P1.3 CHEMICAL GENEALOGY OF AN ATMOSPHERIC CHEMIST: JAMES N. PITTS, JR., A CASE STUDY

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1. INTRODUCTION

It is indeed a desirable thing to be well descended, but the glory belongs to our ancestors.
- Plutarch (AD 46?-120)

Plutarch makes an interesting point. It is important to understand our background and where we came from if we are to really understand the process of creative effort. Mentoring is a key aspect of atmospheric chemistry. Our thesis mentors and colleagues have major influence on us and our research through their discussions and work during the periods in our careers when we study with them.

How far back does this mentoring influence trace? Our mentors influence us, but they were impacted by their mentors, and so on. Presented here is a chemical genealogy of a well-known atmospheric chemist and mentor (thesis mentor for J. Gaffney). This genealogy indicates that the mentoring influence can be traced back for decades if not hundreds of years (Mainz and Girolami, 1998).

2. JAMES N. PITTS, JR. (1921-), Ph.D., UCLA, 1949

I was fortunate to attend the University of California, Riverside, in 1967-1975. I worked as an undergraduate and graduate student in the laboratory of James N. Pitts, Jr. He was at the time, and still is, a very well known photochemist and atmospheric scientist. He has written a number of landmark books on photochemistry and graduate education mentoring with a fellow graduate student and colleague, Jack G. Calvert, and with his student and wife, Barbara J. Finlayson-Pitts (Calvert and Pitts, 1966; Calvert et al., 1972; Finlayson-Pitts and Pitts, 1986, 2000) Pitts taught my freshman chemistry course, and his energy and enthusiasm for science and applications in atmospheric chemistry were indeed a model for all to follow. Having just turned 80 years young, he continues to inspire students at the University of California, Irvine, after his retirement from the University of California, Riverside, in 1988. He has written more papers than I can count and has served on or chaired many key National Academy of Science panels and California state scientific review committees on air quality and air toxics.

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Pitts' group researched the basic chemistry and kinetics of gas-phase reactions involved in air pollution and developed methods for studying and detecting these species. As director of the Statewide Air Pollution Research Center at the University of California, Riverside, he led the development of smog chamber construction and studies on the fundamental processes and production rates of ozone and other oxidants. His early work focused on singlet-oxygen chemistry, while his later work addressed the presence and formation of mutagens in aerosols found in photochemical smog. Here, I explore his mentors and search for links and similar interests in atmospheric chemistry, analytical technique development, physical organic chemistry, and fundamental processes in biological toxicology.

3. THE TWENTIETH CENTURY MENTORS

Pitts obtained his Ph.D. in physical chemistry from the University of California, Los Angeles, in 1949, under Professor Francis E. Blacet. The twentieth century mentors in Pitts' chemical geneaology all influenced their students significantly and were closely tied to the field of photochemistry.

Francis E. Blacet (1889-1990), Ph.D., UCLA, 1931;
Philip A. Leighton, thesis mentor

Blacet was a photochemist of note. He is credited with being the first to propose that the photolysis of nitrogen dioxide is the source of ozone in photochemical air pollution. He also organized a number of informal photochemistry workshops that began in 1952 and are still held every two years. He won the Richard C. Tolman Award from the American Chemical Society Southern California Section in 1968. Blacet was an excellent teacher and mentor and was cited as one of his key teachers by Glenn Seaborg in his autobiography describing his undergraduate days at the University of California, Los Angeles (Seaborg, 1982). Indeed, Francis had estimated that he had taught over 15,000 students during his for years of teaching. During WWII Francis worked for the National Defense Rsearch Committee leading a team that conducted classified research on gas masks for chemical warfare protection. For this work he was awarded the Presidential Certificate of Merit in 1948 from President Truman. Blacet had a number of well-known graduate students, including Jack G. Calvert, David Volman, and Pitts. Blacet also directed Walter Blaedel in his master's degree work before sending him to Stanford to work with Philip A. Leighton, Blacet's

mentor. His research group always referred to him not as Dr. or Professor Blacet but as "Chief", a reference to his wartime nickname of "El Jefe" given him in Panama during his simulated combat work during WWII (Bayes, Pitts, and Volman, 1994). He was a classic example of a true "gentleman and scholar". As an emeritus professor, he worked on handling general questions about chemistry from the public and extended the written history of the UCLA Chemistry Department.

Philip Albert Leighton (1897-1983), Ph.D., Harvard, 1927; G.S. Forbes, thesis mentor

After obtaining his degree at Harvard with G.S. Forbes, Philip A. Leighton joined the faculty of Stanford University. He was well known for his work on photochemistry, chemical kinetics, and aerosols, and he wrote textbooks on photochemistry. The first, *The Photochemistry of Gases*, was written with William Albert Noyes, Jr. (Noyes and Leighton, 1941). This was the first detailed treatise on the photochemistry of the polluted troposphere. The second book, *Photochemistry of Air Pollution* (Leighton, 1961), reveals Leighton's amazing insights at that time into the key radical species and their chemistry. Many senior atmospheric scientists consider this book a classic on the topic.

George Shannon Forbes (1882-1979), Ph.D., Harvard, 1905; T.W. Richards, thesis mentor

Forbes synthesized bromine monochloride and iodine trichloride. He developed very accurate actinometric methods using uranyl salts. He also studied the photochemistry and fluorescent properties of quinine, ozone, diazomethane, and haloalkanes. His research group also actively examined the chemistry of isocyanates and sulfur compounds, as well as the redox chemistry of silver and its salts.

4. THE NINETEENTH CENTURY MENTORS

Theodore William Richards (1868-1928), Ph.D., Harvard, 1888; Josiah Parsons Cooke, thesis mentor

Richards won the 1914 Nobel Prize in chemistry in recognition of his exact atomic weight determinations for more than 30 of the chemical elements. His thesis work with Cooke in 1887 examined the ratio of hydrogen in water. Richards' work confirmed the theory that lead has a number of isotopes. He studied the compressibilties and atomic volumes of elements and invented the adiabatic calorimeter. With this instrument he studied heats of dilution, combustion, dissolution, and neutralization. He even invented a nephelometer for studying trace levels of suspended solids in liquid solutions. The use of optical methods for the study of mixed-phase systems — aerosols — would be the logical next step after this work.

Josiah Parsons Cooke (1827-1894), A.B., Harvard, 1848; no thesis mentor

Cooke was an extraordinary fellow. He was given the job of starting the Harvard Chemistry Department. He initially was hired as a tutor in mathematics but in 1850 was appointed Erving Professor of Chemistry and Mineralogy, a position he held for the rest of his life. He attended chemistry lectures of Benjamin Silliman, Sr., at the age of 16, but he received no formal education in that discipline. After receiving the appointment in chemistry, he traveled to Europe and attended lectures by Jean Baptiste Andre Dumas and Henri Victor Regnault, who influenced him greatly. Cooke studied the properties of the elements, particularly H, O, and Sb. He also wrote a very interesting book titled *Religion and Chemistry* (Cooke, 1880). In the third chapter of that book, he wrote about the testimony of oxygen, as follows:

> *WERE we to limit our regards to those physical qualities of the atmosphere which we studied in the first two chapters, we should overlook the most wonderful adaptations in its divine economy. These properties belong to the atmosphere, in great measure at least, in virtue of its aeriform condition, and, so far as we know, an atmosphere composed of other gases, and still having the same density, would soften the intensity of the light, and diffuse the genial influences of the sun's heat, as well as air. Not so, however, with the chemical qualities of the atmosphere, which we are next to consider. These belong to the atmosphere solely as air, and could not have been obtained with any other known materials.*
>
> *When a chemist wishes to investigate the nature of a new substance, his first step is to analyze it. Let us, therefore, as a preliminary to our present inquiry, ascertain what is the composition of this aeriform matter we call air. The air has been analyzed hundreds of times in every latitude and in every climate; and the result has been uniformly that which is given in the following table:*
>
> *Composition of the Atmosphere*
>
> | | |
> |---|---|
> | *Oxygen* | *20.61* |
> | *Nitrogen* | *77.95* |
> | *Carbonic Dioxide* | *0.04* |
> | *Aqueous Vapor (average)* | *1.40* |
> | *Nitric Acid, Ammonia, Carburetted Hydrogen Traces* | |
> | | *100.00* |

Cooke was very interested in the atmosphere and passed on that interest to his students, including Theodore Richards. Cooke's treatise on the atmosphere predates the work by James Pitts by about one hundred years. Cooke was very meticulous and prided himself on the accuracy of his measurements, a quality that he passed on to Richards and that Richards passed on to his students.

Josiah Parsons Cooke, who had no definite thesis mentor, can be traced by the influences of Benjamin Silliman, Sr., Jean Baptiste Andre Dumas, and Henri

Victor Regnault on his writings. At this point we follow the three lines separately, starting with Silliman.

5. THE BENJAMIN SILLIMAN, SR., LINE

Benjamin Silliman, Sr. (1779-1864), A.B. (Law), Yale, 1796

Silliman was noted as the most eminent teacher of natural science in America. He began as a lawyer but was encouraged to pursue chemistry by the president of Yale. During the winters of 1802-1803 and 1803-1804 he studied with James Woodhouse in Philadelphia. Later he completed his education, attending lectures by Thomas Charles Hope of Edinburgh in 1805. A very astute, influential man, Silliman began the first U.S. scientific journal, *The American Journal of Science*. He also was a co-founder of the American Association for the Advancement of Science, performed the first chemical analysis of petroleum, and discovered the fusion of carbon through the use of electric arcs.

James Woodhouse (1770-1809), M.D., Pennsylvania, 1792; Benjamin Rush, mentor

Woodhouse was a student of Benjamin Rush. He founded the Chemical Society of Philadelphia, the first organization of its kind worldwide. His studies included the demonstration that "heavy inflammable air" was carbon monoxide. He also explained the role of plants in taking up carbon dioxide and maintaining the balance of gases in the atmosphere.

Thomas Charles Hope (1766-1844), M.D., Edinburgh, 1787; Joseph Black, mentor

Hope was the first to introduce Lavoisier's theories to Great Britain. He proposed that strontia contained a new element, studied barium compounds, investigated the behavior of liquids, and disproved the idea that liquids do not conduct heat.

Benjamin Rush (1745-1813), M.D., Edinburgh, 1768; Joseph Black and William Cullen, mentors

One of the founding fathers of the United States of America, Benjamin Rush was a multitalented individual who aided in writing the *Declaration of Independence* and *Common Sense*. He wrote the first chemistry textbook in America, beginning the long tradition of writing books on the subject in his line's future generations. He was the first psychiatrist in America and opened the nation's first free dispensary. Rush also founded the first antislavery society and the College of Physicians. A professor of chemistry at Philadelphia, he is considered by many to be the father of chemistry in America.

Joseph Black (1728-1799), M.D., Edinburgh, 1754; William Cullen, mentor

Black dedicated his thesis to Cullen in 1754, citing Cullen's chemistry teaching in Edinburgh. Black rediscovered fixed air, carbon dioxide, by heating inorganic carbonates and showed that carbon dioxide would not support combustion or animal life. He was one of the first to apply accurate weight measurements to chemical reactions, anticipating the later use of this approach in work on elements by Cooke and Richards. Black was the first to distinguish heat from temperature.

William Cullen (1710-1790), M.D., Glasgow, 1740; Andrew Plummer, mentor

Cullen held the first independent lecture position in chemistry in Great Britain and was the first to teach at Glasgow in English rather than in Latin. He discovered that evaporating fluids cause cooling and suggested examination of soils for nitrate to determine soil fertility. He attended lectures of Andrew Plummer on chemistry in 1734-1736 and was influenced greatly by him.

Andrew Plummer (1698-1756), M.D., Leiden, 1722; Hermann Boerhaave, mentor

Plummer established the first modern teaching of chemistry in the British Isles. He analyzed mineral waters and coal and developed "Plummers Pills" (calomel, antimony sulfide, and mercuric chloride), which were used for over 200 years as a panacea for various diseases. Abraham Lincoln took these pills for ailments.

Hermann Boerhaave (1668-1738), M.D., Hardewijk, 1693; Burchard de Volder, mentor

Boerhaave was an outstanding teacher and writer and is considered the father of physical chemistry. He introduced exact measurements to chemistry, using the best available balances and thermometers. He demonstrated that water is a product of combustion, proved that heat is weightless, and performed the first calorimetric studies.

Burchard de Volder (1643-1709), M.D., Leiden, 1664; Franciscus Sylvius, mentor

An enthusiastic follower of Boyle, Burchard de Volder published studies of the weight of air and invented an improved air pump. He set up the first physics laboratory in Leiden and clearly influenced future students with his interest in gases and the atmosphere.

Franciscus Sylvius (1614-1672), M.D., Basel, 1637; Stupaeus, mentor

Sylvius investigated the heat given off when acid was poured onto iron filings. An anatomist of the brain and cerebral arteries, he defended Harvey's theory of blood circulation. He believed strongly in iatrochemistry (that chemicals could be used to treat illnesses). Little is known of his mentor, Stupaeus.

6. THE JEAN BAPTISTE ANDRE DUMAS LINE

Jean Baptiste Andre Dumas (1800-1884), no formal degree ca. 1823, Geneva; Charles Gaspard De La Rive, mentor

Dumas was an extraordinary organic chemist. Although he obtained no formal degree, he received training in pharmacy from Augustin Le Royer in Geneva. After publishing a book on the physiology of the nervous system, Dumas was invited to Paris, where he assisted Thenard in his lectures on chemistry at the Ecole Polytechnique and later replaced him in a position as professor there. Dumas was also influenced greatly by Charles Gaspard De La Rive. Dumas' work dealt with element vapor densities, the compositions of alcohols and ethers, and the development of a law of substitution reactions in organic compounds (based on his initial work with chlorine and hydrogen in organics). His development of chemical types for organic compounds led to his wide renown as one of the preeminent organic chemists of his time. His research on the atomic weight of carbon influenced Cooke and Richard. He studied the composition of water and of the atmosphere, including the chemical composition of carbon dioxide.

Late in his career, Dumas turned his attention to politics. He was elected a deputy from the department of Nord (1849) and helped to pass laws dealing with recoining of money; stamped paper; forgery of public acts; and taxes on salt, sugar, etc. His abandonment of chemical research for politics was considered a major loss for chemistry, as he ceased his brilliant work when in his prime.

Charles Gaspard De La Rive (1770-1834), M.D., Edinburgh, 1797; John Allen, mentor

De La Rive was an early supporter of the views of Davy (electrochemistry), Dalton (atomic theory), and Berzelius (definite proportions). De La Rive studied the sound produced by burning hydrogen in tubes and invented a galvanometer based on water electrolysis and a qualitative method for arsenic detection. His mentor, John Allen, attributed animal heat to the combustion of food particles in the blood.

Louis Jacques Thenard (1777-1857), M.A., Paris, 1797; Louis Nicolas Vauquelin, mentor

Thenard discovered hydrogen peroxide (an important atmospheric species). He worked with Joseph Louis Gay-Lussac on isolating boron and improving combustion analysis. Thenard was the first to suggest that fermentation was due to living organisms. Gay-Lussac was very interested in the composition of the atmosphere and surely had an influence on Thenard. Gay-Lussac held a world record of 7,019 meters for a balloon ascent, in which he showed that the composition of the atmosphere was the same (i.e., four parts nitrogen to one part oxygen) at this height and at ground level, indicating that the atmosphere is well mixed.

Louis Nicolas Vauquelin (1763-1829), M.A., Paris, 1790; Antoine Francois de Fourcroy, mentor

Vauquelin discovered chromium and the first amino acid, asparagine (from asparagus). He isolated camphoric, quinic, and cyanic acids from natural products and studied the reactions of wine, vinegar, and oil with drinking vessels. He also isolated platinum metal and investigated the respiration of insects. Vauquelin was a prolific writer who described in detail many methods for the analysis of mineral waters, minerals, plants, and other substances.

Antoine Francois de Fourcroy (1755-1809), M.D., Paris, 1780; Jean Baptiste Michel Bucquet, mentor

Fourcroy co-discovered iridium with Vauquelin. He studied the chemistry of chlorine, urea, and mercury and showed that sulfuric acid can act as a desiccant. Fourcroy was an important teacher and an advocate of Antoine Laurent Lavoisier's ideas.

Jean Baptiste Michel Bucquet (1746-1780), M.D., Paris, 1770; Guillaume Francois Rouelle, mentor

Bucquet was a student with Antoine Laurent Lavoisier under Rouelle. Although Lavoisier had no students (because chemistry was not his livelihood), Bucquet trained his students in the concepts and ideas that Lavoisier had developed, and they collaborated and interacted on many projects. Bucquet studied plants and their chemistry and isolated opium and morphine. He was the first to demonstrate that carbon dioxide is acidic.

Antoine Laurent Lavoisier (1743-1794), L.L.B., Paris, 1764; Guillaume Francois Rouelle, mentor

The father of modern chemistry, Lavoisier showed that oxygen is the key to combustion. He also demonstrated the law of conservation of mass, a key concept in the development of chemistry. Lavoisier's interests besides chemistry included mineralogy, economics, and geology, and meteorology was his second love. At the age of twenty, he began making barometric observations from his home, continuing them throughout his life. He developed methods and rules for standardization of temperature measurements and studied natural electricity and its relation to thunder. He considered weather forecasting to be almost as difficult an art as medicine and recognized that daily measurements of atmospheric pressure, the velocity and direction of winds at different altitudes, and the hygrometric state of air would be needed to predict weather. He developed a network of colleagues in France and Europe using selected barometers and wind gauges to predict weather.

> *With all this information it is almost always possible to predict one or two days in advance, within a rather broad range of probability, what the weather is going to be; it is even thought that it will not be impossible to publish daily forecasts which would be*

very useful to society (Imprimerie Nationale, 1864-1893).

Lavoisier was guillotined during the French Revolution. Joseph Lagrange noted at his death that "it took only an instant to cut off that head, and a hundred years may not produce another like it."

Guillaume Francois Rouelle (1703-1770), Apothecary, Paris 1725; J.G. Spitzley, mentor

Rouelle is considered the founder of the French school of chemistry. He proposed the first modern definition of salts and distinguished between neutral, acid, and basic salts. He also proposed a theory of distillation, analyzed plants, and established that the Egyptians had used sodium carbonate, succinic acid, and coal to effect mummification. Amazingly, Rouelle was also a phlogistonist.

J.G. Spitzley (1690-1750?), Apothecary, Paris, 1715(?); Nicolas Lemery, mentor

Little is known of Spitzley. It seems that there is a mystery in everyone's family tree.

Nicolas Lemery (1645-1715), Apothecary, Paris, ca. 1667; Christofle Glaser, mentor

Lemery was the first to distinguish between plant and mineral chemistry, leading to the concepts of organic and inorganic chemistry. He published a very well read book on chemistry and developed a theory of atomic particles based on fundamental shapes.

Christofle Glaser (1615-1678), M.D., Basel, ca. 1640; Etienne de Clave, mentor

Glaser was a professor at the Jardin du Roi. His writings described arsenic trichloride, bismuth oxynitrate, and potassium sulfate. Glaser practiced iatrochemisry in Paris. His book, *Traite de la Chymi*, published in Paris in 1663, is likely the source for much of Lemery's book that was later so well known. Glaser was a physician, pharmacist, and alchemist who treated his patients' ailments with chemicals.

Glaser was imprisoned in the Bastille for supplying arsenic to Sainte-Croix, who used it to poison the Marchioness de Brinvilliers. Little is known about Etienne de Clave, except that he was a professor at the Jardin du Roi in Paris around 1620. Clave accepted the Parcelcus ideas of three principles of mercury, salt, and sulfur, while adding phlegm and earth.

7. THE HENRI VICTOR REGNAULT LINE

We conclude with the last of the major influences on Josiah Parsons Cooke: Henri Victor Regnault and his mentors. These mentors had a strong analytical background and were also very productive in authoring a number of works on mineralogy and chemistry.

Henri Victor Regnault (1810-1878), Ph.D., Paris, 1837; Pierre Berthier, mentor

Regnault's mentor at the Ecole Des Mines was Berthier, an inorganic analytical chemist. Regnault's visit to the laboratories of Justus Von Liebig in 1835 sparked his interests in organic chemistry, at which he excelled. We will trace Regnault's mentoring back through Berthier, but the interested reader can track the Justus Von Liebig connection via Mainz and Girolami (1998).

The Berthier line goes back to the fifteenth century and includes many important scientists and physicians from the Jena and Padua schools. Regnault was the first to prepare carbon tetrachloride, vinyl chloride, and trichloroethene. He carried out detailed studies of the compressibilties, specific heats, and densities of gases. He actually measured the volume of carbon dioxide exhaled per volume of oxygen inhaled by animals in a series of experiments. His interests in how the air around us is used by organisms and the importance of the atmosphere were clearly shared by his followers.

Pierre Berthier (1782-1861), Ing. Ordinare, Ecoles des Mines, 1805; Johann Gottfried Schreiber, mentor

Berthier was very well known metallurgist. He wrote a textbook on assaying and metallurgy that was widely distributed. His interests in that area led to his discovery of bauxite and to studies of beryllium, zirconium, and lithium silicates, along with manganese and nickel oxides. He was one of the many mentors of the past who were authors of very influential works.

Johann Gottfried Schrieber (1746-1847), Academie des Mines, Freiberg; Christian Hieronymous Lommer and Johann Friedrich Wilhelm de Charpentier, mentors

Schrieber was a mining engineer. He studied gold and silver ores and described naturally occurring iron nuggets. He attended the Academie des Mines and likely obtained his degree there in about 1772.

Christian Hieronymous Lommer (? - 1787)

Lommer wrote a number of textbooks on the history of mining and (of all things) the finding of turquoise in petrified animal teeth. He was an expert on silver ores and studied silver chloride found naturally in mines.

Johann Friedrich Wilhelm de Charpentier (1738-1805), Leipzig

Charpentier was trained as a mathematician and was a professor of mathematics. He later established and built the amalgam works in Freiberg. Charpentier wrote a book on the mineralogical geography of Saxony.

8. CONCLUSIONS

We clearly are influenced strongly by our mentors and they in turn by theirs. An examination of the lives and accomplishments of the mentors of James N. Pitts, Jr., shows the continuity of certain interests, particularly in the areas of analytical, organic, and gaseous-species chemistry. Indeed, the links to all the various schools (Edinburgh, Paris, Geneva, Freiberg, etc.) demonstrate a remarkably strong overlap in these areas. One can see that medical influences and interest in chemistry were strong driving forces in understanding the importance of oxygen, carbon dioxide, ozone, and other key atmospheric gases.

We owe much to our mentors. Their dedication and lifelong works are the basis and foundation for all that we are today. Their teaching and advice and excitement for the work have given us the values that we strive to continue to develop.

We owe a lot to our mentors, and they to theirs. Let us hope that we can all continue to develop and expand our understanding of atmospheric chemistry with the thought that we are part of a continuation of this great adventure, the exploration for knowledge.

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