to *daidala* in Greek Antiquity and, of course, to alchemical work. It is such an overworked point that I need not elaborate on it further. An outstanding discussion is that by Roald Hoffmann ("Natural/Unnatural," *New England Review and Bread Loaf Quarterly.* **1990**, *12*, 322-335).
- 10. The first commercial use was in 1851. Schönbein had patented cellulose nitrate in the US in 1846.
- 11. Is there a connexion between the Age of Plastics, that began during the second half of the nineteenth century and the Second Industrialization? Probably, through the rise of the middle class. See below.
- 12. Parkes started commercial manufacture of parkesine in 1866.
- 13. Camphor is a globular molecule. In the solid state, it is a plastic crystal: the spherically-shaped molecules spin

on their lattice sites with little hindrance. This fact about camphor, reached in the mid-twentieth century, is an *a posteriori* justification for the empirical use of camphor, by nineteenth-century inventors, as a plasticizer. See P. Laszlo and E. M. Engler, "New Description of Nuclear Magnetic Resonance Solvent Shifts for Polar Solutes in Weakly Associating Aromatic Solvents," *J. Am. Chem. Soc.*, **1971**, *93*, 1317-1327.

- 14. F. W. Reinhart and G. M. Kline, *Ind. Eng. Chem.*, "Film-Forming Plastics: Effect of Solvents, Diluents, and Plasticizers," **1939**, *31*, 1522-1529.
- J. A. Reilly, "Celluloid Objects: Their Chemistry and Preservation," *J. Am. Inst. Conservation*, **1991**, *30*, 145-162 https://doi.org/10.1179/019713691806066700.
- C. P. McCord, "Celluloid: The First American Plastic— The World's First Commercially Successful Plastic," *J. Occupational Environ. Med.*, **1964**, *6*, 452-457. R. Friedel, *Pioneer Plastic: The Making and Selling of Celluloid*, University of Wisconsin Press, Madison, 1983. R. B. Seymour and G. B. Kauffman, *J. Chem. Educ.*, "The Rise and Fall of Celluloid," **1992**, *69*, 311-314. S. T. I. Mossman and P. J. T. Morris, Eds., *The Development of Plastics*, Royal Society of Chemistry, Cambridge, UK, 1994
- 17. K. Ladha and M. Verma, "19th Century Denture Base Materials Revisited," *J. Hist. Dent.*, **2011**, *59*, 1-11.
- 18. Why dental plates? This is a no-brainer, teeth in both elephants and men are made of ivory.
- A. Sullivan, "Thingamajigs and Whirligigs: A History of Scientific Innovation at UW," *The [University of Washington] Daily*, Jul. 21, 2015, available online at http://www. dailyuw.com/science/article\_5929dd48-3027-11e5-9c0d-03ef0ff15c62.html (accessed May 15, 2019).
- S. J. Mezias and J. C. Kuperman, "The Community Dynamics of Entrepreneurship: The Birth of the American Film Industry, 1895–1929," *J. Bus. Venturing*, 2001, 16, 209-233. See also N. M. Mathews, C. Musser and M. Braun, *Moving Pictures: American Art and Early Film*, 1880-1910, Hudson Hills Press, Manchester, VT, 2005.
- 21. Thus celluloid, an amusement device initially (billiard balls) became the support to a more passive amusement, watching a movie. Because of the personalities of pioneers such as George Eastman and the Lumière brothers, transition to an industry was swift. On Eastman, see *inter alia* R. V. Jenkins, "Technology and the Market: George Eastman and the Origins of Mass Amateur Photography," *Technol. Cult.*, **1975**, *16*, 1-19; R. S. Tedlow, "The Beginning of Mass Marketing in America: George Eastman and Photography as a Case Study," *J. Macromarketing*, **1997**, *17*, 67-81; E. Brayer, *George Eastman: a Biography*, University of Rochester Press, Rochester, NY, 2006.
- 22. See G. Onclincx, "Les débuts du cinématographe des frères Lumière à Bruxelles d'après les journaux du temps

(Novembre 1895-Février 1897)," *Rev. hist. moderne et contemporaine*, **1955**, *2(3)*, 219-225.

- D. Rossell, "A Chronology of Cinema, 1889-1896," *Film Hist.*, **1995**, 7, 115-236. D. Rossell, *Living Pictures: The Origins of the Movies*, SUNY Press, Albany, NY, 1998. M. Chanan and E. Trèves, "La « muse celluloïde » : Le celluloïde et la dialectique de l'invention du cinématographe," *L'Homme et la Société*, **1978**, 47, 77-94. D. Rossell, "Exploding Teeth, Unbreakable Sheets and Continuous Casting: Nitrocellulose from Guncotton to Early Cinema," in R. Smither and C. A. Surowiec, *This Film Is Dangerous: A Celebration of Nitrate Film*, Indiana University Press, Bloomington, 2002, pp 37-51. B. Singer, "Early Home Cinema and the Edison Home Projecting Kinetoscope," *Film Hist.*, **1988**, 37-69.
- 24. T. Shaikh, S. Chaudhari and A. Varma, "Viscose Rayon: A Legendary Development in the Manmade Textile," *Int. J. Eng. Res. Application*, **2012**, *2*(*5*), 675-680.
- 25. W. E. Bijker, "The Social Construction of Bakelite: Toward a Theory of Invention," in W. E. Bijker, T. P. Hughes, and T. Pinch, Eds., *The Social Construction* of Technological Systems, MIT Press, Cambridge, MA, 1987, pp 159-187. M. E. Gorman, *Transforming Nature:* Ethics, Invention and Discovery, Springer, 1998.
- H. Gernsheim, *The Rise of Photography*, 1850-1880: *The Age of Collodion*, Thames and Hudson, New York, 1987.
- 27. G. Bertrand, "Les découvertes scientifiques du Comte de Chardonnet et l'invention de la soie artificielle," *Notices et Discours de l'Académie des Sciences*, **1936**, *1*, 694-709.
- S. S. Sadtler, "Research in the Artificial Silk Industry," Ann. Am. Acad. Political Social Sci., 1925, 119, 32-39.
- E. F. Armstrong, "Charles Frederick Cross, 1855-1935," Obituary Notices Fellows R. Soc., 1935, 1, 459-464.
- C. F. Cross, E. T. Bevan and C. Beadle, "Improvements in Dissolving Cellulose and Allied Compounds," British Patent 8700, issued May 7, 1892. "Thiokohlensäureester Der Cellulose." *Ber. Dtsch. Chem. Ges.*, 1893, 26(1), 1090-1097.
- J. F. X. Harold, "Textiles Go Chemical," *Ind. Eng. Chem.*, 1937, 29(7), 742-746.
- D. C. Coleman, "The Uses and Abuses of Business History," *Business Hist.*, 1987, 29, 141-156.
- 33. P. Farago, "Synthetics v. Natural Fibres," *Australian Quarterly*. **1953**, *25*, 40-52.
- 34. A. Pinton, "La soie artificielle en 1930," *Les Études rhodaniennes*, **1931**, *7(3)*, 333-335.
- 35. There are numerous variations on the internet. For example, The Inventors, Cellophane, http://theinventors.org/library/inventors/blcellophane.htm (accessed May 16, 2019). Another version has Brandenberger himself spill the wine: A. Mangravite, "Cellophane Comes to Buffalo," Disillations, Summer 2012, https://www.sciencehistory.

org/distillations/magazine/cellophane-comes-to-buffalo (accessed May 16, 2019).

- Which would not be forgotten: R. Forster, J. Goergen and A. Mebold, "Ozaphan: Home Cinema on Cellophane," *Film History: An International Journal*, 2007, 19, 372-383.
- J. E. Brandenberger, "Notes on Cellophane," *J. Franklin Inst.*, **1938**, *226*, 797-801.
- J. Brown, "Cellophane Glamour," *Modernism/modernity*, 2008, 15, 605-626.
- P. Selcer, "Standardizing Wounds: Alexis Carrel and the Scientific Management of Life in the First World War," *Brit. J. Hist. Sci.*, 2008, 41(1), 73-107.
- 40. H. N. Holmes, Laboratory Manual of Colloid Chemistry, John Wiley & Sons, New York, 1928. Representative examples: F. H. Johnson, "Cellophane Covers for Petri Dishes for Keeping out Contaminations and Studying the Effects of Ultra-Violet Light." Science, 1931, 73, 679-680; H. L. White, B. Monaghan and F. Urban. "Electrical Factors Influencing the Rate of Filtration of Aqueous Electrolyte Solutions through Cellophane Membranes," J. Gen. Physiol., 1935, 18(4), 515-521; D. Delisa, "Herbarium Mounts in Cellophane," Torreya, 1937, 37(3), 58-59; T. Teorell, "Ionic Transference Numbers in Cellophane Membranes," J. Gen. Physiol., 1936, 19(6), 917-927; A. Dusseau, "Growing Fungi on Cellophane," Science, 1938, 88, 412; I. Bucholz, "Cellophane Cover Slips and a Method for Mounting," Science, 1940, 92, 436; G. W. Harmsen and W. J. Kolff. "Cultivation of Microorganisms with the Aid of Cellophane Membranes," Science, 1947, 105, 582-583; M. B. Templeman and L. M. Marshall, "Dialysis of Certain Sugars through Cellophane." Science, 1960, 132, 153-154.
- 41. Parkesine. Ivorine. Why the -ine suffix? Chemists know that the -ose ending, as in glucose or cellulose, denotes the sugars family, and that the -ine relative was initially introduced by Gay-Lussac as generic to alkaloids. Strychnine (1818), caffeine (1822), codeine (1832), heroin (1898), novocain (1906), yohimbine (1895-1900) are examples, originating in the nineteenth century. In the twentieth, antibiotics came to be given similar suffixation: penicillin, streptomycin, terramycin, tetracyclin, etc. To come back to nineteenth century chemical neologisms, synthetic molecules such as aspirin (1890s) and saccharin (1884) belong to the same lexical family, sharing the identical -in(e) suffix, even though they do not belong to the alkaloid family.
- 42. "Substitute for 'Glos," *New York Times*, Apr. 13, 1924, p E13.
- 43. Is it a mere coincidence if the same times, during the end of the nineteenth century, were those of the introduction of name reactions in the corpus of chemistry? My intuition tells me this is a related historical phenomenon, that might reward further research.

- See the historical chapter by Gary Cross, "Origins of Modern Consumption: Advertising, New Goods, and a New Generation, 1890-1930," in M. P. McAllister and E. West, Eds., *The Routledge Companion to Advertising and Promotional Culture*, Routledge, 2013, pp 11-23.
- F. A. C. Wardenburg, "The Role of Advertising by the Chemical Industry," in *Chemical Marketing in the Competitive Sixties*, American Chemical Society, Washington, DC, 1959, ch. 5, pp 36-40.
- P. Laszlo, *Citrus: A History*, University of Chicago Press, Chicago, 2007.
- P. T. Frankl, Form and Re-Form: A Practical Handbook of Modern Interiors, Harper and Brothers, New York, 1930.
- M. Fuessle, "Elbert Hubbard, Master of Advertising and Retailing," *Advertising World*, **1915**, *20*, 135-144.
- 49. D. Pope, *The Making of Modern Advertising*. New York: Basic Books, 1983, p. 134.
- D. Clemente, "Made in Miami: The Development of the Sportswear Industry in South Florida, 1900-1960," J. Soc. Hist., 2007, 41(1), 127-148. D. Holland, "Volney B. Palmer: The Nation's First Advertising Agency Man," Pennsylvania Mag. Hist. Biog., 1974, 98, 353-381.
- 51. A. J. Liebling and R. Maloney. "The Talk of the Town / Ball of Yarn," *New Yorker*, Nov. 28, 1936.
- E. Applegate, *The Rise of Advertising in the United States: A History of Innovation to 1960*, Scarecrow Press, Lanham, MD, 2012. Reviewed by Q. Yao, *J. Advertising Educ.*, 2013, 17, 51.
- 53. C. Fohlen, (F. M. Abrams, trans.), "Can the French Be Americanized?" *Antioch Review*, **1962**, *22(2)*, 179-188.
- 54. S. Fenichell, *Plastic: The Making of a Synthetic Century*, Harper Business, New York, 1996.
- 55. E. B. White, "Alice through the Cellophane," *New Yorker*, May 6,13, & 20, 1933.
- 56. J. T. Schnapp, "The Fabric of Modern Times," *Critical Inquiry*, **1997**, *24(1)*, 191-245.
- H. Laufenburger, "L'autarchie allemande et les tendances du deuxième Plan Quadriennal," *Politique étrangère*, **1936**, *1(6)*, 72-79.
- For the earlier context in Weimar Germany, see Y. F. Lane, "'No Fertile Soil for Pathogens:' Rayon, Advertising, and Biopolitics in Late Weimar Germany," J. Soc. Hist., 2010, 44, 545-62.
- P. A. Cunningham, "Selling Style: Clothing and Social Change at the Turn of the Century," J. Am. Cult., 2005, 28, 338-339.
- I. Jeacle, "Emporium of Glamour and Sanctum of Scientific Management: The Early Twentieth Century Department Store, *Management Decision*, 2004, 42, 1162-1177.

- 61. J. Whitaker, Service and Style: How the American Department Store Fashioned the Middle Class, St. Martin's Press, New York, 2006.
- As a rule, people were ambivalent about them: B. Rieger, "Modern Wonders': Technological Innovation and Public Ambivalence in Britain and Germany, 1890s to 1933," *Hist. Workshop J.*, 2003, 55, 152-176.
- M. Brady, *Bloomingdale's, the Biography of a Store,* Harcourt, Brace, Jovanovich, New York, 1980. H. C. Klassen, "T. C. Power & Bro.: The Rise of a Small Western Department Store, 1870-1902," *Business Hist. Rev.*, 1992, 66, 671-722.
- 64. C. Becker and J. Gaillard, *Au Bonheur des Dames, Zola: Analyse Critique*, Hatier, Paris, 1982.
- 65. É. Zola, Au bonheur des dames, Hachette, Paris, 1883, p 229. Translation by E. A. Vizetelly, The Ladies' Paradise, Hutchinson & Co., London, 1895, pp 262f. "In the middle of the department, an exhibition of summer silks illumined the hall with an aurora-like brilliancy, like the rising of a planet amidst the most delicate tints: pale rose, soft yellow, limpid blue, indeed the whole scarf of Iris. There were foulards of a cloudy fineness, surahs lighter than the down falling from trees, satined pekins as soft and supple as a Chinese beauty's skin. Then came Japanese pongees, Indian tussores and corahs, without counting the light French silks, the narrow stripes, the small checks and the flowered patterns, all the most fanciful designs, which made one think of ladies in furbelows, strolling in the sweet May mornings, under the spreading trees of some park."
- 66. S. H. Adams, "The Department Store," *Scribner's Magazine*, Jan. 1897, 1-27.
- 67. R. Bowlby, "Modes of Modern Shopping: Mallarmé at the Bon Marché," in Nancy Armstrong and Leonard Tennenhouse, Eds., *The Ideology of Conduct: Essays in Literature and the History of Sexuality*, Methuen, London, 1987, pp 185-205. V. Bourienne, "Boucicaut, Chauchard et les autres," in Jacques Marseille, Ed., *La révolution commerciale en France du Bon Marché à l'hypermarché*, Le Monde-Editions, Paris, 1997, pp 53-70.
- F. Atkinson, "The Selfridge Store, London," *Architectural Rev.*, 1909, 25, 292-301.
- G. Barth, "Department Store," *City People: The Rise of Modern City Culture in Nineteenth-Century America*, Oxford University Press, New York, 1980, ch. 4, pp 110-147.
- S. P. Benson, "Palace of Consumption and Machine for Selling: The American Department Store, 1880-1940," *Radical Hist. Rev.*, 1979, 21, 199-221.
- D. Belisle, "Negotiating Paternalism: Women and Canada's Largest Department Stores, 1890-1960," J. Women's Hist., 2007, 19(1), 58-81.

- 72. B. Bledstein, *The Culture of Professionalism: The Middle Class and the Development of Higher Education in America*, W. W. Norton & Co., New York, 1976.
- 73. R. Bowlby, *Carried Away: The Invention of Modern Shopping*, Columbia University Press, New York, 2002.
- 74. W. R. Leach, *Land of Desire: Merchants, Power, and the Rise of a New American Culture*, Vintage, New York, 2011 (first published 1993).
- 75. J. Klein, "L'industrie française de la rayonne," *Ann. Géographie*, **1939**, *48*, 252-275.
- 76. A. Pinton, "La soie artificielle à Lyon en 1935," Les Études rhodaniennes, **1936**, *12(1)*, 104-107.
- C. E. Mullin, "The Synthetic-fiber Industry of America," Ind. Eng. Chem., 1930, 22, 461-467.
- D. C. Coleman, *Courtaulds: An Economic and Social History* (3 vols), Vol. 2, *Rayon*, Clarendon Press, Oxford, UK, 1969.
- P. Ricard, J.-L. Pelon and M. Silhol, Mémoires de Viscosiers: Ils filaient la soie artificielle à Grenoble, Presses universitaires de Grenoble, Grenoble, France, 1992. M. Blondé, Une Usine dans la guerre: La Société Nationale de la Viscose à Grenoble, 1939-1945, Presses universitaires de Grenoble, Grenoble, FR, 2008.
- 80. This is the part of the story that connects with my family history. My parents left Hungary in 1930 because of the Depression. The three of us settled in Grenoble in March 1940, just a few weeks before the Phony War flared up into real war. My parents, Francois and Magda Laszlo, got in touch with the small local Hungarian community-the worldwide Hungarian diaspora to this day is closely knit, if anything because of the unique Hungarian language they share. Grenoble, initially in the Free Zone, became occupied, first by Italian troops, later by German troops. François Laszlo became active in the Resistance network led by the famous Abbé Pierre, which helped numerous Jews, children in particular, cross the nearby border to escape into Switzerland. These highly dangerous Resistance activities were recorded in his application for French citizenship, that was quickly granted him in 1946. Magda Laszlo also engaged in an underground activity: she organized the Hungarian workers into a union, overwhelmingly female as I have pointed out, in the Grenoble viscose plant. It is perhaps no coincidence if Resistance activities flourished in this plant as a whole, as moreover its director at the time, Mr. Fries, tolerated them instead of cracking down as he might have. I am unable to offer any written document in support of these assertions of the political activities of my mother during World War II, when I was a young child. They are part of the family tradition, just hearsay to the strict historian. I hope they won't be dismissed out of hand.

- D. A. Hounshell and J. K. Smith Jr., Science and Corporate Strategy: Du Pont R&D, 1902-1980, Cambridge University Press, Cambridge, UK, 1988.
- W. F. Mueller, "The Origins of the Basic Inventions Underlying Du Pont's Major Product and Process Innovations, 1920 to 1950," in R. R. Nelson, Ed., *Rate and Direction of Inventive Activity: Economic and Social Factors*, Princeton University Press, Princeton, NJ, 1962, 323-346.
- 83. R. S. Jarmin, "Learning by Doing and Competition in the Early Rayon Industry," *RAND J. Econ.*, **1994**, *25(3)*, 441-454.
- P. Cayez, "Négocier et Survivre: La Stratégie de Rhone-Poulenc pendant la Seconde Guerre Mondiale," *Histoire, économie et société*, **1992**, *11*, 479-491.
- 85. T. Deutsch, Building a Housewife's Paradise: Gender, Politics, and American Grocery Stores in the Twentieth Century, Univ of North Carolina Press, Chapel Hill, 2010.
- R. McAusland, "Supermarkets: 50 Years of Progress," *Progressive Grocer*, **1980**, *59(6)*, 5-155. W. Soper, "Su-permarkets," *Am. Hist. Illustrated*, **1983**, *18(1)*, 40-47.
- K. Humphery, Shelf Life: Supermarkets and the Changing Cultures of Consumption, Cambridge University Press, Cambridge UK, 1998.
- G. A. Nichols, "Enter a New Industrial Giant: Iceless Refrigeration," *Printers' Ink*, Dec. 16, 1926, pp 3-4, 6, 208, 211, 212, 214. O. E. Anderson Jr., *Refrigeration in America: a History of a New Technology and Its Impact*, Princeton University Press, Princeton, NJ, 1953. G. Taubeneck, "Refrigeration Has Come of Age," *Rand McNally Bankers Monthly*, **1937**, *57*, 263-266. S. Isenstadt, "Visions of Plenty: Refrigerators in America around 1950," J. Design Hist., **1998**, *11(4)*, 311-321.
- B. Heggie, "Ice Woman." *New Yorker*, Sept. 6 1941, p 23.
- L. V., "Sur l'emploi de la cellophane pour envelopper les matières alimentaires" [summary of a report by F. Bordas], L'Union Pharmaceutique, 1912, 315-316.
- C. Birdseye, "Some Scientific Aspects of Packaging and Quick-Freezing Perishable Flesh Products. II. Packaging Flesh Products for Quick-Freezing," *Ind. Eng. Chem.*, 1929, 21(6), 573-576.
- 92. C. Bernat, "Supermarket Packaging: The Shift from Glass to Aluminum to Plastic," *Atlantic*, Jan. 25, 2012.
- 93. G. Porter, "Cultural Forces and Commercial Constraints: Designing Packaging in the Twentieth-Century United States," *J. Design Hist.*, **1999**, *12(1)*, 25-43.
- Cellophane Division, E.I. du Pont de Nemours & Company, *Design for Selling: A Study of Impulse Buying*, E.I. du Pont de Nemours & Company, Wilmington, DE, 1946.

- 95. G. L. Urban and J. R. Hauser, *Design and Marketing of New Products,* Prentice Hall, 1980.
- E. B. Halper, "Evolution and Maturity of the American Supermarket During World War II," *Real Property, Probate Trust J.*, 2006, 41(2), 253-356.
- 97. H. R. Simonds, *Extrusion of Plastics, Rubber, and Metals*, Reinhold, New York, 1952.
- Wikipedia has a most informative entry on A. J. Liebling, a great journalist and an excellent writer. https:// en.wikipedia.org/wiki/A.\_J.\_Liebling (accessed May 17, 2019).
- 99. A. J. Liebling, "Comment," *New Yorker*, Jan. 31, 1959, p 17.

100. D. A. Bell, "Total History and Microhistory: The French and Italian Paradigms," in L. Kramer and S. Maza, Eds., *A Companion to Western Historical Thought*, Blackwell, 2002, pp 262-276.

#### About the Author

Pierre Laszlo enjoyed a transatlantic professional academic career, as a physical organic chemist. It led him, early on to history of chemistry which became his main activity after he formally retired in 1999.

## 2020 HIST Award to Lawrence M. Principe

The recipient of the 2020 HIST Award of the Division of the History of Chemistry of the American Chemical Society is Dr. Lawrence M. Principe. This award is the successor to the Dexter Award (1956-2001) and the Sydney M. Edelstein Award (2002-2009), also administered by the Division of the History of Chemistry.

Lawrence (Larry) M. Principe was born in northern New Jersey in 1962. He fell in love with alchemy while studying chemistry at the University of Delaware (B.S. Chemistry, B.A. Liberal Studies, 1983). A "dual approach" to the history of chemistry has characterized his work ever since. He obtained a Ph.D. in Organic Chemistry from Indiana University in 1988, but his interests in the History and Philosophy of Science motivated him to earn a second Ph.D. at Johns Hopkins University in History of Science, from which he graduated in 1996. His dissertation became the acclaimed book, *The Aspiring Adept: Robert Boyle and His Alchemical Quest* (Princeton, 1998).



Meanwhile, the Chemistry Department at Johns Hopkins took advantage of Principe's talents in organic chemistry by hiring him as a Laboratory Instructor. When a tenure-track position in the History of Science opened, he was chosen in 1997 for a joint appointment between Chemistry and History of Science. In 2006 he was honored as the endowed Drew Professor of the Humanities, with Chairs in both Chemistry and the History of Science.

Principe continued his Boyle scholarship and joined with Michael Hunter and Antonio Clericuzio to produce the six volume complete *Correspondence of Robert Boyle* (Pickering and Chatto, 1999-2001). Principe's collaboration with William Newman (Indiana University, 2013 HIST award) examined the laboratory notebooks of George Starkey and Robert Boyle and discovered the actual chemistry they contained. This project produced *Alchemy Tried in the Fire* (Chicago, 2002), which won the History of Science Society's Pfizer Prize (2005), given for the best book in the History of Science in the prior three year period.

Principe has served both adepts in the discipline of history of chemistry and *chymistry* and a broader audience. The 2006 conference on alchemy at the Chemical Heritage Foundation, for which Principe was organizer and editor of its proceedings, *Chymists and Chymistry* (Science History Publications, 2007) is one example of his service to scholarship. His *The Secrets of Alchemy* (Chicago, 2013) delivers exceptional scholarship to a wider audience.

# FORGOTTEN CONTRIBUTION OF V. N. IPATIEFF: PRODUCTION OF BUTADIENE FROM ETHANOL

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#### Introduction

In 1910, the Russian chemist S. V. Lebedev polymerized butadiene from grain alcohol and obtained a synthetic rubber, which was used in the USSR during and after World War II. In the period of 1928-1931 Lebedev investigated the properties of butadiene rubber using sodium as catalyst, found active fillers for it and suggested the composition of rubber products from synthetic rubber. In 1930, an experimental plant was built in Leningrad, and several hundred kilograms of synthetic rubber were produced in it in 1931.

However, it is known that V. N. Ipatieff began to study the properties of butadiene much earlier, in 1900-1903. At that time, the young researcher prepared an article for the journal of the German Chemical Society and made a report in January 1901 to the Russian Physico-Chemical Society (RPhChS) on pyrogenetic reactions by organic substances.

Lebedev's reaction is widely known, but very few people know about Ipatieff's contribution to the study of this reaction. The authors of the present paper want to help restore recognition to one of the greatest chemists of the 20<sup>th</sup> century who worked in the field of organic chemistry and who was unfairly forgotten in the course of history. A historical review on the production of butadiene makes it possible to distinguish some methods for the production of butadiene:

1) Isolation from pyrolysis of amyl alcohol by E. Caventou (1).

2) Production by the steam cracking process used to produce ethylene and other alkenes (2). When aliphatic hydrocarbons are mixed with steam and heated to very high temperatures (above 900 °C) for a short period of time, they undergo dehydrogenation to produce a mixture of unsaturated hydrocarbons, including butadiene.

3) Production by the catalytic dehydrogenation of *n*-butane over  $Al_2O_3$  and  $Cr_2O_3$  at high temperatures (3).

4) Production by catalytic dehydrogenation of *n*butenes. This method was used in the USA during World War II (4). After World War II, this production pathway from *n*-butenes became the major type of butadiene production in the USSR.

5) Production from ethanol. While not competitive with the second method for production of large volumes of butadiene, lower capital costs make production from ethanol a viable option for smaller-capacity plants. There are two processes in use:

a) Lebedev's conversion of ethanol (5-7) to butadiene, hydrogen and water at 400-450 °C over catalysts in one reactor:

$$2CH_3CH_2OH \rightarrow CH_2=CH-CH=CH_2+2H_2O+H_2$$

b) I. I. Ostromislensky working at Russia's main rubber company Bogatyr (Богатырь) in 1915 proposed a conversion method (8, 9) which is dehydrogenation of ethanol over alumina or clay catalysts to acetaldehyde in the first reactor and then conversation of a mixture of ethanol and acetaldehyde to butadiene over a tantalumpromoted porous silica catalyst in the second reactor (Figure 1). The yield of butadiene was 18 % (8).

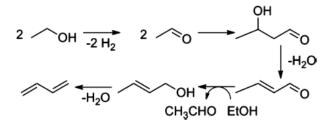


Figure 1. Overall scheme of butadiene production from ethanol via Ostromislensky conversion (10, 11).

Lebedev got a 10-13% yield of butadiene using his reaction (7). In 1928-1931, Lebedev proposed the formulation of rubber products from butadiene. In 1929, he received a patent (12) and submitted to the Soviet Ministry of Chemical Industry (Glavkhimprom) a plan of work necessary for the design of an experimental plant. During 1930, an experimental plant was built in Leningrad where in 1931 several hundred kilograms of synthetic rubber was produced (13) and used in the military industry to produce car tires. Later on, the industrial-scale yield of butadiene was improved to 44 % (7, 14).

A variety of metal oxide catalysts, including silicaand alumina-supported single, binary, or ternary metal oxides such as copper and zirconium (15, 16), mixed metal oxide catalysts such as MgO/SiO<sub>2</sub> (9, 17) or ZnO/ Al<sub>2</sub>O<sub>3</sub> (2) and Ag/ZrO<sub>2</sub>/SiO<sub>2</sub>, Hf–Zn/SiO and ZrBEA zeolite catalysts (16) were investigated.

Based on economic and environment aspects, it has been determined that the Lebedev method holds more potential than the Ostromislensky one (17).

However, it is known that Ipatieff began to study the properties of butadiene much earlier, in 1900-1903. Who was Ipatieff and what did he investigate? What were the reasons that prevented his name from being attached to the reaction?

## Low Yield of Butadiene and Search for Catalysts

In 1900-1903, Ipatieff began to study the properties of butadiene, which had been obtained before him only from the pyrolysis of amyl alcohol by Caventou. The only method then reported in the literature was the passage of alcohol vapours through a heated tube (1). While reflecting on the reasons for the small yield of butadiene, Ipatieff experimented with the tube material, the reaction conditions and composition of pyrolysis products. It turned out that amyl alcohol decomposed to form isovaleric aldehyde and hydrogen when an iron tube was used at approximately 600 °C, whereas it went unchanged at the same temperature in glass and porcelain tubes. When the temperature was increased to 700 °C, smaller amounts of aldehyde formed in these tubes with simultaneous formation of significant quantities of carbon monoxide, methane, ethylene, and hydrogen. Ipatieff made parallel experiments with primary, secondary and tertiary alcohols and found out that:

1) All primary alcohols, when passed through an iron tube, form aldehydes and hydrogen.

2) Secondary alcohols decompose into ketones and hydrogen.

3) Tertiary alcohols do not produce any of these products, but decompose into hydrocarbons and water at high temperatures.

In 1901, Ipatieff made a report to the RPhChS on pyrogenetic reactions of organic substances. In this report, for the first time in science Ipatieff pointed out the influence of the material of the vessel walls on the course and products of the reaction (18). This paper was published in a German journal as well (19), as was common practice at the time for Russian chemical researchers.

In this study, catalytic reaction occurred at very high temperature, and that was new since previously it was believed that at temperatures above 500-600 °C no catalytic effect could be expected. In January of 1901 a new catalytic decomposition reaction of alcohols into aldehyde and hydrogen (aldehyde decomposition), which is related to dehydrogenation catalysis, was discovered.

In September of 1901, at the meeting of the RPhChS Ipatieff made a new detailed report on the catalytic decomposition of ethyl alcohol under the influence of various catalysts and presented a hypothesis about the mechanism of the processes taking place. In this report, an important conclusion had been drawn that if the metal causes an aldehyde decomposition, then its oxide should have the same effect (20). Ipatieff confirmed the correctness of this conclusion experimentally on the example of zinc and its oxide.

By continuing the series of experiments on the pyrogenic decomposition of alcohol, Ipatieff discovered that alumina worked as a catalyst for this reaction and introduced it for obtaining olefins from aliphatic alcohol.

At the end of December 1901, the Eleventh Congress of Russian Naturalists and Physicians was held in St. Petersburg. There Ipatieff made a one-hour report, "Further experiments on the decomposition of alcohols under the influence of various contact agents" (21). M. I. Konovalov and I. L. Kondakov noted that the work had practical value. However, they stated that the author of the report did not indicate the dependence of the amount of decomposing isobutyl alcohol on the reaction time. Kondakov also noted that the product obtained from what he expected to be a bromination reaction after decomposition of isobutyl alcohol was apparently butadiene.

In 1903, Ipatieff investigated the mixture of decomposition products of ethanol using aluminum powder (22, 23). In order to separate unsaturated hydrocarbons from a mixture of products (in addition to those mentioned above,  $CO_2$ , CO,  $CH_4$  and  $H_2$  were also present), Ipatieff carried out the reaction of unsaturated hydrocarbons with bromine water and obtained a dibromide and a tetrabromide, which had different melting points. Then, the reaction of these bromides with hydrogen bromide in an alcohol solution was conducted in the presence of zinc powder. As a result, an unsaturated monobromide  $C_4H_7Br$ discolored bromine water and potassium permanganate solution. The yield of butadiene obtained in Ipatieff's experiments was 1.5-2 %.

During 1904-1907 Ipatieff finally confirmed that at 600 °C in the presence of aluminium powder the pyrolysis of ethyl alcohol yields butadiene in addition to acetaldehyde and ethylene (24-27):

$$\begin{array}{c} \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH} \xrightarrow{\mathrm{Al}, \, \mathrm{p}, \, \mathrm{t}} \mathrm{H}_{2} + \mathrm{CH}_{3}\mathrm{CHO} \\\\ \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH} \xrightarrow{\mathrm{Al}, \, \mathrm{p}, \, \mathrm{t}} \mathrm{H}_{2}\mathrm{O} + \mathrm{C}_{2}\mathrm{H}_{4} \\\\ \mathrm{2CH}_{3}-\mathrm{CH}_{2}\mathrm{OH} \xrightarrow{\mathrm{Al}, \, \mathrm{p}, \, \mathrm{t}} \mathrm{H}_{2} + \mathrm{2H}_{2}\mathrm{O} + \mathrm{CH}_{2} = \mathrm{CH}-\mathrm{CH} = \mathrm{CH}_{2} \end{array}$$

Ipatieff summarized the results of the influence of various catalysts, temperature and pressure on the decomposition of alcohols in his book (28). Thus, in his studies carried out about 115 years ago, Ipatieff found out the possibility of controlling the selectivity of heterogeneous catalytic reactions. He determined that by changing the catalysts, their composition and temperature, different products could be obtained from the same reagent (ethanol): ethylene, diethyl ether, acetaldehyde, butanol, acetone, butadiene, etc.

## Conclusions

The authors of the present paper wanted to help restore recognition to one of the greatest chemists of the 20<sup>th</sup> century who worked in the field of organic chemistry and who was unfairly forgotten in the course of history.

In organic chemistry, there are a number of reactions bearing the name of the researcher who discovered or investigated the reaction. Often the names of several scientists appear in the name of the reaction: it could be the researchers of the first publication, or researchers of the reaction or scientists who simultaneously published the results of the new reaction. Based on the above material, the authors think that despite low yield of butadiene and not very efficient catalysts it would be quite logical and historically fair to call the reaction of butadiene production from ethanol an Ipatieff-Lebedev reaction, and not just Lebedev reaction. In our opinion, the reason that prevented the use of Ipatieff's name for the reaction was the low yield of butadiene and not very efficient catalysts.

In recent years, Ipatieff's life and research during his time in the United State have been described in more detail. His contribution to the study of terpene transformations (29), of various acid-catalyzed processes that yielded ultra-high-octane fuels used for Air Force planes in World War II (4), and investigations in catalysis including high pressure, dispersion of metals on supports, and the use of promoters (30) have been described.

### **References and Notes**

- E. Caventou, "Ueber eine mit dem zweifach-gebromten Brombutylen isomere Verbindung und über die bromhaltigen Derivate des Brombutylens," *Ann. Chem.*, 1863, *127*, 93-97. doi:10.1002/jlac.18631270112.
- E. V. Makshina, M. Dusselier, W. Janssens, J. Degreve, P. A. Jacobs and B. F. Sels, "Review of old Chemistry and new Catalytic Advances in the on-purpose Synthesis of Butadiene," *Chem. Soc. Rev.*, 2014, 43, 7917-7953.

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- J. Grub and E. Löser, "Butadiene," Ullmann's Encyclopedia of Industrial Chemistry Wiley-VCH, Weinheim, Germany, 2012. doi:10.1002/14356007.a04 431.pub2
- M. Jacoby, "Vladimir Ipatieff is the Catalysis Superhero You've never Heard of," *Chem. Eng. News*, 2019, 97(May 11), 22-24.
- S. V. Lebedev, "O Poluchenii Divinila Neposredstvenno iz Spirta [On Obtaining Divinyl Directly from Alcohol]," *Zhizn' i Trudy* [*Life and Works*], Leningrad, 1938, pp 491-514.
- V. F. Tret'yakov, R. M. Talyshinskii, A. M. Ilolov, A. L. Maksimov and S. N. Khadzhiev, "Initiated Conversion of Ethanol to Divinyl by the Lebedev Reaction," *Petroleum Chem.*, 2014, 54, 195-206.
- V. F. Tret'yakov, A. M. Ilolov, R. M. Talyshinskii, A. M. Gyul'maliev and S. N. Khadzhiev, "Quantum-Chemical and Thermodynamic Analysis of Energy Characteristics of Main Reactions and the Initiator Hydrogen Peroxide in Ethanol to Divinyl Conversion on a ZnO/Al<sub>2</sub>O<sub>3</sub> Catalyst" *Petroleum Chem.*, 2017, 57, 423-430.
- I. I. Ostromislensky, "O kondensacii spirtov i aldegidov v prisutstvii vodootscheplaiuschich veschestv i o mechanizme etogo processa," *Zhurn. Rus. fiz.-khim. ob-va*, 1915, 47, 1494-1506.
- G. Pomalaza, M. Capron, V. Ordomsky and F. Dumeignil, "Recent Breakthroughs in the Conversion of Ethanol to Butadiene," *Catalysts*, 2016, 6, 203-208.
- T. De Baerdemaeker, M. Feyen, U. Muller, B. Yilmaz, Feng-Shou Xiao, Weiping Zhang, Toshiyuki Yokoi, Xinhe Bao, H. Gies and D. E. De Vos, "Bimetallic Zn and Hf on Silica Catalysts for the Conversion of Ethanol to 1,3-Butadiene," ACS Catal., 2015, 5, 3393-3397.
- Q. Zhu, B. Wang and T. Tan, "Conversion of Ethanol and Acetaldehyde to Butadiene over MgO-SiO<sub>2</sub> Catalysts: Effect of Reaction Parameters and Interaction between MgO and SiO<sub>2</sub> on Catalytic Performance," ACS Sustainable Chem. Eng., 2017, 5, 722-773.
- S. V. Lebedev, "Procédé pour obtenir des dioléfines directement des alcools," French Patent 665,917, issued May 13, 1929.
- 13. Yu. A. Gorin, Research of S. V. Lebedev in the Field of Synthesis of Divinyl from Ethyl Alcohol and their Further Development, Moscow, 1954.
- 14. A. M. Ilolov, R. M. Talyshinskij and V.F. Tretjakov, "Istoricheskije aspekti odnostasdijijnogo procesa divinila iz etanola," *Istorija nauki i techniki*, **2014**, *4*, 10-14.
- J. L. Cheong, Y. Shao, S. J. R. Tan, X. Li, Y. Zhang and S. S. Lee, "Highly Active and Selective Zr/MCF Catalyst for Production of 1,3-Butadiene from Ethanol in a Dual Fixed Bed Reactor System," *ACS Sustainable Chem. Eng.*, 2016, 4, 4887-4894.

- S.-H. Chung, C. Angelici, S. O. M. Hinterding, M. Weingarth, M. Baldus, K. Houben, B. M. Weckhuysen, P. C. A. Bruijnincx, "Role of Magnesium Silicates in Wet-Kneaded Silica-Magnesia Catalysts for the Lebedev Ethanol-to-Butadiene Process," ACS Catal., 2016, 6, 4034-4045.
- D. Cespi, F. Passarini, I. Vassura and F. Cavani, "Butadiene from Biomass, a Life Cycle Perspective to Address Sustainability in the Chemical Industry," *Green Chem.*, 2016, 18, 1625-1638.
- 18. V. N. Ipatieff, "Pirogeneticheskie kontaktnie reakcii s organicheskimi veschestvami," *Zhurn. Rus. fiz.-khim. ob-va*, **1901**, *33*, 143-149.
- 19. V. N. Ipatieff, "Ueber pyrogenetische Reactionen organischer Substanzen," *Ber. Dtsch. Chem. Ges.*, **1901**, *34*, 596-599.
- V. N. Ipatieff, "Pirogeneticheskie kontaktnie reakcii s organicheskimi veschestvami," *Zhurn. Rus. fiz.-khim. ob-va*, **1901**, *33*, 632-643.
- 21. V. N. Ipatieff, "Dalneichije opiti po razlozeniju spirtov pod vlijanijem razlichnich agentov kontakta," XI Congress of Russian Naturalists and Physicians, St. Petersburg, **1902**, 128.
- 22. V. N. Ipatieff, "Zur Frage über Zersetzung des Äthylalkohols in Gegenwart verschiedener Katalysatoren," *J. Prakt. Chem.*, **1903**, *67*, 420-422.
- V. N. Ipatieff, "K voprosu o razlozeniji spirta pod vlijanijem razlichnich katalizatorov," *Zhurn. Rus. fiz.-khim.*. *ob-va*, **1903**, *35*, 449-452.
- V. N. Ipatieff, "Kataliticeskije reakciji pri visokich temperaturach i davlenijach," *Zhurn. Rus. fiz.-khim. ob-va*, 1904, 36, 786-813.
- V. N. Ipatieff, "Kataliticeskije reakciji pri visokich davlenijach i temperaturach," *Zhurn. Rus. fiz.-khim. ob-va*, **1907**, *39*, 681-692.
- V. N. Ipatieff, "Kataliticeskije reakciji pri visokich davlenijach i temperaturach," *Zhurn. Rus. fiz.-khim. ob-va*, **1907**, *39*, 693-702.
- 27. V. N. Ipatieff, V. N. Zdzitoveckij, "Kataliticeskije reakciji pri visokich davlenijach i temperaturach," *Zhurn. Rus. fiz.-khim. ob-va*, **1907**, *39*, 897-901.
- V. N. Ipatieff, *Kataliticheskie reakcii pri visokich temperaturach i davlenijach. 1901-1907*, M. P. Frolova, St. Petersburg, 1907, p 170.
- 29. C. P. Nicholas, "Terpene Transformations and Family Relations: Vladimir Ipatieff," *Bull. Hist. Chem.*, **2019**, *44*(2), 116-122.
- C. P. Nicholas, "Dehydration, Dienes, High Octane, and High Pressures: Contributions from Vladimir Nikolaevich Ipatieff, a Father of Catalysis," *ACS Catal.*, 2018, *8*, 8531-8539.

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## 2020 Conferences in History and Philosophy of Chemistry: Update

• International Committee for the History of Technology (ICOHTEC): 47th annual meeting scheduled for Eindhoven, the Netherlands July 13-19

https://icohtec2020eindhoven.org

The conference will be an abbreviated online event, July 15-17

• International Society for the Philosophy of Chemistry: 24th annual meeting scheduled for Buenos Aires, Argentina July 21-23 http://www.filoexactas.exactas.uba.ar/ispc2020/ Postponed to 2021, date not yet selected as of late May 2020

• European Society for the History of Science (ESHS): 9th International Conference, hosted by the Centre for the History of Universities and Science at the University of Bologna (CIS) and by the Italian Society for the History of Science (SISS), scheduled for Bologna, Italy, August 31-September 3 https://sites.google.com/view/eshsbologna2020 This conference will be held online

• ACS Division of the History of Chemistry at the Fall 2020 National Meeting of ACS, San Francisco, California, August 16-20

www.acs.org/content/acs/en/meetings/national-meeting.html

HIST has cancelled its program and will reschedule symposia at future conferences. As for the larger conference, ACS states (as of late May):

What we can assure you is that the ACS Fall 2020 National Meeting & Expo will take place in one form or another. We are exploring various scenarios to allow for a safe and meaningful exchange of scientific research and information, as well as networking; all things normally associated with an ACS national meeting. Those scenarios range from an in-person event to a mix of in-person and virtual activities to an all virtual event.

• History of Science Society jointly with the Society for the History of Technology (SHOT), October 7-11 in New Orleans, Louisiana, USA https://hssmeeting.org

As of late May 2020, this event appears to be on schedule to proceed.

• Pacifichem 2020: The International Chemical Congress of Pacific Basin Societies, December 15-20 in Honolulu, Hawaii, USA

https://pacifichem.org

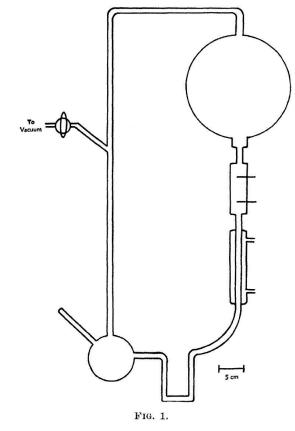
This conference is scheduled to have a historical symposium, and as of late May 2020 it appears to be on schedule to proceed.

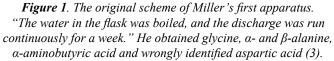
# SCIENCE AND PUBLIC PERCEPTION: THE MILLER EXPERIMENT

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## Introduction

There is hardly a chemical experiment so well known both to scientists and to the general public as the Miller (or Urey-Miller) experiment that was performed in the fall of 1952 by a young American chemist named Stanley L. Miller (1930-2007), who made it as a part of his Ph.D. Thesis (1). By exposing the mixture of gases (CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>, H<sub>2</sub>O), presumed by his mentor Harold C. Urey (1893-1981) to be the constituents of the first Earth atmosphere (2), to electrical sparking he obtained a mixture of organic compounds, and above all of amino acids, "the building blocks of proteins" (3, 4). From a purely chemical point of view, this could hardly be judged as being something new; he simply ran an uncontrolled (or poorly controlled) radical reaction





in the gas phase—similar to Löb's experiments in the beginning of 20<sup>th</sup> century (5, 6). "Löb had been looking for the formation of amino acids, especially glycine, at least as early as 1909," wrote Hubert P. Yockey (7).

Oskar Baudisch (1913) also showed that amino acids are generated by ultraviolet light only in reducing atmosphere. J. S. Haldane (1929) referred to the work of Edward Baly *et al.* (1922), who found glycine using ultraviolet light.

Even the idea of prebiotic synthesis is not Miller's invention. Aleksandr I. Oparin (8) wrote numerous schemes for possible prebiotic syntheses, including those of amino acids. He proposed that amino acids were formed by Trier's reaction of hydroxyl acids with ammonia (9) or by addition of ammonia to double bonds, e.g., conversion of fumaric into aspartic acid (10). "Thus, the primary formation of compounds of the protein type is in no way unusual, exceptional, or different than the formation of other complex organic substances," said Oparin (9). So, what is "unusual, exceptional, or different" in the Miller experiment (Figure 1)? I will try to answer this question in the proceeding paragraphs.

#### The Experiment's Scientific Merit

The leading idea of the experiment is to prove the validity of theory of his mentor, Nobel Prize laureate Harold Urey. This is evident from the very first sentence of his first paper (3):

The idea that the organic compounds that serve as the basis of life were formed when the earth had an atmosphere of methane, ammonia, water, and hydrogen instead of carbon dioxide, nitrogen, oxygen and water was suggested by Oparin and has been given emphasis recently by Urey and Bernal.

Plainly speaking, Miller's idea was to produce amino acids by gas-phase reactions in not just any primordial atmosphere, but in a Jupiter-like one, as proposed by Urey (11). From this point of view his experiment should be judged as obsolete and erroneous, one of many "beautiful theories killed by an ugly fact," as Thomas Huxley (1825-1895) put it. In particular, there are recent geochemical findings (12) suggesting that the primitive Earth's atmosphere was more likely to resemble the one proposed by John B. S. Haldane (1892-1964), composed of  $CO_2$  and  $NH_3$  (13), rather than the atmosphere of the CH<sub>4</sub> and NH<sub>3</sub> type, as were assumed by Oparin and Urey. However, amino acids were obtained from gaseous mixtures of various compositions (14) and there are many ways how organics could originate before the dawn of life (15); there were many primordial soups and many primordial cooks, to use a metaphor by Max Bernstein (15b).

But there are many flaws in such an argument, aimed to disfavor Miller's priority. Oparin did not bother to test his theory of abiotic synthesis experimentally; after all, he was not a chemist (8a). The Russian scientist did not even believe at first in the report of Miller's experiment, as newspapers carried it (16). J. L. Bada and A. Lazcano vigorously opposed Yockey's opinion that Miller just updated Löb's work (17), stating Löb had not the slightest intention to contribute to theories on the origin of life, but to explain nitrogen assimilation (*Stickstoff-Assimilation*), which is evident from the very title of his second paper (6). "Neither Aleksander Oparin, J. B. S. Haldane nor Urey made any mention of Löb's work, which given Oparin's extensive review of early relevant literature suggests it was considered unimportant," stated Bada and Lazcano (17), but it seems that Miller himself found it important because he gave him a credit: "The only work that would have any bearing on the reducing atmosphere would be the experiments of Loeb who obtained glycine by the action of silent discharge on a mixture of carbon monoxide, ammonia and water" (4).

## **Public Perception**

It is true that the Miller experiment "deserves recognition not only because of its intrinsic merits, but also because it opened new avenues of empirical research into the origin of life" (17), as any scientific discovery of real importance does, but it is also true that there is no such a thing as an independent discovery in science. Neither Newton nor Einstein by themselves founded a new physics, and besides Mendeleev and/or Lothar Mayer there were at least four more "co-discoverers" of the periodic system (18). So it was with the theories on the origin of life, or more specifically, with the problem of prebiotic synthesis. *Every* synthesis of organic matter from "inanimate substances," starting from Friedrich Wöhler's (1800-1882) famous 1828 experiment (19), contributed to the solution of the problem.

However, the reason for the exceptional popularity of the Miller experiment is not purely scientific (20):

The finding caught the imagination of scientists everywhere by suggesting that it might soon be possible to reconstruct the emergence of the first living cells from the soup of chemicals generated by natural conditions on the early earth.

Moreover, it is a good story, for the "synthesis of live molecules" in chemical apparatus had a kind of mystical aura, resembling the making of an "artificial man," *homunculus* (21), in a retort, as had been proposed in the 8<sup>th</sup> century by Jabir ibn Hayyan (Geber) and was believed even by Paracelsus (1493-1541). The relation of a notable and respected scientist and his young and anonymous doctoral student is nearly as archetypical as the myth of Daedalus and Icarus: the old man made a miracle and the young one put it to its ultimate test, in Miller's case fortunately not also to the bitter end—and creationists possibly played the role of the Minotaur. The next reason is that in the 1950s, after the end of World War II, public imagination overflowed with scientific and technical discoveries, starting from nuclear bombs and nuclear submarines, synthetic resins and plastics to the impending flight into space, not to mention discoveries in biochemistry, like the double helix of DNA (22). The Miller experiment showed that the problem of the life's origin if not solved, could be solved by scientific means (23):

Published in the May 15, 1953 issue of *Science*, the results galvanized scientists and generated global head-lines. *The New York Times* credited Miller and Urey with inventing "a laboratory Earth." *Time* dubbed the experiment "semi-creation."

Max Bernstein wrote (15b):

The results were breathtaking ... Given that it was also the year that the structure of DNA was published, I am told that it seemed as if the secrets of life were being revealed and that very soon scientists would understand how life had come about.

From another side, all kinds of creationists and believers in intelligent design inevitably refer to the alleged fallacy and insignificance ("much ado about nothing") of his experiment (24), entirely neglecting numerous various and sophisticated similar experiments supporting evolution theory; it was proclaimed simply as an "evolutionistic fraud" (25). In their view, the *icon of evolution* "has little or nothing to do with the origin of life" (26) and, harshly, "The experiments were a ridiculous failure" (27). This is another, bad side of the overwhelming popularity of Miller's abiogenic synthesis.

Amino acids and proteins were, at least in the public imagination, nearly synonymous with life (28), and thus it is hardly surprising that the findings of the young American scientist had "breathtaking" response. Of course, the young chemist didn't obtain proteins in his apparatus, and the polymerization of amino acids in prebiotic conditions is only one of many controversies on the origin of life (29). Obviously, the value of Miller's experiment was exaggerated in general public, but it has to be acknowledged that he knew how to present his results in a popular and attractive way—a capability which was mostly missing in the middle 20<sup>th</sup>-century scientific community (30).

## Conclusion

The story of the Miller experiment is a good example how the valuation of a scientific research depends not only on its intrinsic (scientific) value but also on its acceptance by the scientific community, as well as the general public. In spite of the development of rival theories, like the volcanic "iron-sulfur-world" (31), whose founder Günter Wächtershäuser "held that Dr. Miller's approach was a blind alley" (20), after 65 years the experiment of the young American scientist is still in the public focus. There are hundreds if not thousands of graphical representations of his apparatus on the web and elsewhere (Figure 2). Moreover, his scientific contribution was exaggerated in the public memory stating, wrongly, that he "was the first to demonstrate that the organic molecules necessary for life could be generated in a laboratory flask simulating the primitive Earth's atmosphere" (32), but against all odds "Miller's findings still provide invaluable insight into the formation of essential organic compounds" (33).

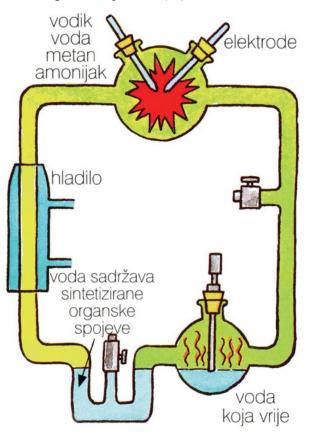


Figure 2. One of many graphical representations of Miller's apparatus—this one in the picture-book style for the fourth middle school grade (European eighth elementary school grade) textbook for an elementary course in organic chemistry. "It is not yet entirely clear how these small molecules organized themselves, created life and obtained the capacity for self-reproduction" (34).

At the end, it has to be said that Miller experiment is undoubtedly a piece of scientific history and it has to be judged as such. It can be judged no more as "the most convincing of all experiments that have been done in this field," as Norman Horowitz (1915-2005) put it in 1963 (35). "The Miller-Urev experiment is now recognized as the single most significant step in convincing any scientists that life is likely to be abundant in the cosmos" (36), as said Carl Sagan (1934-1996), could be perceived as an exaggeration. The experiment may even be judged as "defunct and discredited" (37), but it cannot be denied that "the father of prebiotic chemistry" encouraged other scientists to do as he did, like abiogenic synthesis of nucleic bases in 1960 (38) or thermal polymerization of amino acids in 1956 (39) and clay-catalyzed polymerization of nucleotides in 1989 (40). The work of the young American chemist established a new paradigm (41), to say it in a philosophic way. This is the greatest legacy of the first synthesis of amino acids in the simulated primitive Earth's atmosphere.

## **References and Notes**

- It is a bit misleading to call the Miller experiment "Miller-Urey experiment" because the idea of its performing was originally Miller's, and Urey was not very enthusiastic about it. He did not believe much in its success and therefore in finishing Miller's Ph.D. Thesis. However, Miller acknowledged his mentor for "many helpful suggestions" (3) and "advice and encouragement during the course of this research" (4). a) J. L. Bada and A. Lazcano, "Prebiotic Soup—Revisiting the Miller Experiment," *Science*, 2003, 300, 745-746. b) J. L. Bada and A. Lazcano, "Stanley L. Miller, 1930-2007," *Biogr. Mem. Natl. Acad. Sci. USA* (online), 2012, http://www.nasonline.org/publications/ biographical-memoirs/memoir-pdfs/miller-stanley.pdf (accessed Apr. 9, 2020).
- 2. H. C. Urey, "On the Early Chemical History of the Earth and the Origin of Life," *Proc. Natl. Acad. Sci. USA*, **1952**, *38*, 351-363.
- S. L. Miller, "A Production of Amino Acids under Possible Primitive Earth Conditions," *Science*, 1953, *117*, 528-529.
- 4. S. L. Miller, "Production of Some Organic Compounds under Possible Primitive Earth Conditions," *J. Amer. Chem. Soc.*, **1955**, *77(9)*, 2351-2361.
- W. Löb, "Die Einwirkung der stillen elektrischen Entladung auf feuchtes Methan," *Ber. Dtsch. Chem. Ges.*, 1908, 41, 87-90.
- W. Löb, "Über der Verhalten der Formamids unter der Wirkung der stillen Entladung. Ein Beitrag zur Stickstoff-Assimilation," *Ber. Dtsch. Chem. Ges.*, **1913**, *46*, 684-697.
- H. P. Yockey, "More Light on Pioneers of Electrochemistry," *Nature*, 2002, 415, 833.

- a) S. L. Miller, J. W. Schopf and A. Lazcano, "Oparin's 'Origin of Life': Sixty Years Later," *J. Mol. Evol.*, **1997**, *44*, 351-353. b) N. Raos, "Carbide Chemistry and Oparin's Theory on the Origin of Life," *Bull. Hist. Chem.*, **2017**, *42*(1), 57-62.
- A. I. Oparin, *The Origin of Life*, trans. with annotations by S. Morgulis, 2nd Ed., Dover Publications, Mineola, NY, 1953, pp 134-135. Originally published as translation of Возникновение жизни на земле (*The Upspring* of Life on Earth), 1936. It is noteworthy that Oparin did not mention the better known Strecker synthesis of alpha amino acids from aldehydes, cyanides and ammonia (A. Strecker, "Über die künstliche Bildung der Milchsäure und einen neuen, dem Glycocoll homologen Körper," Ann. Chem. Pharm., **1850**, 75(1), 27-45; A. Strecker, "Über einen neuen aus Aldehyd-Ammoniak und Blausäure entstehenden Körper," Ann. Chem. Pharm., **1854**, 91(3), 349-351.)
- 10. А. I. Oparin, Возникновение жизни на земле (*The Upspring of Life on Earth*), 4th Ed., 1941, p 103.
- 11. "In this apparatus an attempt was made to duplicate a primitive atmosphere of the earth, and not to obtain the optimum conditions for the formation of amino acids. Although in this case the total yield was small for the energy expended, it is possible that, with more efficient apparatus ... this type of process would be a way of commercially producing amino acids" (3); X. Xie, D. Backman, A. T. Lebedev, V. B. Artaev, L. Jiang, L. L. Ilag and R. A. Zubarev, "Primordial Soup was Edible: Abiotically Produced Miller-Urey Mixture Supports Bacterial Growth," *Sci. Rep.*, 2015, 14338.
- a) P. H. Abelson, "Chemical Events on the Primitive Earth," *Proc. Natl. Acad. Sci. USA*, **1966**, *55*, 1365-1372.
  b) J. F. Kasting and M. T. Howard, "Atmospheric Composition and Climate on the Early Earth," *Phil. Trans. R. Soc. B*, **2006**, *361*, 1733-1742.
- 13. "Now, when ultra-violet light acts on a mixture of water, carbon dioxide, and ammonia, a variety of organic substances are made, including sugars and apparently some of the materials from which proteins are built. This fact has been demonstrated in the laboratory by Baly of Liverpool and his colleagues." (J. B. S. Haldane, "The Origin of Life," *Rationalist Annu.*, **1929**, *148*, 3-10.)
- 14. H. J. Cleaves, J. H. Chalmers, A. Lazcano, S. L. Miller and J. L. Bada, "A Reassessment of Prebiotic Organic Synthesis in Neutral Planetary Atmospheres," *Orig. Life Evol. Biosph.*, **2008**, *38*, 105-115. Even in 1957 it was observed that "alanine could be produced in at least seven different ways under conditions which could be considered as prebiological," and that these findings "support the earlier judgment that amino acids could be formed easily." (S. W. Fox, "The Chemical Problem of Spontaneous Generation," J. Chem. Educ., **1957**, *34*(10), 472-479.)

- a) C. Chyba and C. Sagan, "Endogenous Production, Exogenous Delivery and Impact-shock Synthesis of Organic Molecules: An Inventory for the Origins of Life," *Nature*, **1992**, *355*, 125-132. b) M. Bernstein, "Prebiotic Materials from on and off the Early Earth," *Phil. Trans. Roy. Soc. B*, **2006**, *361*, 1689-1702. c) T. M. McCollom, "Miller–Urey and beyond: What Have we Learned about Prebiotic Organic Synthesis Reactions in the Past 60 Years?," *Annu. Rev. Earth. Planet. Sci.*, **2013**, *41*, 207-229.
- 16. Ref. 1b, note 6, p 19.
- 17. J. L. Bada and A. Lazcano, "Miller Revealed New Ways to Study the Origins of Life," *Nature*, **2002**, *416*, 475.
- E. R. Scerri, "The Discovery of the Periodic Table as a Case of Simultaneous Discovery," *Phil. Trans. Roy. Soc. A*, 2015, 373: 20140172.
- a) F. Wöhler, "Über künstliche Bildung der Harnstoffe," Ann. Chim., 1828, 24, 294-317. b) N. H. Warren, "Contemporary Reception of Wöhler's Discovery of Urea," J. Chem. Educ., 1928, 5, 1539-1552. c) D. McKie, "Wöhler's 'Synthetic' Urea and the Rejection of Vitalism: A Chemical Legend," Nature, 1944, 153, 608-610. d) P. S. Cohen and S. M. Cohen, "Wöhler's Synthesis of Urea: How Do the Textbooks Report It?," J. Chem. Educ., 1996, 73(9), 883-886. Also have to pay attention to the first "real" organic synthesis, that of acetic acid in 1848, by Hermann Kolbe (1818-1884). e) A. J. Rocke, "Kolbe Versus 'Transcendental Chemists': the Emergence of Classical Organic Chemistry," Ambix, 1987, 34, 156-168.
- N. Wade, "Stanley Miller, Who Examined Origins of Life, Dies at 77," *New York Times* (online), May 23, 2007, https://www.nytimes.com/2007/05/23/us/23miller.html (accessed Apr. 9, 2020).
- For example see: a) K. R. Snow, "Homunculus in Paracelsus, 'Tristram Shandy,' and 'Faust,'" J. Engl. Germ. Philology, **1980**, 79(1), 67-74. b) M. B. Campbell, "Artificial Men: Alchemy, Transubstantiation, and the Homunculus," J. Stud. Know. Pol. Arts, **2010**, 1(2), 4-14. c) P. Ball, The Devil's Doctor: Paracelsus and the World of Renaissance Magic and Science, Farrar, Straus and Giroux, New York, 2006.
- a) J. D. Watson and F. H. C. Crick, "Molecular Structure of Nucleic Acids: A Structure for Deoxyribose Nucleic Acid," *Nature*, **1953**, *171*, 737–738. b) R. Oldby, "Quiet Debut for the Double Helix," *Nature*, **2003**, *421*, 402-405.
- J. Keats, "Cooking up Early-Earth Conditions," *Discover Magazine* (online), June 19, 2016, http://discovermagazine.com/2016/nov/brewing-life (accessed Apr. 9, 2020).
- 24. "Squeezing the Last Life Out of the Miller Experiment," *Evolution News & Science Today* (online), June 30, 2014, https://evolutionnews.org/2014/06/squeezing\_the\_l/ (accessed Apr. 9, 2020).

- 25. E.g. "This experiment is the only 'evidence' evolutionists have with which to allegedly prove the 'chemical evolution thesis'; they advance it as the first stage of the supposed evolutionary process leading to life. Although nearly half a century has passed, and great technological advances have been made, nobody has made any further progress. In spite of this, Miller's experiment is still taught in textbooks as the evolutionary explanation of the earliest generation of living things." (H. Yahya, The Evolution Deceit: The Scientific Collapse of Darwinism and Its Ideological Background, Ta-Ha Publishers, London, 1999, p 132; see also http://www.darwinismrefuted. com/molecular biology 09.html, accessed Apr. 9, 2020.) "Miller set up a closed glass apparatus ... evacuated it, and replaced air with methane, ammonia, hydrogen and water. (If he didn't clean the apparatus out of air, the next step would be his last.)" ("Evolucionističke prijevare o postanku života na Zemlji (Evolutionistic Frauds about the Origin of Life on Earth)," http://www.novi-svjetskiporedak.com/2013/06/01/evolucionisticke-prijevareo-postanku-zivota-na-zemlji/, accessed Apr. 9, 2020). "When Stanley Miller had analyzed obtained products, he found a huge amount of the tar and traces of certain organic components, among them also amino acids... And that has been taken for certain that life was originated by abiotic way." ("Savremena hipoteza abiogeneze (Contemporary Hypothesis of Abiogenesis)," http://www.cps.org. rs/Cks1/cks14.html, accessed Apr. 9, 2020).
- 26. J. Wells, Icons of Evolution, Rangers Kids, 2000, p 10.
- 27. "However, nothing even remotely indicative of life was produced. Instead, Miller and Urey were able to produce only a few amino acids, the constituents of proteins, as well as some nitrogen bases that are constituents of DNA. They also failed to produce a single molecule of sugar which is required for the creation of genetic material... The experiments were a ridiculous failure." (J. Gabriel, "The Myth of Organic Soup: Only Life Produces Life," http://cosmology.com/MythOfTheOrganicSoup.html.) See also J. Bergman, "Why the Miller-Urey Research Argues Against Abiogenesis," *J. Creation*, **2004**, *18*(2), 28-36; available online at https://creation.com/why-the-miller-urey-research-argues-against-abiogenesis (accessed Apr. 9, 2020).
- 28. It was generally believed that all biological processes were invaluably dependent on proteins, even that *hereditary substance* (genetic material) is a protein, the first and foremost (*protos*) substance of life (e.g., C. Tanford and J. Reynolds, *Nature's Robots: A History of Proteins*, Oxford University Press, 2001).
- J. Peretó, "Controversies on the Origin of Life," Int. Microbiol., 2005, 8, 23-31.
- 30. The need to be visible on the scientific scene reflects itself in ghost authorship (M. Biagioli, "Plagiarizing Names?," *Trends. Chem.*, 2019, 1(1), 3-4). Even the name matters! Croatian-born American inventor Nikola Tesla (1856-

1943) owes much of his popularity to his family name, which is not a typical Croatian (Slavic) cumbersome patronymic, e.g. Tomić, Modrić or Ivičević, but was derived from a nickname (*tesla* is Croatian for adze).

- 31. G. Wächtershäuser, "From Volcanic Origins of Chemoautotrophic Life to Bacteria, Archaea and Eukarya," *Phil. Trans. Roy. Soc. B*, **2006**, *361*, 1787-1808.
- T. H. Maugh II, "Stanley Miller, 77; Chemist was a Pioneer in Studying the Origins of Life," *Los Angeles Times* (online), May 24, 2007, https://www.latimes.com/science/ la-me-miller24may24-story.html (accessed Apr. 9, 2020).
- 33. "NAS Award in Early Earth and Life Sciences," http:// www.nasonline.org/programs/awards/early-earth-andlife-sciences.html (accessed Apr. 9, 2020). The award has two parts, Charles Doolittle Walcott and Stanley Miller Medal. The last was established in October 2008 on the behalf of the 50th anniversary of the Miller experiment.
- M. Bukovac, D. Magdalenić and M. Sikirica, Kemija otkrivanjem 8. Udžbenik za 8. razred osnovne škole (Chemistry by Discovering 8. Textbook for the 8th Grade of the Elementary School), Školska knjiga, Zagreb, 2003, p 31.
- S. Thomas, Men in Space: Profiles of Scientists Who Probe for Life in Space, Chilton Co., New York, 1963, p 249.
- 36. Quoted in R. Shapiro, *Origins: A Skeptic's Guide to the Creation of Life on Earth*, Summit Books, New York, 1986, p 99.
- J. S. Lee, "Is Christianity True?" Science Series: Bill Nye the Pseudo-Science Guy, Apr. 27, 2015, https:// ischristianitytrue.wordpress.com/2015/04/27/scienceseries-bill-nye-the-pseudo-science-guy/ (accessed Apr. 9, 2020).

- a) J. Oró, "Synthesis of Adenine from Ammonium Cyanide," *Biochem. Biophys. Res. Commun.*, **1960**, *2*, 407-412. b) J. Oró, "Mechanism of Synthesis of Adenine from Hydrogen Cyanide under Possible Primitive Earth Conditions," *Nature*, **1961**, *191*, 1193-1194.
- S. W. Fox, "The Evolution of Protein Molecules and Thermal Synthesis of Biochemical Substances," *Am. Sci.*, 1956, 44, 347-359.
- a) J. P. Ferris, G. Ertam and V. K. Agarwal, "Mineral Catalysis of the Formation of Dimers of 5'-AMP in Aqueous Solution: The Possible Role of Montmorillonite Clays in the Prebiotic Synthesis of RNA," *Orig. Life Evol. Biosph.*, **1989**, *19*, 165-178. b) N. Raos and V. Bermanec, "Catalysis in the Primordial World," *Kem. Ind.*, **2017**, *66*(11-12), 641-654.
- 41. T. S. Kuhn, *Structure of Scientific Revolutions*, The University of Chicago Press, Chicago, 1970.

## About the Author

Nenad Raos is a scientific adviser in chemistry, retired from the Institute for Medical Research and Occupational Health, Zagreb, Croatia. He is a very fluent science writer. Besides hundreds of articles on various topics of science, published in newspapers and magazines, he wrote 13 books in popular science, including *The Cookbook of Life—New Theories on the Origin of Life* (2018).

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# LIBERATING R. B. WOODWARD AND THE WOODWARD RESEARCH INSTITUTE FROM ERROR

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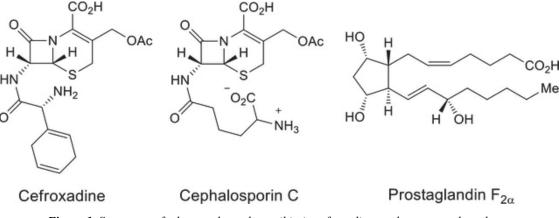
#### Abstract

Insiders' eyewitness accounts correct 14 factual errors and one misleading suggestion in an outsider's history of the Woodward Research Institute. Misrepresented are the recruiting, operations, and accomplishments of the WRI, especially in the syntheses of Cephalosporin C and Prostaglandin  $F_{2\alpha}$ .

### Introduction

The year 2011 saw publication of a review concerning the late R. B. Woodward (RBW) and the erstwhile Woodward Research Institute (WRI) (1). The review, which came belatedly to our notice, proved to contain historical and chemical mistakes that eventually goaded us to write this essay. To the task of correcting the errors (2), we bring eyewitness testimony and firsthand chemical knowledge. Counted among RBW's researchers for several years (3-5), and among his admirers for decades (6), here we seek to liberate the man and his Institute from these errors.

Despite the passage of more than 40 years since the Institute closed, it still rouses international interest, so corrections will serve interested parties, chemical historians among them. Identifying scientific errors needs a chemist, but not necessarily a former WRI postdoctoral researcher. Correcting historical mistakes having to do



with Institute recruiting, operations, and attributions calls for an insider's familiarity with the WRI. We think it important to attack these last mistakes now because correcting them remains possible only as long as insiders abound (7). Otherwise the errors may stand forever to misinform and mislead chemists and historians alike.

Failing to correct the mistakes or publish the corrections may signify indifference, would perpetuate the errors, and might offend our science perhaps more than does erring initially. Such failures would tender miserable tribute to the man whom we think the greatest organic chemist of the 20<sup>th</sup> century.

## The PGF<sub>2α</sub> Synthesis: Misconstrued Accomplishments

From September of 1971 to April of 1972, WRI chemists began and completed Woodward's novel synthesis of Prostaglandin  $F_{2\alpha}$  (PGF<sub>2\alpha</sub>) (Figure 1). A crucial intermediate was protoprostaglandinal **1** (Figure 2), so named by RBW himself, and embodying the 2-oxabicy-clo[3.3.0]octane ring system (4). Ref. 1 incorrectly states, "[Woodward] developed an innovative synthesis of the pivotal bicyclic aldehyde **1** (Fig. 17) in Corey's early syntheses of PGE<sub>2</sub> and PGF<sub>2α</sub> (Ref. [37] in 1)." What is incorrect here is the supposition that the bicyclic aldehyde **1** played any role in either of Corey's two prostaglandin syntheses; it did not.

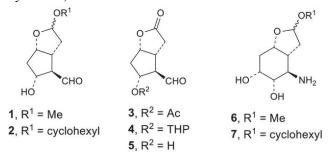


Figure 2. Selected intermediates in prostaglandin syntheses

Ref. 1 erroneously indicates that p. 278 of "The Logic of Chemical Synthesis" depicts the intermediacy of protoprostaglandinal **1** in Corey's work (8). However, that page (Figure 3) does not show this precursor, nor does any other page in the book do so. The failure of Figure 3 to depict this structure is akin to the dog's curious failure to bark in the night (9). It is the absence of the barking and the structure that is significant. Protoprostaglandinal **1** plays *no* role in Corey's work, but is unique to Woodward's. So, RBW's achievement does not entail an

"... alternative synthesis of Corey's bicyclic aldehyde," as Ref. 1 inaccurately states.

Mediating Corey's prostaglandin syntheses (10-13) but not RBW's are other 2-oxabicyclo[3.3.0]octane-6-als (**3-5** (Figure 2)). None of these intermediates is a methyl acetal like protoprostaglandinal **1** but all except one (**2**) are C-3 lactones.

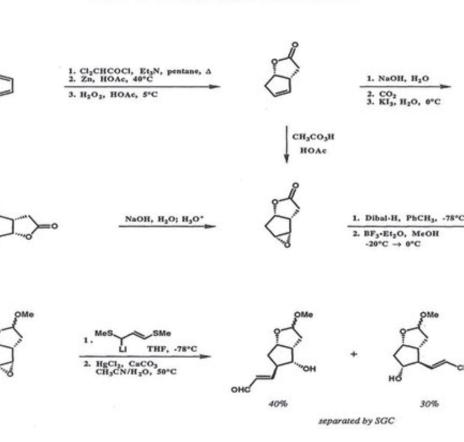
Attributions matter; and mistakenly to assert that the WRI made one of Corey's intermediate lactones diminishes Woodward's originality. In part, it lay in appreciating that any two hydroxyl groups of *cis,cis*-1,3,5cyclohexanetriol contained the relative stereochemistry of the cyclopentane hydroxyls in PGF<sub>2α</sub>. At the same time, the remaining carbinol carbon of the triol pledged functionality enough ultimately to contract the cyclohexane of **6** to the cyclopentane of **1** (Figure 2). Compound **1** contains in the correct relative stereochemistry four of the five stereogenic centers of PGF<sub>2α</sub>.

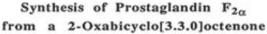
Ref. 1 erroneously suggests that RBW borrowed his key intermediate 1 from one of Corey's prostaglandin syntheses. However, the opposite—that Corey took advantage of RBW's protoprostaglandinal synthesis—is true, as we show below.

Another 2-oxabicyclo[3.3.0]octane-6-al, compound 2 (13), arises from an alternative synthesis Like protoprostaglandinal 1, compound 2 is an acetal, but one derived from cyclohexanol rather than methanol. Also like intermediate 1, which arises from the acetal-amine 6 (Figure 2), precursor 2 comes from a Tiffenau-Demjanov ring contraction following diazotization of the derivative acetal-amine 7 (Figure 2).

Corey and Snider acknowledge that "T[heir] procedure [for making compound 2] follows one applied by Professor R. B. Woodward and coworkers to an analogous prostaglandin intermediate [compound 1] prepared by a different route (13)." By April of 1972, the WRI had made the first sample of racemic PGF<sub>2a</sub>. RBW's synthesis of it and the intermediates 6 and 1 were disclosed some weeks later to Professor Corey (14), after CIBA-Geigy applied to patent these compounds in Switzerland, naming Woodward as the inventor (15, 16). The dates of disclosure and application came a year before Corey and Snider submitted their article concerning compounds 7 and 2 to Tetrahedron Letters (13). The disclosure, application, and dates together show that RBW did not emulate Corey. They suggest that Corey's preparation of 2 took advantage of Woodward's synthesis of 1 (17), and it is this suggestion that Ref. 1 inverts.

11.12





*Figure 3.* Page 278 of Corey and Cheng's The Logic of Chemical Synthesis (8), in which protoprostaglandinal 1 does not appear. Reprinted with permission of J. Wiley & Sons.

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#### **Ivan Ernest's Insight**

1. n-AmLi

2. separation of diastereomers

The insight of Ivan Ernest (Figure 4), which Ref. 1 neglects, solved the synthetic problem preoccupying the WRI chemists in 1971-1972. Their challenge was to contract the six-membered ring of 6, 8, or some other tricyclic acetal to a 5-membered carbocycle bearing an aldehyde group. An examination of molecular models showed that the vicinal, axial amino and hydroxyl groups in the tricyclic 8 would become equatorial in the bicy-

clic **6**, adopting an antiperiplanar arrangement (Figure 5). Ernest then supplemented analysis with experiment, subjecting the tricyclic **8** to methanolysis and the bicyclic product **6** to diazotization. The diazonium salt **[6a]** formed (Figure 5) and ruptured, and protoprostaglandinal **1** resulted.

PGF20



Figure 4. Ivan Ernest (1922-2003). Photo by K. F. Burri.

Ernest's other contributions to the WRI were numerous but overlooked by Ref. 1. In the 11½ years he worked at the Institute, he became a co-inventor of 17 patents, a co-author of 12 papers, and the sole author of a book chapter, four papers (6), and a textbook. The chapter (18) and one of those four papers dealt with the chemistry of penicillin-derived diazoketones (19) while two of the others concerned the synthesis and antibacterial properties of 2-oxocephems (20, 21). The textbook set forth bonding, structure, and reaction mechanisms in organic chemistry (22). In terms of authorship and inventorship, Ernest was the more productive of the two full-time administrative directors of the WRI during their appointments, which were unequal in duration.

However, the notion that Ernest "...followed up research ideas in search of novel PGs...." was mistaken by Ref. 1. On the contrary, he never reported attempts to make prostaglandins other than PGF<sub>2α</sub> (23).

## Other Misrepresentations of the PGF<sub>2α</sub> Synthesis

Ref. 1 misrepresents RBW's  $PGF_{2\alpha}$  synthesis in another respect. Fig. 17 in Ref. 1 erroneously shows direct conversion of the *tricyclic* aminoalcohol **8** (Figure 5) to protoprostaglandinal **1** by a Tiffenau-Demjanov ring contraction. Such a contraction was never realized or tried (24), so the claim is erroneous; the effective ring contraction of 6 to 1 is published (4). Indeed, successful diazotization of the tricyclic aminoalcohol 8 followed by loss of nitrogen would have yielded the tricyclic  $\alpha$ epoxide 9 (Figure 5), from which 8 was prepared.

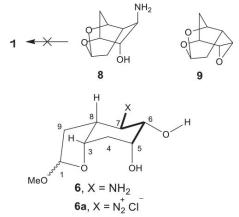


Figure 5. The antiperiplanar disposition of bonds (emboldened) in a key intermediate (6a)

In Ref. 1 the text below Fig. 17 contradictorily reads, "The crucial step, Tiffenau-Demjanov rearrangement (step 6, Fig. 17) involved a stereospecific ring contraction from the *bicyclic* amino alcohol with *four* contiguous stereogenic centers ... [emphasis added]." However, Fig. 17 does not show *any* bicyclic amino alcohol, and certainly *not* the bicyclic aminoalcohol 6, that possesses *five* contiguous chiral centers and does form protoprostaglandinal 1. What step 6 of Fig. 17 depicts is the *tricyclic* aminoalcohol 8 (not a bicyclic aminoalcohol) undergoing a ring contraction that was not in fact part of the synthesis.

## The Cephalosporin C Synthesis: Miscellaneous Chemical Errors

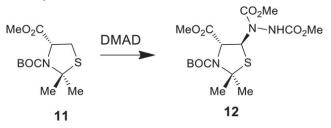
Fig. 19 of Ref. 1 portrays RBW's Cephalosporin C synthesis, carried out at the WRI during 1963-1966 (25) and becoming the subject of his Nobel Prize address (26). Four mistakes flaw Fig. 19 of Ref. 1. (+)-L-Cysteine is a carboxylic acid, not a methyl ester as Ref. 1 mistakenly shows in Fig. 19. In the synthesis, methyl N-t-butyloxycarbonyl-2,2-dimethyl-thiazolidine-4-carboxylate **11** (Figure 6) reacts with dimethylazodicarboxylate (DMAD) (25). Fig. 19 of Ref. 1 says that cysteine does so and shows its methyl ester doing so, but neither undergoes such a reaction as part of the synthesis. This startling, crucial reaction with DMAD yields the hydrazo compound **12** bearing three carbomethoxy groups, not the azo compound with two carbomethoxy groups mistakenly shown in Ref. 1 (25). Ref. 1 mistakes

the product of this reaction with DMAD as well as one of the reactants, which became an early intermediate compound in the synthesis.

Ref. 1 not only mistakes this intermediate but the structure of the final product as well. Fig. 19 in Ref. 1 shows a glutamic acid sidechain in the final product, but the natural substance (Figure 1) derives from  $\alpha$ -aminoadipic acid, not glutamic acid (25). The mistaken Cephalosporin C drawing (1) is shy one methylene group. In Fig. 18, however, Ref. 1 does show the full complement of six methylene groups.

#### Recruiting

After listing the first WRI postdocs Ref. 1 reads, "Almost all of the later members of WRI were previous postdoctoral students [*sic*] of Woodward at Harvard." However, only seven researchers (20%) worked for RBW at Harvard as postdocs or graduate students before joining the WRI (6). The postdocs were Ernest, Jacques Gosteli, Karl Heusler, Robert Ramage, and Subramania Ranganathan while the graduate students were Robert Sitrin, and James Whitesell.



#### Figure 6. A crucial stage in the synthesis of Cephalosporin C: stereoselective introduction of nitrogen. (DMAD abbreviates dimethylazodicarboxylate.)

Postdoctoral researchers at the WRI represented ten nations including the five mentioned by Ref. 1 in an obsolete listing (27). These nations were Austria, Canada, Czechoslovakia, France, Germany, India, Israel, Switzerland, the United Kingdom, and the United States. In 1980, Ernest noted all the postdocs' national origins in his final report from the WRI (6, 28). The five countries listed by Ref. 1 were those of the first seven postdoctoral workers, all of whom joined the WRI before 1966. Heusler's article "The Woodward Institute" from which Ref. 1 drew, appeared in that year (27).

#### **Operations**

"At WRI, the chemists worked in the American style of postdoctoral research accompanied by long

hours with [the] usual discussions late into the night" (1). This claim misrepresents history in two respects. First, Ref. 1 invokes what we think a non-existent but colorful style of American industrial postdoctoral research; and second, it mistakenly claims the fanciful style governed operations at the WRI.

In general, the WRI chemists labored in the colorless, international style of industrial postdoctoral researchers in North America and Europe. They began each day at about 8 AM and ended it at 5-6 PM. Neither long hours nor late nights were customary during our tenures at the WRI. Working hours did include some evenings when RBW visited Basel (29). The postdocs' practice had changed by 1968 or earlier. In contrast, before 1966, "Oft und besonders während der Besuche von Professor Woodward... Brennen die Lichter im Institute bis spät in die Nacht hinein" (27, 30).

#### **Chemistry Spinoffs?**

In a section entitled Chemistry Spinoffs, Ref. 1 misattributes J. Gosteli's indigo syntheses (31) to the WRI. They were carried out on the premises of what had been Geigy AG before the 1970 merger with CIBA AG. Gosteli writes, "My work on indigo was entirely done there [Geigy] and had not the least to do with the WRI (32)." The syntheses were completed before Gosteli became the administrative director of the Institute, but not published until he after had taken up the new post. Each of the three papers gives his WRI address. Ref. 1 cites the WRI not Geigy, because determining the correct attribution was impossible without interviewing a knowledgeable WRI veteran.

A previous section of this essay, namely Ivan Ernest's Insights, summarizes some of his accomplishments in the WRI and refutes a mistaken notion concerning his contribution to the  $PGF_{2\alpha}$  synthesis. His search for novel prostaglandins appears as a topic in Ref. 1's Chemistry Spinoffs, but he undertook no such search.

In Chemistry Spinoffs Ref. 1 also cites throughspace oxidations and devotes to them ca. 275 words and drawings of two steroid structures. These were reactions studied by Barton (1960), Arigoni (1958), Jeger (1958), Corey (1958), and Heusler and Kalvoda (1964). However, this work had no influence on the WRI according to an alumnus (32) whose appointment ran from June of 1963 when the Institute began until May of 1967.

What the present essay reveals about these oxidations, Gosteli's indigo syntheses, and Ernest's contributions to WRI projects implies that Ref. 1's Chemistry Spinoffs discloses no spinoffs whatsoever. By contrast, genuine influences exerted by RBW and the WRI on organic and medicinal chemistry inform a published history (6). For example, the WRI did spin off an extensive, international effort devoted to making pharmacologically active analogs of the penems, a Woodward invention. In 1988 the work culminated in a review of nearly 100 references, detailing the *in vitro* activity of the new class of antibiotics (33). Ref. 1, published in 2011, does illustrate a penem (Fig. 18).

## **A Misleading Suggestion**

In Ref. 1, Fig. 29 and its legend are misleading. The photograph in the figure shows the multi-story Building 401 at Klybeckstrasse 200 in Basel. The legend claims that the photograph depicts the WRI. While the WRI was housed in this building, the Institute occupied only one-half of one floor, in contrast to what Ref. 1 suggests in the legend accompanying Fig. 29. In defense of Ref. 1, we note it states obliquely that "...the WRI was separated from the rest of the research floor by a glass door...."

### Summary

Fourteen errors and a misleading suggestion, which we recount below, inform a review concerned with R. B. Woodward and the Woodward Research Institute (1). In what follows here, these errors are assigned lower-case Roman numerals; parenthetical page and figure numbers refer to Ref. 1.

**Chemical Errors** — Errors in the discussion of RBW's PGF<sub>2 $\alpha$ </sub> work begin with a claim (p. 934) that (i) one of E. J. Corey's prostaglandin syntheses entailed use of protoprostaglandinal **1**. That (ii) the structure of **1** was illustrated in a book reviewing a published Corey synthesis of PGF<sub>2 $\alpha$ </sub> from 2-oxabicyclo[3.3.0]octenone (p. 934, Fig. 16) is untrue. The writer also mistakenly claimed (p. 935, Fig. 16) that (iii) RBW's preparation of **1** represented an alternative synthesis of an intermediate first made by Corey and his coworkers.

In presenting the ring-contraction that RBW's  $PGF_{2\alpha}$  synthesis entails, the author mistakes the substrate undergoing the contraction (p. 935, Fig. 17). (iv) It is neither the tricyclic aminoalcohol **8**, nor (v) an unidentifiable bicyclic aminoalcohol with four contiguous stereogenic centers. Discussing the Cephalosporin C synthesis, Ref. 1 (p. 936, Fig. 19) mistakenly depicts as part of the work (vi) cysteine or (vii) its methyl ester reacting with DMAD, and (viii) it depicts a different product of the DMAD reaction than was actually obtained in the synthesis. Containing a glutamic acid sidechain instead of an  $\alpha$ -aminoadipic acid group (25), (ix) the structure of Cephalosporin C is erroneously drawn (compare Figure 1 in this work).

*Historical Errors* — WRI recruiting of postdoctoral researchers, operations, spinoffs, and an affiliation are all subject to errors.

*Recruiting.* Claiming (pp. 932-933) that (x) "Almost all of the later members of WRI were previous postdoctoral students [*sic*] of Woodward at Harvard" is false. That (xi) five nations only were represented by the postdoctoral researchers (34 in number) who passed through the WRI is a mistaken underestimate (p. 932).

*Operations.* The author of Ref. 1 invents (p. 933) a non-existent American style of postdoctoral research, and (xii) mistakenly claims (p. 933) it governed WRI operations. (xiii) He asserts (p. 937) that Ernest at the WRI sought to make novel prostaglandins.

*Chemistry Spinoffs.* The eponymous section in Ref. 1 fails to reveal any spinoffs.

*Affiliation.* (xiv) The remaining misattribution (p. 937) deals with J. Gosteli's affiliation, which appears in articles detailing new indigo syntheses.

*Misleading Suggestion.* The WRI did not occupy all of the Ciba building at Klybeckstrasse 200 (p. 943, Fig. 29), but only about half of one floor.

Readers interested in an accurate account of WRI research may wish to read "A School for Synthesis: R. B. Woodward and the Woodward Research Institute Remembered" (6).

Sources of Error — A concatenation of deficiencies explains why the errors in Ref. 1 were uttered and committed. We think editor, referee(s) if any, and author share responsibility, albeit unequally. Adequate editing and refereeing would have averted the publication that ensued. Thoughtlessness in writing, carelessness in researching, and negligence in verifying factual claims inform its flaws, as does a shortfall in interviewing WRI alumni. Failures to discover or confirm published or unpublished information, especially concerning RBW's prostaglandin  $F_{2\alpha}$  synthesis and Ernest's insightful role in it, result from neglecting to interview more than one WRI veteran. Indeed, more than two years before the attempts to make  $PGF_{2\alpha}$  (Figure 1) began in 1971, the only veteran (K. Heusler) interviewed for Ref. 1 had left the Institute (6). Errors in presenting the first crucial step of the Cephalosporin synthesis and in discussing the  $PGF_{2\alpha}$ synthesis we attribute to insufficient self-criticism of the manuscript or lack of a colleague's help in vetting it.

*Lessons* — Valuable but well known lessons may be drawn from Ref. 1. In a roundabout way, its errors testify to the importance of consulting the available literature, of attentive reading and note taking, of many interviews when the published literature is insufficient, and of colleagues' critical reading of drafts. They also demonstrate indirectly the importance of painstaking refereeing and editing. Editing would have prevented publication of mistakes, while refereeing would have encouraged the author to correct errors. An error that escaped a referee's notice might have been corrected by the editor or brought to the author's notice. Of course, an author's responsibility to submit for publication an error-free manuscript is paramount.

Consulting Ernest's final report from the WRI (Schlussbericht (28, 34) available through the Novartis Archive) would have prevented errors x-xi. Attentive reading of three articles presenting the PGF<sub>2 $\alpha$ </sub> and Cephalosporin C syntheses (4, 23, 25) and other sources (8, 10) would have prevented nine chemical errors. A reading of Ernest's "A Synthesis of Prostaglandins; Strategy and Reality" (23) would have avoided the mistake (xiii) of thinking he tried synthesizing prostaglandins other than PGF<sub>2 $\alpha$ </sub>. Interviewing more WRI veterans than one would have averted five historical errors and a misleading suggestion, all associated with operations, recruiting, and affiliation.

Whether journalists writing an article embrace a standard for the minimum number of interviewees is arguable. Tom Rosenstiel, executive director of the American Press Institute and a co-author of "The Elements of Journalism," says there is no rule (35). Other journalists favor three interviewees (36, 37), while Rosenstiel also states that more verification is best given a static story, ample time, and available experts (35).

We suggest that finding WRI veterans to have interviewed for Ref. 1 was feasible. At least five of them lived and worked in and near Basel from the time they left the WRI until or after publication in 2011. The author of Ref. 1 was employed nearby at the time. *Epilog* — In writing this article, we confined our efforts to relatively simple topics both chemical and historical. We restricted our criticism to subjects about which we had knowledge acquired during our WRI appointments, which began in 1968. Offering no comments on RBW's pre-WRI syntheses, beginning in 1944 and illustrated (Figs. 8, 11, and 12 in Ref. 1), was therefore appropriate. Nor do we remark on the unfinished synthesis of quinine from various azatwistanes, which Figs. 23-26 illustrate in Ref. 1. To chemical historians we leave opportunities to elucidate the choices of relevant figures and photographs that Ref. 1 presents.

#### Acknowledgments

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#### **References and Notes**

- 1. G. W. Craig, "The WRI, Robert Burns Woodward (1917-1979) and Chemistry behind the Glass Door, "*Helv. Chim. Acta*, **2011**, *94*, 923-946.
- 2. We lack any reason to believe that these errors arose either from falsification or fabrication.
- R. B. Woodward, K. Heusler, I. Ernest, K. Burri, R. J. Friary, F. Haviv, W Oppolzer, R. Paioni, K. Syhora, R. Wenger, and J. K. Whitesell, "Synthetic Analogs of β-Lactam Antibiotics. Biologically Active 2-Alklylidene-3-Deacetoxymethyl Cephalosporins," *Nouveau J. Chim.*, **1976**, 1, 85-88.
- R. B. Woodward, J. Gosteli, I. Ernest, R. J. Friary, G. Nestler, H. Raman, R. Sitrin, Ch. Suter, and J. K. Whitesell, "A Novel Synthesis of Prostaglandin F<sub>2α</sub>," *J. Am. Chem. Soc.*, **1973**, *95*, 6853-6855.
- K. Heusler, "Total Synthesis of Penicillins and Cephalosporins," in E. H. Flynn, Ed., *Cephalosporins and Penicillins*, Academic Press, New York, 1972, ch. 6, pp 255-279.
- K. F. Burri and R. J. Friary, "A School for Synthesis: R. B. Woodward and the Woodward Institute Remembered," *Bull. Hist. Chem.*, 2019, 44 (1), 37-50.

- 7. In 2020, the median age of 28 of the 29 living WRI veterans is 78 years (6).
- E. J. Corey and Xue-Min Cheng, Ch. 11, "Prostanoids" in *The Logic of Chemical Synthesis*, Wiley, New York, 1989, pp 250-307.
- A. Conan Doyle, "The Adventure of Silver Blaze," in *The* Memoirs of Sherlock Holmes, Oxford University Press, 1993 (originally 1892), p 274.
- 10. E. J. Corey, N. M. Weinshenker, T. K. Achaaf, and W. Huber, "Stereo-Controlled Synthesis of Prostaglandin  $F_{2\alpha}$  and  $E_2$  (*dl*)," *J. Am. Chem. Soc.*, **1969**, *91*, 5675-5677.
- E. J. Corey, S. MAlbonico, U. Koelliker, T. K. Schaaf, and R. K. Varma, "New Reagents for Carbonyl Reductions. An Improved Synthetic Route to the Primary Prostaglandins," *J. Am. Chem. Soc.*, **1971**, *93*, 1491-1493.
- 12. E. J. Corey, Z. Arnold, and J. Hutton, "Total Synthesis of Prostaglandin  $E_2$  and  $F_{2\alpha}$  (*dl*) via a Tricarbocyclic Intermediate," *Tetrahedron Lett.*, **1970**, 307-310.
- E. J. Corey and Barry B. Snider, "New Synthetic Route to Prostaglandins," *Tetrahedron Lett.*, **1973**, 3091-3094.
- Personal communication from J. Gosteli to the postdoctoral researchers dated June 1973, in Basel at the WRI. At the time, Gosteli was the administrative director of the WRI.
- R. B. Woodward, "Oxabicyclononanes," *Chem. Abstr.*, 1974, 80, 59850g; Swiss Appl. May 10, 1972.
- R. B. Woodward, "Oxabicyclooctanes," *Chem. Abstr.*, 1974, 80, 598513k; Swiss. Appl. May 10, 1972.
- 17. The confluence of synthetic routes may have resulted from coincidence, and we thank a referee for pointing this out.
- I. Ernest, "Penicillin-Derived Diazo Ketones: An Intramolecular Carbene Reaction," in J. Elks, Ed., *Recent Advances in the Chemistry of β-Lactam Antibiotics*, The Chemical Society, Burlington House, London, 1977, pp 252-259.
- 19. I. Ernest, "Penicillin-derived Diazoketones: Copper (II) Catalyzed Decomposition in Aprotic Media," *Tetrahedron*, **1977**, *33*(5), 547-552.
- I. Ernest, "2-Oxocephems. Synthesis and Properties of 7-Acylamino-2-oxocephem-4-carboxylic Acids," *Helv. Chim. Acta*, 1979, 62(8), 2681-2694.
- I. Ernest, "2-Oxocephems. II. Synthesis of 2-Oxocephalexin from Hetacillin," *Helv. Chim. Acta*, **1980**, *63*(1), 201-213.
- 22. I. Ernest, *Bindung, Struktur und Reaktionsmechanismen in der organischen Chemie*, Springer, Wien, 1972.
- 23. I. Ernest, "A Synthesis of Prostaglandins: Strategy and Reality," *Angew. Chem.*, *Int. Ed.*, **1976**, *15*, 207-214.

- 24. The 53 weekly issues of the *WRI Progress Reports* dated September 6, 1971, to July 1973, reveal no such experiment. These issues include the period when  $PGF_{2\alpha}$  was made. A collection of *WRI Progress Reports* with call number HUGFP 68.45 resides in the Harvard University Archives, Pusey Library, Cambridge, MA.
- R. B. Woodward, K. Heusler, J. Gosteli, P. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan, and H. Vorbrüggen, "The Total Synthesis of Cephalosporin C," *J. Am. Chem. Soc.*, **1966**, *88* (4), 852-853.
- R. B. Woodward, "Recent Advances in the Chemistry of Natural Products" in *Nobel Lectures, Chemistry 1963-1970*, Elsevier, Amsterdam, 1972, pp 100-121.
- 27. K. Heusler, "The Woodward Institute," *CIBA Blätter*, **1966**, 202, 1-6.
- I. Ernest, "Woodward Research Institute. Schlussbericht. Liste der in den Jahren 1963-1979 im Woodward Forschungsinstitut arbeitenden Chemiker (in chronologischer Reihenfolge)," Basel, May, 1980, pp 17-25. This final report forms part of the Novartis Firmenarchiv, Bestand CIBA-Geigy, PH 3.03; Novartis Campus, WSJ-433.6.15, CH-4056 Basel, Switzerland.
- 29. The frequency of RBW's visits to the WRI ranged from about one week in four to about one week in seven or eight.
- 30. *Trans*.: Often, and especially when Professor Woodward visited, the Institute's lights burned late at night.
- 31. J. Gosteli, "New Indigo Syntheses," *Helv. Chim. Acta*, 1977, *60*, 1980-1983.
- 32. J. Gosteli, private communication, Dec. 31 2017.
- S. W. McCombie and A. K. Ganguly, "Synthesis and *In Vitro* Activity of the Penem Antibiotics," *Medicinal Res. Rev.*, **1988**, 8(3), 393-440.
- Ernest's last report lay in the Novartis Archive in Basel from 1996 onward. Private communication from F. Wicker, Archivist, Nov. 27, 2019.
- 35. Tom Rosenstiehl, private communication, Mar. 6, 2020.
- Tyler Christensen, opinion-page editor of the Missoulian, Missoula, MT, private communication, Feb. 25, 2020.
- A. J. Coyne, The 18 Essential Rules of Journalism, https://writerswrite.co.za/the-18-essential-rules-ofjournalism/ (accessed Mar. 21, 2020).

#### About the Authors

Kaspar F. Burri was born in 1941, raised in Switzerland and received in 1968 his Ph.D. in Natural Sciences from the University of Bern, Switzerland. In 1968 he joined the Woodward Research Institute in Basel, Switzerland, as a postdoctoral fellow. He immigrated to the USA in 1971, where first he worked on the Vitamin  $B_{12}$  synthesis as a research fellow at Harvard University. Then, from 1973 to 1978 he served as a senior scientist at Hoffmann-La Roche Inc. in Nutley, N. J. From 1979 to 1995, back in Switzerland, he did research as a chemical project leader for F. Hoffmann-La Roche AG in Basel. From 1996 to 1999 he acted as chairman of the board for Lipomed AG in Arlesheim, Switzerland. From 1999 to 2007 he directed the chemical development of Iclaprim, a clinical candidate of the (now defunct) start-up company Arpida AG in Reinach, Switzerland.

Burri's research focused mostly on medicinal chemistry, especially in the fields of antibiotics and cardiovascular agents, where he is an inventor of many patents. He has published as the main author in *J. Am. Chem. Soc.* (1978) and in many issues of *Helv. Chim. Acta*, as well as in *Chimia*. He has co-authored in several international scientific journals, including *Nature*.

A native of Biddeford, Maine, born in 1942, Richard J. Friary became a synthetic organic and medicinal chem-

ist. He earned bachelor's and master's degrees in chemistry and organic chemistry from Colby and Dartmouth Colleges, respectively. Fordham University conferred his doctor's degree in June of 1970. Richard W. Franck, now Emeritus Professor of Chemistry, supervised Friary's doctoral research. Friary joined the Woodward Research Institute in February of 1970, serving for 3 1/2 years. There he made Cephalosporin C analogs and worked on the PGF<sub>2 $\alpha$ </sub> synthesis. Leaving Basel for New Jersey, he worked 27 years at the Schering-Plough Pharmaceutical Research Institute, where he became one of that Institute's most prolific inventors. Twenty-five patents name him as an inventor or co-inventor. Friary is the author or coauthor of 32 publications in the chemical literature. He wrote two trade books, Skate Sailing: A Complete Guide (1996) and Job\$ in the Drug Industry: A Career Guide for Chemists (2000). He retired in 2000 and writes about himself in the third person.

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## **BOOK REVIEWS**

Antimony, Gold, and Jupiter's Wolf, Peter Wothers, Oxford University Press, 2019, xv+273 pp, ISBN 978-0-19-965272-3, \$25.95.

"How the elements were named" precedes the unusual title of this book on its title page. The author, Peter Wothers of St. Catharine's College, Cambridge, elaborates a bit on this description in the preface: the book isn't an etymological table but a series of brief explanations of how some names became attached to their elements. "For example, while it's easy to find out that selenium was named after the goddess of the moon, why did the discoverer choose to do that in the first place?" (vii-viii) The names examined include not just those one can find on a current periodic table, but some discarded names, some attached to discoveries that were not accepted, and a few of important compounds or groups of elements. The vignettes are arranged and connected in a way that recapitulates many key episodes in the discovery of elements and their classification. And the tales are abundantly illustrated, mainly from the author's own library, including many from alchemical and early metallurgical texts.

Organized topically, the book contains interesting digressions into all manner of chemical trivia. In the first chapter, for example, we read that gold, associated with the sun, was sometimes prescribed as a medical remedy for the heart, because the sun was thought to govern the heart. One such remedy was the explosive compound, fulminating gold. Today, a different explosive compound, nitroglycerine (containing no gold), is often prescribed for angina, chest pain related to heart disease.

That first chapter, Heavenly Bodies, treats elements associated with celestial objects. It begins with the seven ancient metals, which were linked to the seven planets of geocentric astronomy and astrology. The metals (gold, silver, mercury, copper, iron, tin and lead) and their corresponding planets (Sun, Moon, Mercury, Venus, Mars, Jupiter and Saturn) shared symbols. Planets, asteroids and dwarf planets discovered more recently also had elements named for them, namely uranium, cerium, palladium, neptunium, and plutonium. Tellurium is another element named for a planet, namely the one on which we live.

The second chapter, Goblins and Demons, moves back in time to the days of Basil Valentine (if he existed) and Georgius Agricola, when miners were plagued and sometimes confused by gnomes and goblins and metals that seemed to be not quite the ancient ones they knew. The names cobalt and nickel are derived from mining demons according to the 19<sup>th</sup>-century philologists and folklorists, the brothers Grimm. Or perhaps cobalt comes from the ancient Greek cobathia, the toxic white smoke produced by roasting arsenic-containing minerals in air. Nickel certainly comes from Kupfernickel, where the Kupfer clearly refers to copper; perhaps the Nickel part derives from the Latin nichelus, a name applied to agate and sometimes onyx.

From minor demons in the second chapter, we pass to the devil's elements, sulfur and phosphorus, in the third, Fire and Brimstone. Brimstone is an older English word for sulfur, literally meaning burning stone. It was long associated with subterranean fires, both natural (volcanoes) and infernal. A delightful 15<sup>th</sup>-century woodcut of the destruction of Sodom and Gomorrah ornaments this section.

Pneumatic chemistry is the theme of the fourth chapter, "H two O" to "O two H." Among the terms examined here are the word gas, coined by van Helmont with chaos in mind, but related by Lavoisier to spirit (Goast, Ghost, Geist). Several examples of specific gases are treated, both compounds and elements, some as named by their discoverers (fixed air, inflammable air), and some under the new nomenclature of Lavoisier and Guyton de Morveau (oxygen, azote). The name "azote" was displaced in English, but not by the name proposed by American chemist Samuel Mitchill, "septon;" we call the element "nitrogen."

Nitrogen means nitre-former, and when the name was coined, nitre referred to potassium nitrate. But the word nitre and variations like nitron, nitrum, and natrun referred to other salts, rich in compounds we know as sodium carbonate and sodium bicarbonate. The Wadi El Natrun in Egypt shares its name with such materials, although it is not clear whether the place or the material was named first. That is where the element symbol Na comes from (for Latin natrium). Chapter five, Of Ashes and Alkalis, treats names and symbols of sodium and potassium among others.

The next chapter, Loadstones and Earths, addresses the names of a great number of metals, most of them isolated in the early 19th or later 18th century. In this chapter we encounter Jupiter's wolf, of the book's title. This ore robbed or spoiled tin (Jupiter), as it was too dense to be separated from tin ore in slurry tanks. This heavy ore was variously called Wolfrumb, Wolffschaum (wolf foam) or Wolffshar (wolf hair). We call the metal of this mineral tungsten, Germans call it Wolfram and we all use W as its symbol. The end of the chapter draws attention to the end of a couple of element names. The name silicon was proposed by Thomas Thomson early in the 19<sup>th</sup> century for the element recently isolated by Berzelius. Before its isolation, it had been widely expected to be a metal, as were the bases of many other earths, and it had been called silicium. Thomson proposed to change its ending to emphasize similarity to carbon and boron rather than to metals. Most metallic elements' names end in -ium, including aluminium according to IUPAC but not to ACS.

Chapter seven is called The Salt Makers, and its title gives the meaning meaning of the term halogens, the subject of the chapter. The convoluted path to the name chlorine for the prototypical halogen is outlined in the first few sections of the chapter. The mineral acid we know as hydrochloric acid was known for centuries as spirit of salt or oyle of salt. The gaseous compound was isolated in reasonably pure form in the 18<sup>th</sup> century, and dubbed marine acid air or muriatic acid. Scheele isolated a related gas, the dephlogisticated acid of salt, later recognized to be an element. But Lavoisier's theory of acids, which held oxygen to be part of all acids, prevented its recognition as an element until the early 19<sup>th</sup> century. In the meantime, it was known as oxygenated muriatic

acid or oxy-muriatic acid. Davy recognized the elemental nature of the gas, and he named it chlorine after its color.

Elements discovered by spectroscopy and the noble gases are the two main subjects of chapter eight, From under the Nose. That chapter begins with the first few elements discovered by spectroscopy. Caesium (cesium to Americans), rubidium, thallium, and indium were named after colors-not for the colors of the elements but the colors of distinctive spectral lines. The name helium also comes from spectroscopy, not because of color but because of its origin from a line identified in the spectrum of the sun (Greek helios). Helium, the second noble gas discovered on earth, is the link between spectroscopy and the noble gases. Most of the latter were discovered in the atmosphere, so they were literally under the nose. Shortly before argon was isolated, William Ramsay speculated that there might be a trio of such gases, for which he had the names anglium, scotium and hibernium in mind, echoing the nationalistic names of elements discovered in the previous two decades, gallium, scandium and germanium.

The last chapter, Unstable Endings, is a brief one, treating the last four element names approved by IUPAC, namely nihonium, muscovium, tennessine, and oganesson.

Antimony, Gold and Jupiter's Wolf is above all an interesting and entertaining collection of elemental and etymological anecdotes organized and assembled into a coherent order. Wothers points interested readers to plenty of additional material. In addition to an extensive bibliography of primary sources, he includes a page of books for further reading on related topics. These include classics from past Dexter Award winners such as Mary Elvira Weeks's Discovery of the Elements and Maurice Crosland's Historical Studies in the Language of Chemistry. More recent titles like Kit Chapman's Superheavy and The Lost Elements by Marco Fontani, Mariagrazia Costa, and Mary Virginia Orna are also recommended.

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Women in Their Element: Selected Women's Contributions to the Periodic System, Annette Lykknes and Brigitte Van Tiggelen, eds., World Scientific, New Jersey, London, 2019, xxiv + 531 pp, ISBN 978-981-120-628-3, \$128; 978-981-120-768-6, \$45 (softcover), 978-981-120-630-6, \$19.90 (ebook).

Despite the fact that this volume was developed as one of the core initiatives of the European Chemical Society (EuChemS), in celebration of the International Year of the Periodic Table 2019 (IYPT2019), the many contributors to the 38 women-featured chapters, in a true international spirit, hail from very disparate places: 23 from nine different European countries, 8 from North America, and one each from Australia and Japan. Pilar Goya, the 2019 President of the EuChemS, acknowledged in her foreword to the volume that women had, at best, complicated and limited access to scientific investigation, but were often discouraged, discriminated against, and denied access simply on the basis of their gender. Natalia Tarasova, Co-Chair of the IYPT2019 Management Committee and Past-President of the IUPAC, seconds this assessment in her own foreword by advocating that structural issues and legal frameworks that present barriers to women's empowerment be dismantled and that those promoting gender equality be advanced. She cited the fact that chemistry has had a long and honorable tradition of participation by highly creative women but that the percentages of women scientists remain shockingly low. She sees the celebration of IYPT2019 and its aftermath as an extraordinary opportunity to right these wrongs and to promote science education for all women at every level, particularly in developing countries.

The editors, Annette Lykknes, of the Norwegian University of Science and Technology, Trondheim, and Brigitte Van Tiggelen, of Mémosciences, Louvainla-neuve, Belgium and the Science History Institute, Philadelphia, USA, present us with a brief preface (6 pages) and a very lengthy introduction (54 pages!). In the former, they speak of the target readership for the volume: science-curious adults with a taste for history, as well as professional historians of science. They provide reference lists and bibliographies to satisfy the professionals, but in such a way as to not overwhelm the merely curious. The authorship of the chapters was deliberately drawn from many different disciplines to represent the community at large. They remind us that when Mendeleev devised his system (and they deliberately use system, not table), there were still many chemists who did not believe that atoms really existed. Yet, over the centuries, there was a continued effort to understand the elements and to grapple with the complexity presented by the periodic system. Though the pathway was not smooth, this volume, by design, documents an uninterrupted progression from the twilight of alchemy to the discovery of the superheavy elements. The major section of this introduction is titled, and appropriately so, "Women Discovering and Mastering Elements." Subdivisions summarize women's roles in the discovery of artificial radioactivity and the synthesis of the superheavy elements, their move into the development and use of advanced analytical methods, and their ever-present awareness of the social implications of "big science." Male leaders who provided opportunities for women scientists by mentoring, collegial recognition, providing a welcoming and friendly atmosphere, and promoting an egalitarian attitude in the profession are mentioned, among them Dmitri Mendeleev (1834-1907), Ernest Rutherford (1871-1937), and Harold Urey (1893-1981). While not every scientist who did so could be listed, curiously, three outstanding leaders who welcomed women into their research groups when it was still fashionable to criticize them for this practice, were omitted: William Henry Bragg (1862-1942), William Lawrence Bragg (1890-1971), and F. Gowland Hopkins (1861-1947). In closing the introduction, the editors note that the 38 vignettes of women scientists that comprise the book are as diverse as the elements in the periodic system itself; much of the information contained in the volume is based not only on written documents, but, whenever possible, on interviews and oral histories.

In Part 1, "Old and New Understandings of the Elements," three women are featured: Dorothea Juliana Fischer Wallich (1657-1725), Marquise Émilie Du Châtelet, née Gabrielle Émilie le Tonnelier de Breteuil (1706-1749) and Marie-Anne Pierette Paulze-Lavoisier (1758-1836). All three, whose lifetimes span almost two centuries, were very different in their approaches to and interests in science. Wallich was held in high esteem by Georg Ernst Stahl (1659-1734), developer of the phlogiston theory, for her ability to extract silver from its ores. She published three books in the years 1705-1706 describing her work with "minera," a putative precursor of the philosopher's stone. In the course of her experiments, which involved treating this substance, which we now infer was native bismuth mixed with some cobalt compounds, with nitric acid, she produced impure cobalt(II) chloride. (Cobalt was only discovered and recognized as an element in 1735, ten years after Wallich's death.) She subsequently noted the thermochromic effects of the latter, interpreting them as a step along the way toward discovering the philosopher's stone. If she had concentrated on the chemistry involved instead of the

alchemy, she may have been the first woman to discover an element. Our second proto-chemist in this section is Madame Du Châtelet, a woman who was obsessed with defining the nature of fire. An experimentalist who concentrated on fire's properties, including light, color, and heat, she published a dissertation on this topic, replete with faithfully recorded original observations, in 1744. Endowed with a lively curiosity and unbiased spirit, she was in the midst of writing a French exposition of Isaac Newton's (1643-1727) ideas when she died in childbirth in 1749. Her various works, which actually dealt with inchoate fields such as thermodynamics and the nature of energy, incorporated thinking that was far ahead of her time. Marie Paulze-Lavoisier is best remembered as a para-scientist since she worked side-by-side with her husband, Antoine-Laurent Lavoisier (1743-1794)-painting, drawing, describing his experiments; translating the ideas of others; and disseminating the anti-phlogiston ideas of the Chemical Revolution. She studied and absorbed the new ideas and nomenclature of her husband and his colleagues to such a degree that she was able to write not just a translation of the phlogistic ideas of Richard Kirwan (1733-1812), but a definite counter-attack that promoted Lavoisier's oxygen theory. She was an important protagonist in ushering in the dawn of quantitative chemistry.

Part 2, "The Glory of Analytical Chemistry: The Elements Multiply," contains seven chapters. Four of them highlight the contributions of individuals: Jane Haldeman Marcet (1769-1858), Julia Lermontova (1846/47-1919), Astrid Cleve Von Euler (1875-1968), and Ellen Swallow Richards (1842-1911). Each of these four women was remarkable in her own right. Jane Marcet's very popular book, Conversations on Chemistry, was an intercontinental phenomenon, with tens of thousands of copies printed through many editions, each of which was meticulously updated to contain the latest discoveries personally collected by the author from the actual scientists themselves. Though she had no formal training in science herself, Marcet gleaned and repackaged cutting edge science from informal meetings, meticulous lecture notes, experiments done at home in company of her husband, Alexander (1770-1822), contact with leading scientists, and access to books and journals. An early edition of her book is what enticed Michael Faraday (1791-1867) into science when he read it as a bookbinder's apprentice. (A series of articles in This Journal traces the evolution of the various editions of Conversations on Chemistry in detail.) Julia Lermontova made a substantial contribution to separation and atomic weight determinations of the platinum metals. Astrid Cleve Von Euler's book,

The Wonderful Element Selenium, served to popularize science by its unusual style: the use of simple metaphors to make abstract concepts understandable. However, during her marriage she found that her time was to be made entirely at her husband's disposal, and after her divorce, she found herself, tragically, without a home, a laboratory, and an income. Ellen Swallow Richards was the first woman to enroll at MIT; she is best known for her efforts to promote science for the common good, thus becoming an activist for women's education and for a healthy environment. She put her chemistry to work by doing the major portion of the analytical work on the study of industrial pollution of Massachusetts waterways. Three other chapters in this part review (a) the contribution of women analysts whose work helped map the different elements in the periodic table, (b) the work of three Spanish women scientists in fluorine chemistry and (c) the contributions of four women chemists to the chemical literature of the elements.

Part 3, "New Fields and Instrumental Methods," highlights the contributions of six outstanding women to the evolution of the periodic table. They are Clara Immerwahr Haber (1870-1915), Cecilia Payne-Gaposchkin (1900-1979), Ida Tacke Noddack (1896-1978), Erika Cremer (1900-1996), Dame Kathleen Yardley Lonsdale (1903-1971) and Yvette Cauchois (1908-1999). Clara Immerwahr Haber's collaborative work with Richard Abegg (1869-1910) broadened and clarified the concept of electronegativity, although her later life with Fritz Haber (1868-1934) led to grief and her eventual suicide. Astronomer Cecilia Payne-Gaposchkin, a specialist in the study of stellar spectra, was the first person to recognize the true composition of the stars, mainly hydrogen and helium. Ida Tacke Noddack is famous for two reasons: her co-discovery of the element rhenium, and her 1934 hypothesis that shook the scientific world (belatedly): "When heavy nuclei are bombarded by neutrons, it is conceivable that the nucleus breaks up into several large fragments..." This first-ever proposal of nuclear fission went ignored, and even ridiculed, by the scientific community which was unprepared to imagine a process unsubstantiated by theory. Erika Cremer was the first person to apply quantum tunneling theory to heterogeneous catalysis; she also pioneered the new analytical technique of gas-solid chromatography. Dame Kathleen Yardley Lonsdale, a crystallographer whose mentor was William Henry Bragg, confirmed the planar structure of benzene, thus enabling the evolution of modern organic chemistry. Yvette Cauchois' major contribution to science was the development of her eponymous curved-crystal spectrograph that improved luminosity and resolving

power, making it possible to observe spectral lines never seen before. This invention enabled the measurement of the low intensity X-ray emission lines typical of rare earths, rare gases and heavy elements.

Part 4, "Clusters of Women in Radioactivity," begins, naturally, with a chapter on Marie Skłodowska Curie (1867-1934) of whom so much has been written that it is unnecessary to add to that mountain of information at this point, except that the author observes that her life and career are testimony to the importance of family support and the careful management of a personal and a professional life. Nine additional chapters highlight the lives of ten additional women, none of whom have the iconic celebrity traction of Marie Curie except, perhaps, Lise Meitner (1878-1968), who now "inhabits" the periodic table as meitnerium. Meitner, next to Curie, has been acknowledged as one of the greatest women scientists (perhaps, greatest without the "women" appellation?) of the twentieth century; her long career exemplifies the difficulties of a life in science, but also the ways in which women sought and managed to overcome them. Other women in the "radioactivity club" are Harriet Brooks Pitcher (1876-1933), who worked with Ernest Rutherford on the discovery of "emanation," later found to be the element radon; Dr. Margaret Todd (1859-1918), a physician who coined the word "isotope" for Frederick Soddy (1877-1956), though it went unacknowledged by him; Stefanie Horovitz (1887-1942) who, by her very precise measurements, provided the first authoritative evidence for the concept of isotopes; Ellen Gleditsch (1879-1968), whose most celebrated achievement was the exact determination of the half-life of radium; May Sybil Leslie Burr (1887-1937), whose experiments with thorium emanation helped clarify the process of radioactive decay and the nature of the decay products; Elizabeth Róna (1890-1991), who became the world's leading expert on polonium, crossing the borders between chemistry, physics, biology and medicine for most of her career; Marguerite Perey (1909-1975), who discovered francium (element 87), the last element that could be extracted chemically from minerals, and the Austrian duo, Berta Karlik (1904-1990) and Traude Bernert (1915-1998), who discovered the isotopes 215, 216, and 218 of element 85, formerly "eka-iodine," known today as astatine-the rarest naturally occurring element on earth.

The final three parts, "Manufacturing Elements: From Artificial Radioactivity to Big Science," "Instrumental Revolution and Interface Between Chemistry and Industry," and "Social Activism, Sisters in Arms" (parts 5, 6, and 7 respectively) bring us into the modern era-complete with several color photographs. Beginning with the discovery of artificial radioactivity by Irène Joliot-Curie (1897-1956) and her husband, Frédéric (1900-1958), an event that led to greater understanding of nuclear processes and the production of the transuranics, Part 5 documents the role of Isabella Lugoski Karle (1921-2017) in plutonium research, Chien-Shiung Wu's (1912-1997) identification of Xe-135 as the "nuclear poison" that kept shutting down nuclear reactors, Darleane Christian Hoffman's (b. 1926) role in pioneering "atomat-a-time" chemistry as the leader of the Heavy Element Nuclear and Radiochemistry Group at the University of California at Berkeley, and, following in Hoffman's footsteps, Dawn Shaughnessy's (b. 1972) collaborative work in identifying six superheavy elements as the group leader at the Lawrence Livermore National Laboratory. Part 6 examines instrumentation's role in cementing the relationship between chemistry and industry. Five women are featured in this part: Sonja Smith-Meyer Hoel (1920-2004), whose work in the Norwegian metals industry and patent system boosted her country's postwar recovery; Toshiko Kuki Mayeda (1923-2004), whose mass spectrometric expertise helped establish methods to use oxygen isotopes to study the history of the solar system; Mary Almond Pickering (b. 1928), whose paleomagnetism work provided the first-ever crucial step to confirming continental drift; Barbara Bowen (b. 1932), whose collection and digitization of atmospheric data led to the detection of the "ozone hole" over Antarctica; and Reatha Clark King (b. 1938) who, at the U.S. National Bureau of Standards (presently the National Institute of Standards and Technology), developed the apparatus and procedures to control and measure the combustion of dangerous gases that were later used as rocket propellants by the National Aeronautics and Space Administration (NASA). The women whose avowed vocation as social activists are highlighted in Part 7 include Gertrud Johanna Woker (1878-1968) who warned against the dangers of using tetraethyl lead as an anti-knock agent in automobiles as early as 1932 and warned against using scientific research for military purposes. Alice Hamilton, M.D., (1869-1970) had research interests in bacteriology, pathology and public health and social activist interests in the settlement house movement, which described its goals as residence, research and reform. These two thrusts eventually led her to become a pioneer of occupational epidemiology and industrial hygiene resulting in new legislation, new insurance requirements and modifications to industrial methods. An American Chemical Society National Historic Chemical Landmark (https:// www.acs.org/content/acs/en/education/whatischemistry/ landmarks/alicehamilton.html) recognizes these contributions. And finally, we come to the formidable Ida Freund (1863-1914), the first woman to be appointed to a university lectureship in the UK. Through her books, Freund's impact remains strong to this day with respect to her educational ideas and the history of chemistry. Though she was a no-nonsense lady who deplored the and publications—without any citation whatsoever. Perhaps the most egregious example of this behavior was that of Otto Hahn (1879-1968) who could possibly be excused from omitting Lise Meitner's name from their collaborative papers during the Nazi regime, but certainly cannot by failing to acknowledge her contribution to the discovery of fission after the war. Nowadays, we might



Figure 1. Periodic Table of Cupcakes, momentarily intact. Periodic Table People Science Café, October 5, 2019, Saint John's University, Queens, NY. Photograph: Mary Virginia Orna

association of chemistry with the kitchen, she nevertheless became famous for her whimsical promotion of the "periodic table of cupcakes" that became a staple of chemical education. In fact, this author and Sally Mitchell, Rye High School, Rye, NY, recently employed this same "hook" to draw students into an ACS New York Local Section Science Café called "Periodic Table People" during the #IYPT2019 (Figure 1).

If you have managed to reach the end of this very long review, you no doubt realize that this volume is a rewarding exposition of the role of women in the development of chemistry, worthy of being read over and over again. Each reading reveals new riches and insights. One comes to understand that not only were women denied access to science for the reasons elaborated upon in the preface of this book, but in many other ways that were both systematic and the fruit of personal animosity, fear, and the simple opinion that women did "not count"-factors that come to light in many of the chapters in this volume. Among the former are the laws that many countries had in place that forbade women's entry into higher (and, in some cases that even persist today, to elementary) education. Among the latter, we note the failure of renowned scientists, among them Nobel laureates, to recognize the priority of women who preceded them or collaborated with them in their work, simply ignoring and yet building upon their ideas find these individuals with intellectual property rights lawsuits on their hands. Another way of "putting down" these women was to simply dismiss their work as "not innovative" or "routine," missing the point that most research is apparently routine and not very innovative until a breakthrough occurs, the importance of which may dawn on the scientific community many years later because the work was ahead of its time. One very fine feature of the volume is that each chapter contains a rich set of endnotes and bibliography for further research. It is also completely indexed with a General Index, a Name Index, and an Element Index, and contains an appendix of authors' biographies (though without email addresses).

Some picky little errors: p. 71, 1749, not 1742, was the death-date of Madame Du Châtelet; pp. 101-111, Jane Marcet's book is variously referred to as *Conversations* on *Chemistry* and *Conversations* in *Chemistry*; and perhaps a dozen additional typos caught my eye. For a book numbering 531 pages, this is trivial!

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## **The Back Story**

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January 21, 2020

I learned today that Sir Jack Baldwin, FRS died on January 4, 2020.

Jack was a force.

A hungry British lion.

Some would say that he lived to intimidate others. Some would say that he was a narcissistic SOB. Jack would say they were all right. He was those things and a lot more.

I was rather surprised when Jack was knighted. He so very loudly despised authoritative figures and anyone else who feigned authenticity. I imagined that he had burned so many bridges, not to mention metaphorical buildings of all sizes and shapes, that he was politically too hot to handle. Congratulations to the Queen and her ministers.

I studied Jack during my 1983-1984 sabbatical at Oxford's Dyson Perrins Laboratory. I personally encountered his not-always-so-whimsical imperialism when he commanded that I carry out physical organic chemical research with him-though we had agreed the previous year and he officially had stipulated on my immigration forms that I would work on penicillin biosynthesis. How could I say no to Professor Baldwin, the Waynflete Professor of Chemistry? Simple. I was a young, naïve American, ignorant of the power of the Professor at Oxford. I chose not and found (mostly) another area to study. True, I did work on Jack's project and, together with Laurence Harwood and Rolf Bohlmann, published a paper on olefin stereospecific isomerizations. I also published a series of papers with a then up-and-coming Steve Davies who, several decades later, would become Jack's successor as the Waynflete Professor of Chemistry.

I watched as Jack would ask questions at seminars that made visiting professors shake in their boots. However, I also realized that Jack was not trying to intimidate, he was seeking information. Jack could pluck seemingly disparate chemical information out of the air, blend the parts effortlessly, and produce great creativity. I knew each piece of Jack's data but it was he who produced the brilliance. I watched Jack deal with his competitors; it was not a game. I watched Jack play, at times menacingly, with his junior colleagues—they were all junior to him—and we would all wince. Later, however, we would tell those tales with respect, even with admiration. Maybe not with admiration ...

Eighteen months ago, at the invitation of Tony Barrett, Jack and I participated in a celebration of Derek Barton's centenary at Imperial College. Barton was Jack's (and Tony's) professor and a friend to all of us. At the end of one evening, Jack's limo was an hour or two late (!), so he and I chatted in a corner of the bar. I had hoped, for this unexpected occasion, to review my



Jack Baldwin in a car that did not fit his oversized personality, in front of the Dyson Perrins Laboratory, 1986. Photograph courtesy J. I. Seeman

experiences of that sabbatical with Jack. I asked him, "How did you manage this paradox, of wanting the DP to be great, thereby wanting to provide resources—excellent graduate students and other resources—to the DP's staff, while wanting to succeed yourself?" In his deep growling voice, he laughed. "Simple. I took all the best students and all the space for myself."

The undeniable fact is, Jack brought life and great science into a department that, before him, was characterized by Barton as "sleepy." Jack Baldwin was an infinite source of energy and passion that invigorated the entire Dyson Perrins Laboratory. He was lightning fierce. He was lightning. And I can still feel the power that was Sir Jack Baldwin. The world is a bit dimmer and a lot less exciting without Jack.

## **BULLETIN FOR THE HISTORY OF CHEMISTRY**

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