THE ART OF DISTILLATION AND THE DAWN OF THE HYDROCARBON SOCIETY

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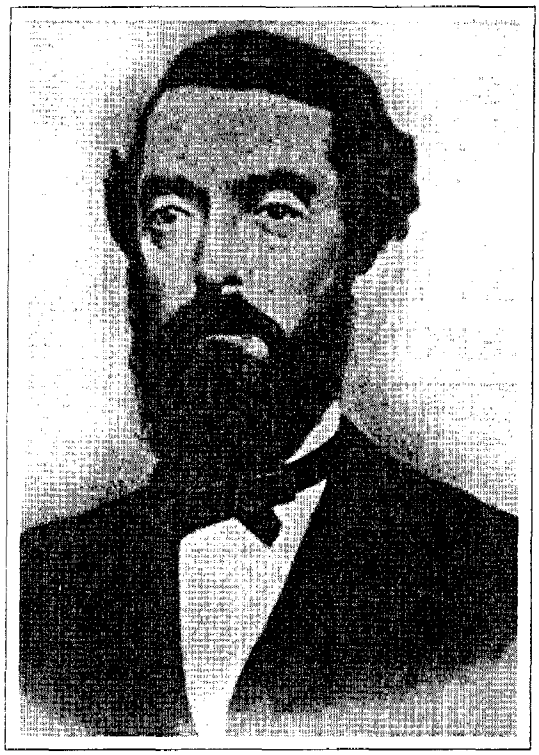
Of all the techniques employed in the laboratory none has such an ancient lineage as that of distillation. The first uses of distillation are shrouded in antiquity, but certainly by the Middle Ages a body of literature existed describing various aspects of the technique. The Encyclopedia of Denis Diderot (1713-1784), which appeared in seventeen volumes from 1751-1772, contains an extensive entry on distillation with many references to various treatises on the subject. R. J. Forbes has produced perhaps the most definitive study of the subject from antiquity through the nineteenth century in his book *A Short History of the Art of Distillation* (1).

The product that most immediately comes to mind that is associated with distillation is alcohol. However, another product, petroleum, has had far greater consequences for our society. The beginning of the hydrocarbon society (2) is usually associated with the well drilled at Titusville, Pennsylvania, by Edwin L. Drake (1819-1880) on behalf of the Seneca Oil Company. This well first produced crude oil on August 27,1859, and thus the oil industry began as we know it today. Ida Tarbell has written, however (3):

> ...The development of the American oil industry does not begin, as is commonly said, with the discovery of oil in August, 1859, near Titusville, Pennsylvania. Dating a discovery, like dating the beginning of a war or a revolution, is one of history's most misleading short cuts. Discoveries like wars and revolutions have long backgrounds.

Stock Certificate of the Seneca Oil Company

The roots of the oil industry can be traced back to the fourth century B.C. in the Middle East. In Mesopotamia, petroleum products were available from bitumen seeps, oil springs, and oil-bearing rock. Bitumen was used by the Sumerians, Assyrians, and Babylonians as caulking for their boats, irrigation systems,



Edwin L. Drake

and in making bricks. The Egyptians used bitumen in their mummification procedures. The material was obtained from the Dead Sea where huge balls periodically rise to the surface. The Egyptian trade was controlled by Arabs who gave the Arabic name "naft" to this product, from which is derived the modern term naphtha. Naft became a fearsome weapon in the arsenals of the Byzantine and Muslim armies and navies, which were contending for dominance in this region in the 7th century. It is believed that the weapon which became known as the "Greek Fire" may have been a distillate rather than crude oil. The weapon was used with great effect by the Byzantines at the Battle of Kyzikos in 680 BC in which the Muslim fleet suffered enormous casualties from burning.

The first recorded reference to distillation of crude oil appears in the writings of Muhammad al-Razi (1149-1210), a Persian physician and chemist, in his *Book of Secrets*. The process described involves the device called an al-imbig, which has been transliterated into English as alembic. The alembic became a standard piece of apparatus throughout the Middle East and Europe for simple distillation (Fig. 2). The distillate al-Razi described seems to resemble kerosene, that fraction of crude oil used for heating and lighting and the impetus for drilling the first oil well. A later reference to the distillation of crude oil is found in the writings of Hassan Al-Dimashki (1310-1370), a Syrian historian and man of letters (4):

> Many types of naft are water white by nature and so volatile that they cannot be stored in open vessels. Others are obtained from a kind of pitch in a turbid and dark condition, but by further treatment they can be made clear and white by distilling them like rose water.

There are many reports in the Arabic literature of the medicinal value of naft as a curative for various illnesses. Crude oil was continually refined in the Middle East, particularly in the region surrounding the city of Baku in present day Azerbaijan from the seventh century AD onward.

Petroleum seeps in the United States had been discovered as early as 1627 in western New York near the present town of Cuba. The best sites were found in western Pennsylvania along a stream appropriately named Oil Creek, near the town of Titusville. These oil seeps were discovered by a Moravian missionary, David Zeisberger, in 1768. The Senecas had been using crude oil for medicinal purposes, and it soon became an item of trade with the European settlers. Physicians routinely prescribed crude oil in the first part of the nineteenth century as a cure for a variety of illnesses.

There were two major problems in the use of petroleum for lighting and heating. First, there was not an efficient burner for this material; and second, a supply of refined product was not available at a cost competitive with the other fuels available. In 1780 Francois-Pierre Ami Argand (1750-1803) invented a burner that produced an intensity of light that had never been possible before (5). The Argand burner was too expensive to produce for the mass market, but the development in the early 1850s in Austria of a burner with a flat wick which was much cheaper to produce solved the first problem. The flat wick became the standard in kerosene lamps and lanterns from that time onward and is still produced today in much the same way.

In 1850 one had the choice of a variety of liquid fuels of varying lighting ability and price. The best was sperm oil, but the American whaling industry had so decimated the sperm whale population that the cost of this product became prohibitive for the general population. Rosin oil, burning fluid, and camphene then became the principal fuels. Camphene, a mixture of purified turpentine and alcohol, was very popular even though it was particularly dangerous because of the volatility of its components and required a special burner. A

much better fuel was needed; and this was produced by Abraham Gesner (1797-1864), a Canadian physician by training but also a geologist, chemist, and inventor (6). Sometime in 1845 Gesner began experiments to produce a better fuel by dry distillation from a black mineral named albertite found in New Brunswick. He obtained a liquid whose use as a fuel for lighting he demonstrated as early as 1846 in public lectures on Prince Edward Island.

A similar material could be obtained by distillation of pitch found on the island of Trinidad (Fig. 3) and also of certain types of English fuel called cannel coal. In 1853 Gesner moved to New York to superintend the construction of the first commercial plant to produce this new hydrocarbon fuel, generically named rock oil. Gesner's patent (US Patent 70525, Jan. 29,1850) covered a process to produce a volatile fraction to which he gave the name keroselain, from the Greek *keros* for wax and *elain* for oil. For public relations reasons the name was changed to kerosene so that it resembled the name camphene. Kerosene was shown to be a much better value for money than any other of its competitors. This even included coal gas, both in terms of the cost and the resulting brilliance of the illumination. Kerosene became an instant success; by 1859 between fifty and sixty plants, representing an investment of four million dollars, had been built. These were based on Gesner's process as well as a similar one that had been invented and patented by the Scotsman James Young (1811-1883) in Britain and the United States (US Patent 8833, March 21, 1852) (7). No one, however, at this time was producing kerosene in any significant quantities because of the lack of a supply of crude oil.

Circular Used by Kier to Advertise Petroleum as a Medicine

In parts of Pennsylvania wells had been drilled for some time which produced salt water as a source of salt. In many of these wells besides the salt water quantities of crude oil came to the surface. In 1849 Samuel Kier (1813-1874) conceived the idea of selling oil from the salt wells for medicinal purposes; but "Kier's Petroleum or Rock Oil," put up in half-pint bottles, was not a commercial success (Fig.4). Having an excess of crude oil in his possession, Kier turned his attention to its use as an illuminant. Crude oil itself was unsatisfactory because of its odor and the smoke it produced when burned. Kier sought the advice of James C. Booth (1810-1888), a consulting chemist in Philadelphia, who suggested he distill the crude. A small-scale refinery was built in Pittsburgh in 1850; and Kier's product, which he named "carbon oil," was a local success. That prompted this pioneer oil refiner to build a larger scale plant outside Pittsburgh. The major drawback to the use of Kier's product was a disagreeable odor, but yet 1,183 barrels (each 31 1/2 gallons) were sold at very high prices. Demand exceeded supply, but every attempt to produce more oil by drilling additional salt wells proved a failure. The value of hydrocarbon fuels for lighting and heating had been well established; the major problems were still the supply and the cost. The solution to this dilemma began in the fall of 1853.

Francis B. Brewer (1820-1881), a physician and graduate of Dartmouth College, had moved to Titusville in 1851 to join the firm of Brewer, Watson, and Company, which had been established by Brewer's father Ebenezer in 1844 to produce lumber from a large tract of land he owned on Oil Creek. After having completed his medical studies at Jefferson Medical School in Philadelphia, Brewer began the practice of medicine in Barnet, Vermont. He had used petroleum oil in his medical practice beginning in 1848. In 1850 Brewer decided to give up the practice of medicine and become an active part-

Francis B. Brewer

ner in the family business. Brewer, Watson, and Company used the crude oil collected from trenches as both a lubricant and for lighting in the saw mill. Dr. Brewer was fascinated by the prospect of the commercial value of oil and persuaded his partners to try to develop this product.

In the fall of 1853 Brewer visited his alma mater with a sample of the rock oil that had been collected from the oil springs on the Brewer property. This was shown to Dr. Dixi Crosby of the Medical School and Professor O. P. Hubbard, a chemistry professor, and left for their evaluation. Hubbard believed the material to be potentially very valuable, but the limited supply made its prospects dim. Skimming the oil could at best produce eighteen gallons per day from the Brewer lands. By sheer coincidence in the fall of 1853, a few weeks after Brewer's visit to Dartmouth, George Henry Bissell (1821-1884) (Fig. 5), a native of Hanover and an 1845 graduate of Dartmouth, happened to be visiting his birthplace. Bissell had been recently admitted to the bar in New York after a varied career which included serving as superintendent of public schools in New Orleans before becoming a lawyer. Bissell and his law partner Jonathan G. Eveleth were active promoters for the sale of the shares in newly formed companies. Bissel by chance happened to see the bottle of rock oil in Crosby's office and asked about it. Crosby related to Bissell that he had done a few simple experiments and was convinced this material could be a superior illuminant. Bissell recognized the connection between Brewer's rock oil and Gesner's coal oil now coming into general use. Ever on the lookout for a profitable venture, Bissell commissioned Dixi Crosby's son Albert to go to Titusville in the summer of 1854 to obtain first-hand information and to evaluate the oil springs. The younger Crosby was impressed by what he saw, and Bissell and Eveleth began a plan to establish a joint stock company to purchase the oil-bearing properties in Titusville and to bring the product to market. In September, 1854 the Pennsylvania Rock Oil Company was founded with offices at 346 Broadway in the D. Appleton and Company building in New York. Brewer, acting on behalf of his partners, came to New York in the fall of 1854 to sign the papers at the offices of Bissell and Eveleth; and the company was officially incorporated in New York on December 30, 1854. In conversations with Brewer it became evident that Crosby had exaggerated greatly the quantity of oil present. Bissell and Eveleth became somewhat skeptical and hesitant about proceeding. However, Brewer proposed an offer to Bissel and Eveleth they could not refuse. Either Bissell or Eveleth could personally inspect the property, and if they were not satisfied, the agreement would be canceled; and Brewer, Watson and Company would pay all the expenses so far incurred. Before either of them could go to Titusville, a letter arrived from New Haven. Anson Sheldon, a retired minister who had heard about the new venture, suggested that Bissell and Eveleth should visit New Haven, as there were parties who might be interested in

George M. Bissell

investing in their company. One of these was James M. Townsend, president of the City Savings Bank. Townsend and his partners, however, specified two conditions before any shares would be bought: a visit to the property by a representative of their group, and a scientific analysis to determine the commercial value of petroleum. Thus the rationale for one of the most important landmark analyses by distillation came about. Two men were chosen for this enterprise, Luther Atwood of Boston and Benjamin Silliman, Jr., of Yale College. On November 4, 1854 Eveleth and Bissell wrote to Frank Brewer the following (8):

> Dr. Atwood of Boston is analyzing the oil, and it is in the hands of Prof. Silliman of Yale College. We shall have it analyzed by several of the best chemists in the country, and shall make use of their analysis and get some of your best western men to examine and to testify as to facts there.

Luther Atwood (1826-1868) was a partner with his brother William and Samuel Philbrick in 1854 in the US Manufacturing Company in Waltham, Massachusetts in 1854 (9). This company had been organized to exploit a patent of Luther Atwood to make a lubricant for machinery by the distillation of the coal tar residues produced by gas works (US Patent 9,630 March 29, 1853). Atwood in 1856 established the coal oil business in Boston and succeeded Abraham Gesner as chief chemist of the Kerosene Company in New York. Atwood seems to have given the Brewer oil sample a fairly cursory examination and pronounced it to have potential as an illuminant.

Benjamin Silliman, Jr. (1816-1885) was the son of Benjamin Silliman (1779-1864), professor of chemistry at Yale College(10). Silliman, Jr. had studied with his father at Yale, where he received his undergraduate degree in 1837 and an MA in 1840. After a short period spent in Boston with the chemist Charles T. Jackson, Silliman returned to New Haven and acted as a laboratory instructor for his father's advanced students. In 1846 the Yale Corporation created a professorship in applied chemistry to which Silliman Jr. was appointed. Because the position had no salary attached to it, Silliman was forced to leave Yale and went to the University of Louisville. In 1854, with the retirement of his father, he assumed the latter's position; and it was in this year he was approached to analyze the oil sample provided by Brewer. It seemed logical to the New Haven investors that a chemist of Silliman's stature should analyze the oil. His was a very thorough analysis; and it was his report, dated April 16, 1855, that was the key in getting Sheldon's group to back the oil venture. Silliman wrote to Eveleth and Bissell on December 21, 1854 the following, which was relayed to Frank Brewer (11):

> I am very much interested in this research and think I can promise you that the results will meet your expectations of the value of this material for many most useful purposes. The oils which I have so far obtained are perfectly fluid...As yet the quantities I have obtained have all been distilled in glass from an original weighted quantity, and the weights of the several products have been carefully noted. That operation has consumed from 2 to 3 weeks and is still in process.

Silliman reported further progress which was passed on by Eveleth and Bissell to Brewer (11):

> Since the above letter was written from which the extract has been taken, the analysis has been extended and six different oils produced, making in all that has thus far been obtained 50 per cent...the Professor is of the opinion that the yield will be at least 75 or 80 per cent of pure oil.

On February 17, 1855 Eveleth reported to Brewer (11):

> Silliman is progressing with the analysis, we have been obliged to get all new apparatus for him, they had an explosion, but we hope to have the report soon.

This was followed on April 10, 1855 by a letter from Anson Sheldon to Brewer with further news of Silliman's work (11):

> Professor Silliman has not yet completed his photometrical examination of the Rock Oil in comparison with other burning fluids, but will probably wind up his analysis in all this week....The value of the oil depends mostly on its properties as a burning fluid. In this respect the analysis and its results, has [sic] been highly satisfactory.

On April 21, 1855 Eveleth wrote to Brewer (11):

> Have rec'd. Prof. Silliman's Report. Bill is $526.08. We had paid out for other things for him, over $100. Could not have the report till paid for....It is now in the hands of the Printer. Will be ready for middle of next week....It is a great report.

Anson Sheldon wrote to Brewer about the report on April 23, 1855 (11):

> Silliman's Report is now in my hands, and is favorable to our enterprise, but as Bissell and Eveleth had failed to meet the Professor's wishes in placing $100 to his credit in the Bank of New York...he placed the Report in the hands of a friend in New York with instructions not to deliver it up until satisfactory arrangements were made for the payment of his bill which amounts, (including the expense of his appa-

> ratus employed in the analysis), to the round sum of $526.08 about $75 had been previously paid....making the whole expense exceed $600.This sum may at first appear exorbitant, but when we take into account the time consumed, the nature of the experiments, and the value of the Report, I think those concerned will be satisfied....Several gentlemen here of known ability have assured me that they should take some stock, if Silliman's Report should be favorable to the oil. That point is settled, the Report is more favorable, even, than I had dared to hope.

Anson Sheldon reported to Frank Brewer on May 11, 1855 that "Prof. Silliman proposes to take some stock (11)." The report, printed in New Haven, amounted to twenty 5" x 8" pages.

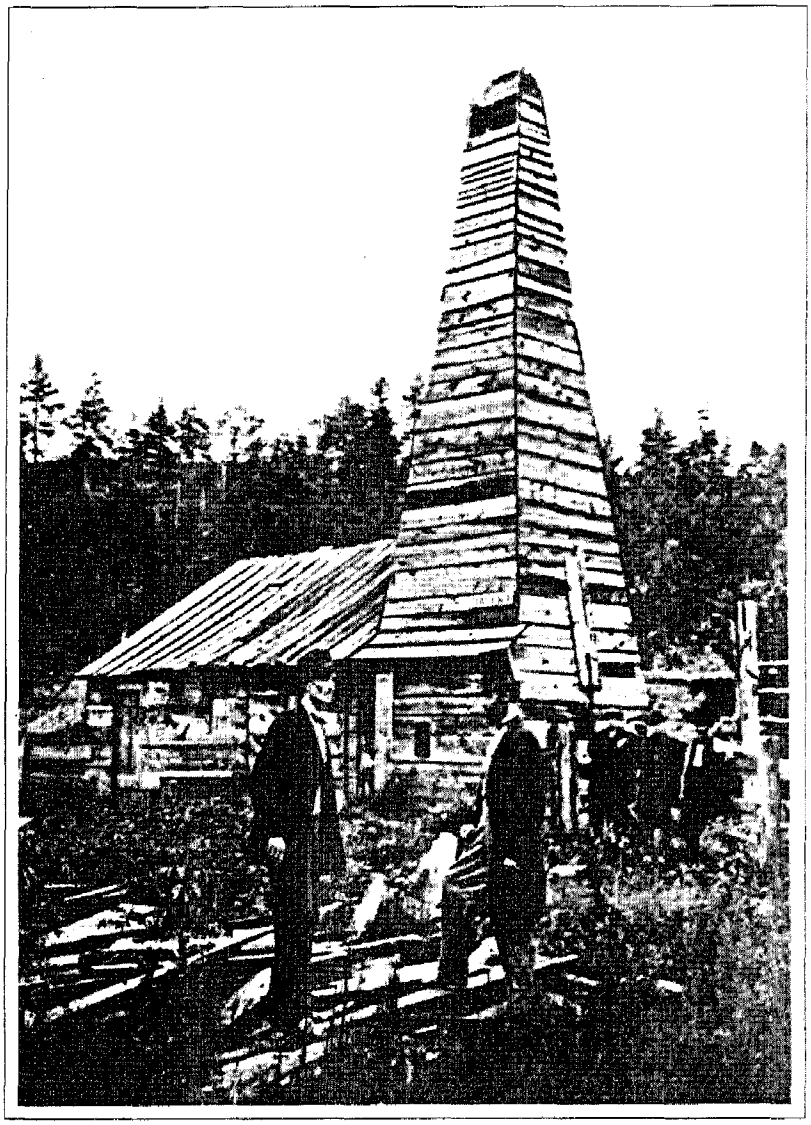
How did Silliman do this most important analysis? His own words provide the answer (12):

> To determine what products might be obtained in the oil, a portion was submitted to fractional distillation.*..*(Fractional distillation is a process intended to separate various products in a mixture, and having unlike boiling points, by keeping the mixture contained in an alembic at regulated successive stages of temperature as long as there is any distillate at a given point, and then raising the heat to another degree, etc.).

From a sample of 304 grams of crude, Silliman was able to distill 160 grams into several different fractions (12):

> We infer from them (boiling points) that the Rock Oil is a mixture of numerous compounds, all having the same chemical constitution, but differing in density and boiling points, and capable of separation from each other, by well-regulated heat.

Silliman performed various chemical tests such as elemental analysis, tests for acidity and corrosive action on copper, inertness to hydrochloric, chromic, and acetic acid, as well as the action of metal oxides. Lack of reaction with calcium chloride, potash, sodium carbonate, and calcium oxide was also observed. Reaction with bleaching powder produced a product resembling in character that of chloroform. The oil was slightly soluble in alcohol but easily soluble in ether. Silliman did a second distillation of the crude oil, this time on a much larger scale and with a copper still. The temperature was raised to 280° C initially and then to 300° C. In this narrow range over 43% of the crude oil distilled. The temperature was raised again, this time to above 360° C, and another 31% of the crude distilled. This fraction, after treatment by boiling with water, was used as the material for the illumination tests. Thus close to 75% of the crude oil was separable into distillates by using external temperatures ranging from 280-360° C. Further distillation at even higher temperature in the end led to a recovery close to 90%. Silliman concluded (12):



The Drake Well in 1866.
Peter Wilson and E. L. Drake are shown standing in the foreground.

> It is safe to add that, by the original distillation about 50 per cent of the crude oil is obtained in a state fit for use as an illuminant without further preparation than simple clarification by boiling a short time with fair water.

The report concluded with a discussion of the naphtha as an illuminant and photometric studies. Silliman stated that the fraction from the high-temperature distillation, that which boiled below 360° C, burned without smoking and gave a light which was (12):

> .....pure and white without odor. Its rate of consumption was one-half of those of most oils such as camphene which was in common use. I have submitted the lamp burning Petroleum t the inspection of the most experienced lampists who were accessible to me, and their testimony was, that a lamp burning this fluid gave as much light as any which they had seen, that the oil was spent more economically, and the uniformity of light was greater than in camphene.

To test the intensity of the light Silliman constructed a photometer. The standard used was Judd's Patent Sixes Sperm Candles which were assigned a value of 1. Compared to coal gas light, sperm oil, and camphene, the Rock Oil produced the highest value for the light intensity and possibly the best value for cost. At this time it was difficult to fix a value for the Rock Oil because it was not yet in commercial production. Silliman noted that preliminary results indicated the oil was also a good lubricant (12):

> In conclusion, gentlemen, it appears to me that there is much ground for encouragement in the belief that your Company have in their possession a raw material from which, by simple and not expensive process, they may manufacture very valuable products. It is worthy of note that my experiments prove that nearly the whole of the raw product may be manufactured without waste, and this solely by a well directed process which is in practice, one of the most simple of all chemical processes.

The report created considerable interest in New York and New Haven, and two-thirds of the shares were sold reasonably quickly. For legal reasons the Pennsylvania Rock Oil Company of New York was reincorporated in Connecticut on June 25, 1855, with offices in New Haven and Benjamin Silliman (13)) as president.

All did not go smoothly with the attempts to obtain oil in commercial quantities. The method of surface collection was abandoned in favor of the novel approach of drilling a well. Edward Drake (14) was hired in December, 1857 by the New Haven group to act as superintendent at the Oil Creek site and to begin the drilling. Various delays postponed drilling until May, 1859; and there was little confidence that drilling for oil in solid rock would ever amount to anything. The shareholders became increasingly disenchanted, and the money raised by the stock offering was running out. Frank Brewer traded his shares for cigars, which he gave out freely to young men in Titusville. What a mistake he had made became very evident on the weekend of August 27, 1859, when the first oil came in. Although Drake is usually given most of the credit for the dawn of the hydrocarbon society, would it have started in 1859 if not for Benjamin Silliman, Jr. and his application of the art of distillation?

ACKNOWLEDGMENT

I would like to thank the Drake Well Museum and the Pennsylvania Historical and Museum Commission for assistance in obtaining copies of the Brewer papers. A special note of appreciation goes to my colleague Mario DiNunzio of the History Department of Providence College for his help in preparing this paper.

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4. Ref. 1, p 53.
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14. Edward L Drake was by trade a railroad conductor on the New York & New Haven Railroad. Forced by ill health to retire, he retained a pass for free travel. For this reason he was hired by Eveleth and Bissell in 1857 to go to Titusville to obtain some legal papers. He was introduced as "Colonel" to impress the locals and forever has been known as such. He studied the salt well drilling operations near Syracuse and Pittsburgh on his trip and became convinced that this was the best way to extract the petroleum. His persistence in drilling led to the birth of the oil industry in Pennsylvania. Although not trained as an engineer, Drake was the inventor of the idea of using pipe to prevent the filling of the hole driven in the bed rock by sand and clay.,

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The Dexter Prize Committee of HIST has selected **Dr. Mary Jo Nye**, the Thomas Hart and Mary Jones Horning Professor of the Humanities and Professor of History at Oregon State University, as recipient of the **1999 Dexter Award for Outstanding Achievement in the History of Chemistry**. Professor Nye is the author of four books and more than three dozen articles on the history of chemistry and its interactions with physics. For 25 years she participated actively in the formation of leading undergraduate and graduate programs in history of science at the University of Oklahoma, and she served for three years as President of the History of Science Society. The award will be presented at a luncheon at the conclusion of the Dexter Award Symposium at the 219th National American Chemical Society meeting in the spring, 2000, in San Francisco.