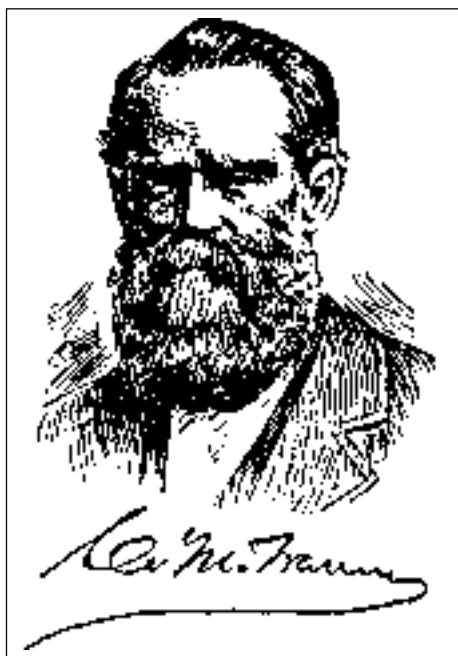


THE CONTRIBUTIONS OF CYRUS MOORS WARREN TO THE ANALYSIS OF HYDROCARBONS

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Saturday, August 27, 1859 was a day that profoundly changed the world, for on that afternoon in the small town of Titusville, Pennsylvania, the first well drilled specifically to produce liquid oil came in. Petroleum offered a simpler and cheaper way to produce kerosene than the method of that time, which involved the destructive distillation of certain types of coal (1). Kerosene, introduced in the early 1850s, had revolutionized industrial societies by offering a source of light that allowed for a longer working day. Even the humblest homes could be lighted in a way that was previously unavailable.

Hydrocarbons that had been produced by the distillation of various substances such as tars, pitch, and coal remained a mystery because of the failure to separate and analyze these mixtures(2). Cyrus Moors Warren (1824-1891) made significant contributions to the development of techniques for fractional distillation and their application to the analysis of complex hydrocarbon mixtures. He did his work in the early 1860s in his own private laboratory in Boston and reported the results at meetings of the American Academy of Arts and Sciences (3). Much of the work was later published in the academy journals (7,13,15,17,18,19,20).



Warren's life combined careers as a basic research oriented chemist and as a successful industrialist.

Warren was born on January 15, 1824 in West Dedham, Massachusetts, the fifth son and eighth of eleven children born to Jesse and Betsey (Jackson) Warren. His father was a blacksmith by trade and an inventor by avocation, who for all his ability was never very successful financially. In 1829 the family moved to Peru, Vermont, in hopes of improving their situation. This was followed by another move to Springfield, Vermont, where his father started a foundry business. The foundry was destroyed by fire in 1839, leaving the family in dire financial straits. Cyrus' formal education to this

point was spotty at best, but both he and his older brother Samuel spent as much time as possible continuing their education by self-study. The brothers pledged to each other that if they became successful, first one and then the other would be able to complete his education. In 1846 Samuel Warren perfected a process to improve the manufacture of a waterproof roofing material made by coating paper with coal tar. He opened a plant to make the "tar paper" in Cincinnati in that year, and Cyrus joined him as a partner in the business in 1847.

Coal tar is the byproduct of the process used to produce coal gas for lighting. This process had been invented by William Murdoch (1754-1839) in the late 18th century, and plants to manufacture this gas were found in cities all over Europe and the United States after 1810. When the Warrens entered the tar paper business, coal tar was thought to have little commercial value; and the brothers were able to enter into long term contracts to purchase it at very low prices.

The tar paper business proved to be an almost immediate success. Samuel was the first to leave and pursue his education (4). As the business prospered, other Warren brothers were brought in; and finally, in 1852, at the age of 28 Cyrus, by this time married with a family, began his higher education. Because of his interest from childhood in the natural sciences, he chose to pursue his studies at the Lawrence Scientific School, affiliated with Harvard University. His initial interests were both in zoology and chemistry, and his studies were supervised by the eminent Swiss naturalist Louis Agassiz (1807-1873). Although attracted to natural history, Warren decided his interest really lay in chemistry. Warren received his S.B. degree in 1855 with high distinction and was elected to Phi Beta Kappa. He had the unique honor of being the first graduate of the Lawrence Scientific School ever elected to this scholarly society.

Wishing to complete his education and being of independent means, Warren embarked on the chemical grand tour of Europe with stops in London, Paris, Heidelberg, Munich, and Berlin. He carried out various research projects in the laboratories of such titans as Emil Kopp, Justus Liebig, Robert Bunsen, and Heinrich Rose. His work in Rose's laboratory on titanium and zirconium resulted in the publication of several papers in 1857 (5). This European sojourn was to last for several years before Warren finally returned to America in 1858. There were few American chemists who had achieved as extensive training in various aspects of chemistry as Cyrus Warren had by 1858.

In 1855 the Warrens had moved their industrial operations to New York, establishing the Warren Chemical and Manufacturing Company to produce coal tar products. Contracts had been secured from the numerous gas works in the city to provide the raw material at very low cost. When William Henry Perkin's synthetic aniline dye mauve, introduced in early 1858, became an instant success, the Warrens profited handsomely by being a major source of benzene, aniline, and other coal tar intermediates used by the aniline dye industry (6).

Cyrus Warren remained in New York until 1861, when he moved to Boston with the intention of producing the highly profitable aniline dyes himself. As the center of the American textile industry, New England was a logical location for a dye plant. With the raw materials available at very low cost from the Warren coal tar distilleries in New York, this venture seemed a logical extension for the Warren Company. However, this was not to be. When it became obvious to the English manufacturers such as Reed & Holliday that an American firm was going to compete in the lucrative American market, they proceeded to unload their aniline dyes on the American market at prices with which the Warren Company could never compete. With failure of the dye venture, Warren turned his attention from business to basic research at the laboratory he had built as an addition to his Boston home. It had always been Warren's intention to devote himself to chemical research as a part of this new venture in Boston. Warren was able to outfit his laboratory with the latest and best equipment available and set to work. One of the first problems to which Warren turned his attention was the development of better methods of fractional distillation, with an eye towards its application to the analysis of hydrocarbon mixtures. As Warren wrote (7):

...simple fractional distillation...affords but very imperfect and unsatisfactory results, and not infrequently leads to gross errors and misconceptions... The want of a more efficient process for effecting such separations has long been recognized. There are numerous natural and artificial products, of the highest scientific interest, such as petroleum...of which it may at least be said that we have but very imperfect knowledge

The innovation that Warren introduced was the control of the temperature in the still head. This was achieved by a worm coil whose temperature was controlled independently and through which the distillate had to pass. Figure 1 is the drawing of the apparatus shown in Warren's paper (7):

In the belief that no process of fractioning at all analogous to mine has ever been employed in scientific research, and that I am not in any way directly indebted to any devices of my predecessors,...I may say, however, that I have found no record of any one's ever having employed the oil bath and a separate fire to regulate a heated condenser, this being the essential feature on which the superiority of my process is based; adapting it at once to both high and low temperatures, and for the most delicate work.

The worm coils used by Warren were made of copper in various sizes from 10 feet by 1/2 inch to as small as 1

foot 6 inches by 1/4 inch in length. A complete description of the procedures used to conduct fractional distillation is given in the paper. Warren concluded his paper with the following remarks (7):

...I can say that as regards bodies not decomposed by heat in distillation, I have not yet found a mixture so complex that it cannot be resolved by this process into its proximate constituents so completely, that these shall have almost absolutely constant boiling points.

The fractional distillation technique was so successful that Warren was able to separate benzene from coal tar naphtha in such a state of purity after several distillations that it froze upon cooling in the receiver into a solid mass of crystals. Warren's fractional distillation technique would be used in the research laboratory as well as in the chemical industry particularly in Europe (8):

...an expert traveling in Europe in 1870 found the process in common use there in the distilleries of tar. In some instances, the managers of these works knew that they were using Warren's invention, while others professed ignorance as to its origin, while freely admitting its excellence.

Warren had received a patent for his technique (9), but this did not seem to deter those who infringed upon it without paying any royalties.

Having developed this efficient method of fractionation, Warren began to apply it to various types of hydrocarbon mixtures. Among the first studied were the volatile hydrocarbons found in light coal tar naphtha. The first attempt to analyze these low-boiling fractions (bp 80-175°C) had been done in 1849 by Charles Mansfield, a student of Hofmann at the Royal College of Chemistry in London (10). Mansfield reported (11) that there were four major components that showed a constant incremental difference of 30° in boiling point. Mansfield believed these four components to be aromatic hydrocarbons, with the first of the series being benzene. Faraday had isolated benzene in 1825 from oil gas, and Hofmann had shown it to be present in coal tar naphtha in 1845. Mansfield proposed the other three components, in order of increasing boiling point, to be toluene (113°), cumene (140-145°), and cymene (170-175° C). The only compound that could be definitively identified in the mixture was benzene, the lowest-boiling component. The others had not been obtained in a sufficient state of purity for any kind of definitive analysis. In 1855 Church, reporting his analysis of this mixture, proposed (12) that there are five components, each having a constant difference in boiling point of 22°.

Warren hoped to produce a definitive analysis of the light coal tar naphtha by using his fractional distillation technique. In addition, he had developed what he thought to be a better and more accurate method for determining boiling points. To ensure the accuracy of his study he used a mixture of coal tars produced by six different gas works, derived from different varieties of coal, both imported and domestic. Since the gas works produced coal tar residues in quantities of upwards of 50,000 barrels per annum, Warren firmly believed that the naphtha he was to fractionate contained all the possible components (13):

...fractioning in this case was conducted in all respects as there described, and continued until the whole of the naphtha taken, boiling between 80° and 170° C had accumulated at the four points...80°, 110°, 140°, and 170°, or so nearly the whole that the intermediate quantities had become too small to admit of being further operated upon...I may here remark that each of the sample gallons employed, when subjected to my process of fractioning, was found to contain, in variable proportion, all of the constituents of the naphtha.

The compounds isolated by Warren were identified in order of increasing boiling points as benzene (80°), toluene (110°), xylene (140°) and cumene (170° C). This paper seemed to verify the preliminary work that had been done by Mansfield and cast doubt upon the analysis published by Church.

An early empirical discovery was that the hydrocarbons in a homologous series had boiling points that differed by a constant increment. Hermann Kopp (1817-1893) reported in papers published in 1842 and 1845 (14) that there was a definite 19°C increment for each member of the homologous hydrocarbon series he studied. In 1855 (15), Kopp, revisiting the question of the correlation of boiling points in homologous series of hydrocarbons, noted that there seemed to be certain exceptions for a difference of C₂H₂ in some cases. Other contemporaries of Kopp had suggested various rationales for calculating the differences in boiling points by using certain structural assumptions. Warren was concerned with the lack of reliability of boiling points reported in the literature and hence the confusion concerning the effect on physical properties in an homologous series (15):

It may be hoped, however, that the superior means which my process furnishes for separating mixtures of liquids, will lead to the accumulation of reliable facts of sufficient number and variety for a profitable review of this question in its different bearings, which, from its importance, it clearly merits.

Warren obtained his boiling points by immersing the bulb of the thermometer in the liquid rather than in the vapor, as was the standard procedure. He argued that the temperature of the boiling liquid and the vapor should be the same as long as there is a regular pattern of boiling. To ensure uniform boiling Warren used as boiling stones pieces of sodium when possible or else coke (15):

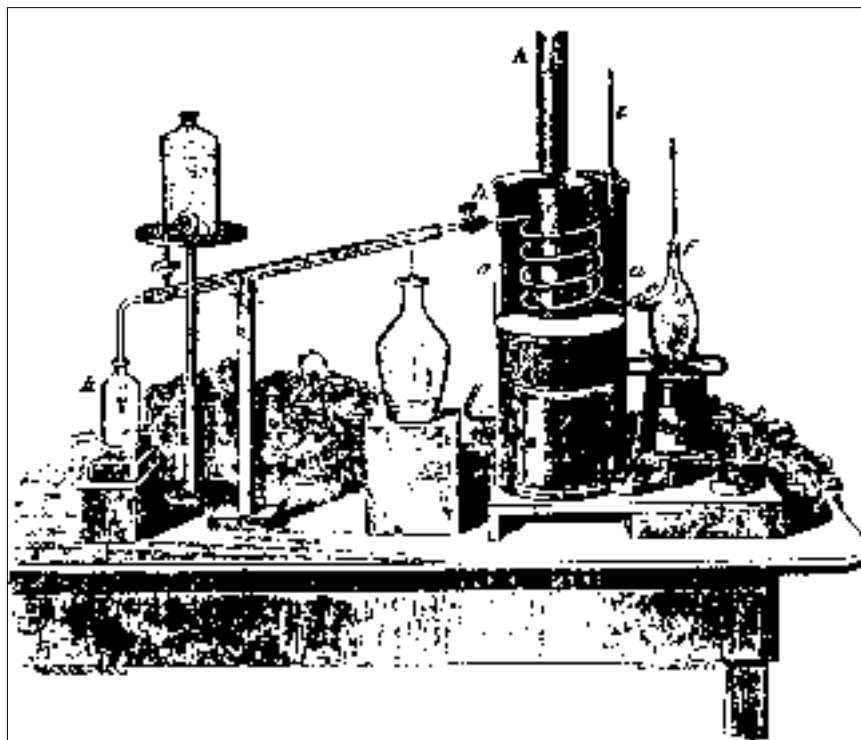
My experience has shown that, when irregular ebullition is effectually prevented, the temperature of the vapor from a boiling liquid is more liable to lead to an erroneous determination of the boiling-point, than the temperature of the liquid itself.

Warren used Pennsylvania petroleum as the source of homologous series of hydrocarbons in one of his studies. Prior to the beginning of Warren's study in 1861 there had not been any complete analysis of the volatile hydrocarbons from petroleum. The more volatile components had little commercial value at this time and would only become important in the 20th century with the development and increasing use of the internal combustion engine. Warren thought it would be of great interest to fractionate the most volatile hydrocarbons from crude petroleum as well as from the synthetic coal oil, which had been used to make kerosene prior to the availability of liquid petroleum. The question was whether the mixture of hydrocarbons found in Pennsylvania crude and that produced by distillation of coal were the same or different in view of the contrasting sources. In all of his studies Warren pointed out that each of the fractions isolated boiled within, at most, a 1.5° range and left no residue. Two identical series of hydrocarbons were obtained from both sources, which differed by 30° for each increase of CH_2 , thus showing that the petroleum (also known as rock oil) and coal oil were identical mixtures of hydrocarbons. These hydrocarbons were identified as pentane, bp (30.2°), hexane (61.2°), heptane (90.4°), octane (119.5°) and nonane (150.8°C). In a truly Baconian manner, Warren wrote of his accomplishment as follows (15):

As no one had preceded me in the investigation of these substances, my mind was as far as possible un-

biased as to the boiling points of the constituents of these mixtures. I was, however, aware of the beautiful relation between elementary constitution and boiling point, which Kopp had discovered.

Thus it would appear that no matter the source of the hydrocarbon mixture the homologous series of hydrocarbons were identical and had an incremental boiling



Warren's distillation apparatus

point of 30°. Seeking to extend his investigations further, Warren studied the boiling points of the nitro compounds of the aromatic series. These showed a difference of only 14°, much less than the 30° for the hydrocarbons. Warren had no proper explanation for these results.

The fractional distillation technique was also used to determine the composition of petroleum produced in Burma, known in the trade as Rangoon petroleum. Crude oil that seeped to the surface in Burma, just as in Pennsylvania, was collected and distilled at a refinery in Rangoon to produce kerosene for the Asian market. The British chemists Warren De La Rue and Hugo Muller had attempted to determine the composition of the crude Burmese petroleum but without success. They had reported (16) their failure in being able to separate the naphtha fraction into its components in 1857. Warren wrote (17):

The labors of De La Rue and Muller at once occurred to us as furnishing an extreme instance, and it was determined to test the new process with materials which, as these chemists had shown, could not be unraveled by the old processes of analysis.

Volatile components from the Rangoon petroleum were collected in a range from 150° to 270°. The light naphtha fraction was not included in the sample Warren had obtained from a London merchant, and therefore the volatile components started to boil at 150°. A sample of the light naphtha fraction could not be obtained, and thus only the fraction above 150° was subjected to fractional distillation. This produced seven distinct fractions boiling between 170° and 240°C. Each of the fractions was treated with sodium until no further reaction occurred and then analyzed for carbon-hydrogen content. The entire volatile fraction had approximately 86% carbon and 14% hydrogen, corresponding to an empirical formula of CH_2 . As to the composition of this mixture Warren speculated that it was a series of homologous aliphatic hydrocarbons, C_{10} - C_{14} . The presence of naphthalene in the mixture was also inferred.

Warren was not satisfied with the methods available for the analysis of carbon and hydrogen content by combustion in air. He modified the usual method of combustion, substituting pure oxygen for air for the analysis (18):

By a very simple device I entirely obviate the danger of explosion; viz. the combustion tube is closely packed with asbestos, or other inert substance, and yet so loosely as to leave free passage for gases through the interstices.

Warren provided a thorough and detailed description of the apparatus and procedures that led him to conclude that "the results obtained are extremely accurate and uniform." This method, Warren believed, was superior to the conventional methods in use (18):

...its greater convenience, economy of time, avoidance of excessive heat, neatness, etc.; it will, at least, not be found inferior to other methods; but, on the contrary, I think preferable, as affording greater security against failures and errors.

In the course of his work on petroleum, Warren isolated several sulfur and chlorine containing compounds. The present methods for the analysis of chlorine and sulfur in organic compounds were not satisfactory in Warren's opinion. Sulfur analysis involved a problem that some of the element present in the compound was converted to sulfuric acid rather than sulfate. Warren turned this problem to his advantage by employing the reaction of

sulfur compounds with lead peroxide (PbO_2) to ensure that sulfuric acid would be the only product formed. With some modification Warren was able to use the same apparatus he had developed for carbon-hydrogen content to analyze organic compounds simultaneously for carbon, hydrogen, and sulfur. The method gave excellent results for the known compounds such as carbon disulfide (19).

The analysis of chlorine in organic compounds presented the problem of the conversion of the whole of the chlorine content, but without allowing absorption of the carbonic acid and water produced from the carbon and hydrogen in the sample. Oxides of the heavy metals were known to have a strong affinity for chlorine, but they did not interfere with the carbon analysis. After trial and error, Warren found that the "brown oxide of copper" ($\text{CuO}_2 \cdot 2\text{H}_2\text{O}$) was the best reagent to use for the analysis of chlorine. He also obtained excellent results by using known compounds (20).

In 1866 Warren accepted an appointment as Professor of Organic Chemistry at the Massachusetts Institute of Technology, but he resigned the position after two years because it involved excessive demands upon his time. His ability to continue his research and his continued involvement in the chemical industry as a consultant were seriously hampered by his duties at MIT.

The chaotic business cycles that followed the Civil War finally claimed all of his time, and so the grand program for the separation and analysis of petroleum was never realized. Though independently wealthy, he felt a continuing obligation to his partners, especially after the death of his brother in 1880. The strain of overwork broke his health and eventually led to a debilitating stroke in 1888. He died on August 13, 1891 at his home in Manchester, Vermont.

In his will he generously provided funds for the American Academy of Arts and Sciences as well as Harvard University for the funding of basic chemical research. In addition, his will provided funds toward the construction in Boston of a permanent library and meeting hall for the American Academy of Arts and Sciences. Although Cyrus Warren's career in basic research spanned only a few years, he made significant inroads into an understanding of complex hydrocarbon mixtures, but his contributions do not appear to be widely known by the American chemical community.

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