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Rachel Lloyd (1839-1900), early Nebraska chemist,
see page 9

"Instructions for Authors:" see Issue 15/16

THE 1993 DEXTER ADDRESS

Thomas Burr Osborne and Chemistry

Joseph S. Fruton, Yale University

I count it an honor to appear before a meeting of the Division of the History of Chemistry. My talk will deal with the place of Thomas Burr Osborne in the historical development of protein chemistry (1). To begin with, I will describe briefly the state of that field in the late 1880s and the circumstances that brought Osborne into it. I will then try to summarize his work in relation to that of his principal contemporaries. Finally, I will speak about Osborne's qualities as a leader of his research group.

Osborne was a Connecticut Yankee who spent his entire life in New Haven. He was born there in 1859, went to Yale for his undergraduate and graduate studies, and studied chemistry there with William Gilbert Mixer. He was the only son of a prominent New Haven banker, who wanted young Osborne to join him in the Second National Bank, but at Yale he had become interested in analytical chemistry. A year after he had received his Ph.D., Osborne joined the staff of the Connecticut Agricultural Experiment Station, located in New Haven, where he headed the Biochemical Laboratory until 1928. He died in New Haven in the following year (2).

When Osborne came to the Station in 1886, its director was Samuel William Johnson [1830-1909], whose daughter Osborne married in the same year (3, 4). His first publications dealt with such matters as soil analysis, but in 1888, at the suggestion of his father-in-law, he turned to the chemistry of plant proteins, and published his first paper on the subject in 1891. The stimulus provided by Johnson was a consequence of the fact that he was an assiduous reader of the European literature on agricultural chemistry, and had come to admire the contributions of Heinrich Ritthausen [1826-1912] (5). During the 1850s, Johnson had worked in Leipzig and had met Ritthausen at that time.



T. B. Osborne

Over a thirty-year period, beginning in 1862, Ritthausen published an extensive series of papers on the preparation and characterization of proteins from plant seeds. When he began this work, the only amino acids thought to be generally present in proteins were glycine, leucine, and tyrosine. Ritthausen added glutamic acid and aspartic acid to the list and showed that hydrolysates of proteins which Liebig had considered to

be identical substances differed greatly in their content of these amino acids. Along with others of his time, Ritthausen crystallized the seed globulins from several plants. The procedures were very simple: a sodium chloride solution was allowed to cool slowly, or dialyzed against water, whereupon well-developed crystals appeared. Some physiological chemists considered such crystalline proteins to be important. For example, in the 1887 (first) edition of his textbook, Gustav von Bunge wrote (6): "The analysis and investigation of the pure protein crystals and the various products of their cleavage should provide the groundwork for all of physiological chemistry." Apparently Johnson shared this view, but it should also be noted that his decision to encourage Osborne to engage in basic research on the chemistry of plant proteins reveals vision and courage in the face of the down-to-earth objectives of the Experiment Station, namely to provide reliable chemical analyses of commercial fertilizers.

At Johnson's suggestion, therefore, Osborne undertook to repeat and extend Ritthausen's studies, and between 1888 and 1901 Osborne's chief aim was the isolation and purification of the proteins of plant seeds. Beginning with oat seeds, from which he obtained crystalline avenin, he proceeded to study the proteins of over 30 different seeds; indeed, bottles containing samples of his preparations are still tucked away in the vault of the Johnson Laboratory at the Experiment Station. During this early phase of Osborne's work, his aim was to prepare what he considered to be pure proteins, and his principal criterion for purity was a reproducible elementary analysis for carbon, hydrogen, nitrogen, and sulfur. Accordingly, he set himself the task of checking the discordant reports in the earlier literature on the elementary composition of the seed proteins. As he expressed it in 1892 (7):

The fact that these proteid substances can be artificially crystallized is not only interesting in itself, but is important as presumably furnishing a means for making preparations of undoubted purity which will afford a sure basis for further study of their properties. The contradictory statements made by various investigators, not only in regard to the properties and composition of these bodies but also in respect to the value of the methods of solution and separation which have been employed hitherto, render an exact knowledge of all the facts relating to these substances a matter of the highest scientific and practical importance.

Osborne's confidence in crystallization as a means of preparing pure proteins was not shared by some of his contemporaries. Thus, Louis Pasteur, who began his sci-

entific work as a crystallographer, had stated in 1883 (8): "You know that the most complex molecules of plant chemistry are the albuminoid substances. You also know that these immediate principles have never been obtained in a crystalline state. May one add that apparently they cannot crystallize." Pasteur, by that time the great healer, apparently did not know of the work of Ritthausen and others on crystalline proteins from plant seeds, or chose to ignore it. After egg albumin had been crystallized by Franz Hofmeister [1850-1922] in 1889, the noted crystallographer Arthur Wichmann examined them, and wrote ten years later (9) that "There is scarcely a crystalline substance which, like a sponge, soaks up dissolved substances as does albumin." And in 1913, the great organic chemist Emil Fischer [1852-1919], of whom I shall have more to say shortly, wrote about crystalline proteins as follows (10): "... the existence of crystals does not in itself guarantee chemical individuality, since isomorphous mixtures may be involved, as is frequently the case in mineralogy for the silicates." Indeed, for most of the German organic chemists of Osborne's time, the proteins were included among the natural products which they chose to denote as *Schmiere*.

Also, at the turn of the century, leading biochemists had turned to the study of proteins as colloids, which Thomas Graham had defined as noncrystalline and non-diffusible substances, and they preferred to apply the new physical chemistry to the study of adsorption phenomena exhibited by proteins. It would seem, therefore, that Osborne chose to disregard prevalent opinion and, as a well-trained analytical chemist, to begin his work on proteins by single-mindedly pursuing his goal of purifying them by crystallization and of drawing conclusions about their identity or individuality from their elementary composition and their solubility properties.

In 1892, Osborne reported his findings on the crystalline globulins from six different kinds of seeds - Brazil-nut, oat-kernel, hemp-seed, castor-bean, squash-seed, and flax-seed. He concluded that the first two globulins are distinct proteins, and different from the other four, which appeared to him to be the same protein. Two years later, Osborne found the seed globulins from wheat, maize, and cotton to have the same elementary composition as the four seemingly identical proteins; and he considered the seven kinds of seeds to contain the same globulin, which he named "edestin." By 1903, however, he was obliged to revise this opinion, but in the meantime he continued to amass data on many other seed proteins, including the alcohol-soluble prolamines such as zein and gliadin. In those intervening years, important advances had been made in protein chemistry,

and Osborne changed the direction of his research program accordingly.

The most important of these advances was the addition of many amino acids to the list of regular protein constituents. Those added between 1880 and 1903 included the basic amino acids lysine, arginine, and histidine, as well as phenylalanine, cystine, alanine, valine, isoleucine, proline, hydroxyproline, and tryptophan (11). In particular, the finding that the basic amino acids form sparingly-soluble salts with phosphotungstic acid led Walter Hausmann, a student in Hofmeister's laboratory, to develop in 1900 a method for the determination of the partition of the nitrogen in acid hydrolysates of proteins among the so-called ammonia-nitrogen, basic-nitrogen, and nonbasic nitrogen fractions. Osborne seized upon the Hausmann method, and in 1903 he reported that (12):

We have found by its use that some of our preparations from different seeds which were so nearly alike in composition and reaction that no difference could be detected between them sufficient to warrant the conclusion that they were not the same chemical individual, yield such different proportions of nitrogen in the several forms of binding that there can be no longer any doubt that they are distinctly different substances. On the other hand, many preparations of different origin, which we have heretofore considered to be identical, have yielded the same proportion of the different forms of nitrogen and consequently our former opinion respecting the identity of these protein preparations is very greatly strengthened.

The next step in the development of Osborne's research program was his acceptance, in 1906, of the necessity of determining the amino acid composition of protein hydrolysates by means of the methods developed by Albrecht Kossel and Emil Fischer. In 1900, Kossel [1853-1927] had introduced a procedure for the quantitative estimation of the three basic amino acids, and in the following year Fischer described his so-called ester method for the separation of other amino acids present in acid hydrolysates of proteins. Because Fischer's name figures so prominently in the history of protein chemistry, I digress briefly from the account of Osborne's work.

By 1906, Fischer was widely regarded as the leading organic chemist of his time. He had received the Nobel Prize for Chemistry in 1902 for his outstanding achievements in the synthesis of sugars and purines; and, soon after entering the protein field in 1899, he had initiated an ambitious program to effect the synthesis of proteins. Apart from his lock-and-key analogy to describe the specificity of enzyme action, Fischer is per-

haps best known for his synthesis of polypeptides. In December 1905, he wrote to his teacher Adolf von Baeyer as follows (13):

On January 6th I will present a lecture at the Chemical Society summarizing my work on amino acids, polypeptides and proteins, and then early next year I will publish the collected papers in the form of a book. The material has grown splendidly and there is much detail in it. Recently I have also prepared the first crystalline hexapeptide and hope to obtain a matching octapeptide before Christmas. Then we should be close to the albumoses....My entire yearning is directed toward the first synthetic enzyme. If its preparation falls into my lap with the synthesis of a natural protein material, I will consider my mission fulfilled.

Although the accounts of Fischer's lecture in newspapers and in popular science journals encouraged the belief that the preparation of synthetic proteins was around the corner, by 1910 the enormous effort of his assistants had produced much less than he had hoped for, and his disappointment may be inferred from the fact that after that date there were no further experimental papers on peptide synthesis from his laboratory (14).

In Fischer's ester method, the mixture of amino acids in an acid hydrolysate of a protein was esterified with ethanol, alkali was added to generate the free esters, which were then extracted with ether. The ether extract was concentrated and subjected to fractional distillation under reduced pressure, and the esters in the individual fractions were converted to free amino acids, which were crystallized, weighed, and characterized. It surely must have been clear from the start that this method was not likely to give reliable quantitative data for the amino acid composition of proteins. Nevertheless, many protein preparations were analyzed in this way in Fischer's laboratory; and, apart from demonstrating the general occurrence of amino acids such as alanine or phenylalanine, three new protein constituents were found: proline, hydroxyproline, and diaminotrioxododecanoic acid. Much of this work was done by Emil Abderhalden [1877-1950], who had come to Fischer's laboratory in 1902, after receiving his Dr.med. degree at Basle. Two years later, in a letter to a Berlin colleague, Fischer wrote (15):

Because of his unusual capacity for work, in a short time Abderhalden has become so adept in the difficult methods of organic chemistry that I was able to accept him last fall as a collaborator in my private laboratory. I note that I had not dared to do this be-

fore with a medical man. He is a good observer, and is an enemy of all superfluous hypotheses. Regrettably, biological chemistry is that part of our science in which imprecise and incomplete experiments are often heavily padded with the dazzling ornamentation of so-called ingenious reflections to produce pretentious treatises. For this reason, people like Abderhalden are needed.

These opinions led Fischer to turn over to Abderhalden the succession of post-M.D. students who flocked to Fischer's laboratory at that time, and most of them worked under Abderhalden's direction on the application of the ester method to the analysis of a great variety of protein preparations, including plant proteins such as edestin and gliadin. However, Fischer's initial assessment of Abderhalden's chemical talent proved to be incorrect, for much of his work both as a member of Fischer's group and in later years as an independent investigator proved to be irreproducible. In particular, Fischer was obliged to withdraw diaminotrioxododecanoic acid from his list of protein amino acids.

I now return to Osborne's work on proteins. By 1906, he had begun to receive financial support from the Carnegie Institution of Washington. This grant enabled him to hire more assistants and to purchase equipment for the preparation of the sizable amounts of proteins then needed for the analysis of their amino acid composition. Osborne applied the methods of Kossel and Fischer to the analysis of several seed proteins and also used other procedures to estimate the content of such components as tryptophan or sugars, which are destroyed upon acid hydrolysis. By 1908, these newer studies led Osborne to revise further his earlier views about the chemical individuality of the proteins he had purified (16):

We are now well past the time when agreement in solubility, ultimate composition and color reactions are to be accepted as evidence of the identity of two preparations of protein... On the basis that agreement in ultimate composition affords no evidence of identity of two similar proteins, but that distinct and constant differences in composition are conclusive evidence that they are not alike, I ... have since subjected them to careful comparison in respect to their physical properties and the proportion of their decomposition products, so that those which are alike in their more apparent characters have been still further distinguished from one another.

Even though the use of the Fischer ester method had revealed new differences among the seed proteins, Osborne, as a well-trained analytical chemist, did not accept the limitations of the method, but proceeded to

subject it to a more rigorous examination than that conducted in Fischer's laboratory, and improved it greatly (17). In this connection I cannot forbear from citing a passage from a letter from Fischer to Abderhalden in 1912 (18):

I consider it likely that because of their greater wealth the Americans will beat us in several fields, and I have expressed this opinion at every opportunity. However, we can withstand this competition for a time because of our greater inventiveness and more distinguished individual achievements. That the gentlemen in America are also rather presumptuous is nothing new to me, but one can defend oneself against this at a suitable opportunity. As soon as I find the time, I will discuss this question in a retrospect on chemical research on proteins during the past ten years.

Although his name is not mentioned, Osborne is the most likely candidate for Fischer's displeasure, as he was the leading protein chemist in the United States at that time.

Osborne's contributions to the analytical chemistry of proteins may perhaps best be illustrated by means of Table 1, taken from his review article in 1910 (19). The first column of numbers contains the data (grams per 100 g of protein) reported for zein by Ritthausen in 1872, the second column the data in 1903 of Langstein who used the Fischer ester method, and the third column the values given by Kossel and Kutscher in 1900 for tyrosine and the three basic amino acids. The fourth and fifth columns give the values reported from Osborne's laboratory in 1906 and 1910, respectively.

In addition to the contributions of Kossel, Hausmann, Fischer, and Abderhalden to the analytical chemistry of proteins, there was another series of developments which influenced the course of Osborne's research. The first was the discovery in 1901 by Otto Cohnheim [1873-1953] of the enzymatic conversion of peptones to amino acids by the intestinal mucosa. Before that time, many physiologists believed that, in the metabolic utilization of food proteins, the peptones formed by the action of pepsin and trypsin are taken up at the intestinal wall and converted there into blood proteins. The next blow to this doctrine came from Otto Loewi [1873-1961], who showed in 1902 that completely digested (peptone-free) pancreatic protein can replace intact protein in the animal diet. Osborne appears to have recognized at once the importance of these findings, for in 1903 he wrote (20): "The animal... can synthesize protein from a mixture of the crystallizable products produced by the decomposition of proteins." However, he did not pursue the consequences of this idea until 1909, when he and Lafayette Benedict Mendel

Table 1. Products of the Hydrolysis of Zein

Component	Ritthausen (1872)	Langstein (1903)	Kossel & Kutscher (1900)	Osborne & Clapp (1906)	Osborne & Jones (1910)
Glycine		0.00		0.00	0.00
Alanine		0.50		2.23	8.98
Valine				0.29	
Leucine	17.25	11.25		18.60	17.95
Proline		1.49		6.53	9.01
Phenylalanine	6.96		4.87	6.23	
Aspartic acid	1.43	1.04		1.41	1.73
Glutamic acid	10.00	11.78		18.28	26.17
Serine				0.57	1.00
Tyrosine	3.20		10.06	3.55	3.55
Arginine			1.82	1.16	1.35
Histidine			0.81	0.43	0.82
Lysine			0.00	0.00	0.00
Tryptophan				0.00	0.00
Ammonia			2.56	3.61	3.64
				61.53	80.43

[1872-1935] initiated their famous joint studies on animal nutrition. In the meantime, Frederick Gowland Hopkins [1861-1947], the discoverer of tryptophan, had noticed Osborne's report that the seed protein zein lacked this amino acid. In 1906, Hopkins and Edith Gertrude Willcock [1879-1953] published a paper (21) showing that young mice fed zein as a sole source of protein did more poorly than comparable animals to whose diet tryptophan had been added.

A few words about Mendel and his relationship to Osborne. Mendel received his Ph.D. at Yale in 1893 for work with Russell Henry Chittenden [1856-1943], and ten years later he



L. B. Mendel

succeeded Chittenden as head of the Yale laboratory of physiological chemistry (22, 23). An outstanding teacher, Mendel made that laboratory the principal seedbed for the next generation of American biochemists. His collaboration with Osborne in the field of animal nutrition lasted nearly twenty years and produced more than one hundred joint papers, with special emphasis on the so-called indispensable amino acids and on vitamins. In this work, Osborne's highly purified protein preparations played a decisive role. Among Mendel's students at that time was William Cumming Rose [1887-1985], who later discovered threonine during the course

of his sustained nutritional studies along the lines initiated by Osborne and Mendel (24).

Osborne collaborated to a lesser degree with other American scientists, for example Francis Gano Benedict [1870-1957] and Donald Dexter Van Slyke [1883-1971], but the most fruitful of these additional joint efforts was the one with noted pathologist Harry Gideon Wells [1875-1943]. Wells had worked in Fischer's laboratory with Abderhalden, and his interest in protein chemistry led him to examine the specificity of the anaphylactic response of sensitized guinea pigs to the injection of purified seed proteins supplied by Osborne. These experiments, reported in 1911, revealed further cases of the individuality of proteins previously thought to be identical (25).

To summarize briefly, the most important features of Osborne's research until about 1915 were successively the purification of seed proteins, the amino acid analysis of these proteins, and their use for studies of animal nutrition and immunological specificity. Afterward, Osborne and Mendel were led increasingly into such areas as the vitamin content of various foods and some medical aspects of nutrition.

I turn now to Osborne's research group. At any given time, it was quite small and composed almost entirely of Yale graduates (see Table 2). It seems that when one of his assistants was about to leave, Osborne would ask a professor in the Yale Chemistry Department (usually the organic chemist Treat B. Johnson) to recommend someone. Only one of these men - Hubert

Vickery - may be said to have achieved scientific distinction. A Canadian who had come to Yale as an 1851 Exhibition Scholar, Vickery had begun graduate work with Johnson, who recommended him to Osborne. In 1928, "Vic" (as he was known to his friends) succeeded Osborne as head of the Biochemical Laboratory at the Experiment Station, and in the years that followed he instituted a fruitful program of research on the metabolism of leaves (26, 27). Except for Breese Jones, who continued to work productively on proteins after he left Osborne, none of the others listed in Table 2 appear to have made a significant mark in the scientific literature. I should note, however, that in 1913 Frederick Heyl became the first research director at Upjohn and during the 1930s he initiated that company's pioneering program on steroid hormones (28).

Osborne attracted few post-doctoral guests, but among them was Edwin Cohn later [1892-1953], who was in New Haven in 1917. At Harvard, Cohn led a research group which made many important contributions to the study of the physical chemistry of proteins (29). Only one post-doctoral associate came to the Osborne laboratory from abroad. He was Albert Charles Chibnall [1894-1988], who had received his Ph.D. in 1921 at Imperial College London for work on leaf proteins. When Chibnall arrived in New Haven, Osborne was still in Vermont for his summer vacation - the partridge season had not yet ended - so Chibnall made contact with Mendel, who impressed him greatly. Vickery later recalled that (30):

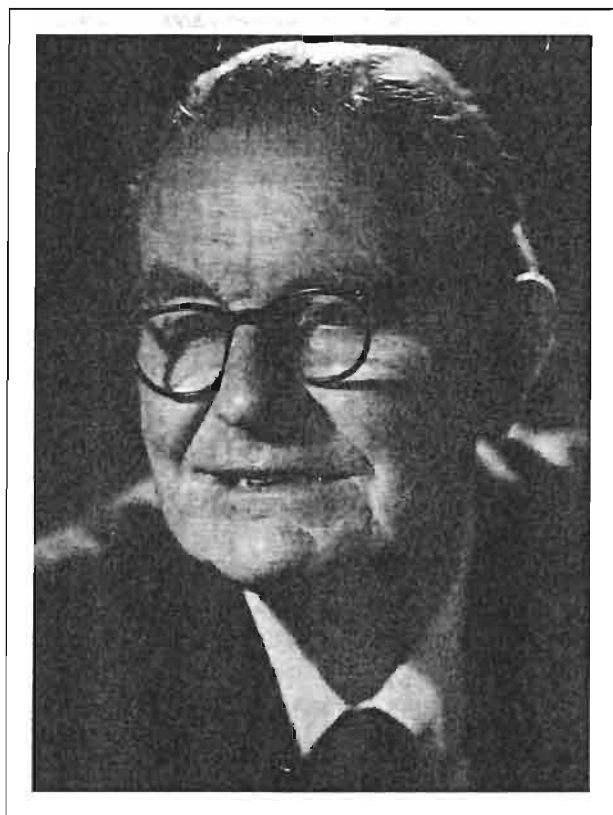
Table 2. Osborne's Research Assistants

1891-92	Voorhees, Clark Greenwood [1871-1933]	Yale Ph.B. 1891
1894-1900	Campbell, George Flavius [1870-1902]	Yale Ph.B. 1892
1901-07	Harris, Isaac Faust [1879-1953]	Yale Ph.D. 1915
1906	Gilbert, Ralph Davis [1878-1919]	Yale Ph.D. 1904
1906-08	Clapp, Samuel Hopkins [1876-1952]	Yale B.A.; Ph.D. 1908
1906-09	Brautlecht, Charles Andrew [1881-1964]	Yale Ph.B.; Ph.D. 1912
1908	Heyl, Frederick William [1885-1968]	Yale Ph.B.; Ph.D. 1908
1908-28	Leavenworth, Charles Stanley [1879-1948]	Yale Ph.B. 1902
1908-10	Jones, David Brees [1879-1954]	Yale Ph.D. 1910
1909-10	Liddle, Leonard Merritt [1885-1920]	Yale Ph.D. 1909
1910-11	Guest, Herbert Hartley [1884-1956]	Yale Ph.B.; Ph.D. 1912
1916-23	Wakeman, Alfred John [1865-1956]	Yale Ph.B. 1887
1920-28	Nolan, Owen L. [1888-1958]	
1921-28	Vickery, Hubert Bradford [1893-1978]	Yale Ph.D. 1922
1924-28	Nolan, Laurence S. [1890-1984]	

When Osborne returned a few weeks later, I told him of this Englishman who wanted to join us. Osborne was very busy that morning, and my tale was greeted with a succession of grunts and finally, "Well, is he any good?" Assured on this point, he finally said, "All right, bring him out." Chibnall succeeded in charming Osborne within the hour, and I was instructed to install him in the laboratory at once. As soon as Osborne saw his command of technique, his original approach, and his industry, he happily turned over all of the work on leaf proteins to him.

To this report should be added Chibnall's own later recollections (31):

I had been warned by Mendel of [Osborne's] nervous temperament, and the possibility that he might



A. C. Chibnall

be taciturn when we met, but he greeted me cordially and in a very short while I felt quite at ease. I think I touched a chord to which his nature readily responded, for in our first talk I mentioned my home background, and he recognized in me someone who had taken the same path as himself, embracing science in spite of family efforts to divert him to more practical pursuits. As I got to know him better I learned to appreciate the warmth of his interest in things that he cared for, and the scarcely less con-

spicuous indifference to matters which lay outside the well defined boundary lines of his sympathies.

In a later memoir, Chibnall noted (32):

I was surprised to find how narrow his interests were. Almost as soon as I came into touch with him I was to learn, to my surprise, that plant physiology made no appeal to him at all.

I have quoted these recollections about Chibnall's association with Osborne for several reasons. The most important is that they reveal something of Osborne's style of leadership in his latter years, especially in his ability to recognize scientific talent, as was also evident in his treatment of Vickery. They also confirm the impression that Osborne was a man of limited scientific outlook.

To these reasons I must add an obligation to pay tribute to Chibnall's role in the development of modern protein chemistry (33). In his later research on proteins, as professor at Imperial College from 1929 until 1943, and then as the successor of Hopkins at Cambridge until 1949, Chibnall followed the trail charted by Kossel, Fischer, and Osborne. By about 1940, however, with the advent of the chromatographic method introduced by Martin and Syngé, Chibnall had begun to see the demise of that approach. At Cambridge, he suggested to a young post-doctoral student named Frederick Sanger that fluorodinitrobenzene might be a good reagent for the determination of the amino-terminal groups of proteins, and that insulin (whose amino acid composition Chibnall's group had determined) might be a good protein to start with.

The rest is well-known history. The analytical chemistry of proteins, begun during the 1830s by Gerrit Mulder and Justus von Liebig, was completed during the 1950s by Sanger and by Stanford Moore and William Stein. In this transmission of a chemical heritage, the role of Thomas Burr Osborne deserves to be remembered.

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ABOUT THE AUTHOR

Professor Fruton, recipient of the Dexter Award in 1993, earned the Ph.D. in biochemistry at Columbia University in 1934 with Hans T. Clarke. He worked in the research group of Max Bergmann at Rockefeller Institute for Medical Research, 1934-1945, and then joined the faculty at Yale, where he served as Chairman of Biochemistry from 1951 to 1967. He was elected a member of the National Academy of Sciences in 1952 and of the American Philosophical Society in 1967.

RACHEL LLOYD: EARLY NEBRASKA CHEMIST

Mary R. S. Creese and Thomas M. Creese, University of Kansas

The lead editorial in the University of Nebraska student newspaper for June 9, 1894 concerned the resignation of chemistry professor Rachel Lloyd (1):

[Dr. Lloyd] has seen develop, largely by her efforts and under her eye, one of the largest chemical laboratories in the West. She has seen her lecture rooms crowded by enthusiastic students of all courses and departments. She leaves in Lincoln many warm, social friends, but it is by the students that her absence will be most keenly felt ... She is one of those instructors who stands not only for a science or a language, but for ideals and all higher culture. We can ill afford to lose one of these, for their name is by no means legion ...

In all likelihood Lloyd was the first American woman to take a Ph.D. in chemistry and the first to hold a full professorship in any science at a co-educational state university. She was in Nebraska for only seven years, her career being cut short by failing health, but the time was one of development and opportunity, and her contributions to the university and the regional agricultural community were notable. Her story has remained elusive, however; her early life unknown, and the question of how she got her chance in Nebraska, a matter of special interest to students of the history of women in chemistry, has gone largely unasked.

When Lloyd joined the faculty in 1887 the University of Nebraska had been in operation for only sixteen years (2). Student numbers had increased from twenty regular students in the first year (1871-72) to 334 (3). Most of the chemistry classes during the first ten years were taught by the professor of natural sciences, Samuel Aughey, a clergyman like many of the early faculty, who had little formal scientific training but a vast amount of miscellaneous knowledge, tremendous energy, and unbounded optimism in the future of Nebraska. In 1882

the first well-trained chemist, H[enry] Hudson Nicholson, was hired. The son of Wisconsin farmers, Nicholson had taken an A.M. at Lawrence College in



Rachel Lloyd
(University of Nebraska Archives)

Appleton, Wisconsin, in 1872 and was to supplement his chemical education with further studies throughout the 1880's at Harvard Summer School and the Universities of Heidelberg and Berlin (4). His description of the facilities awaiting his arrival at Lincoln is graphic (5):

[Equipment] consisted of a plain pine table on the top of which was a rack of bottles. In one corner of the room was a cupboard for supplies and in the upper part of the room, near the ceiling, was installed a barrel tank for the water service. There were numerous bottles, jugs, demijohns and carboys—mostly empty and unlabeled [sic]—scattered about the room, and various packets and bottles of chemicals, generally open and unmarked, stuffed in the cupboards. Of reference books, journals, or even texts, there were none ...

Fortunately he brought with him his private collection of apparatus.

In the fall of 1883, 295 students, more than ninety percent of those on the campus, requested chemistry courses. Nicholson's laboratory could accommodate twenty (6). The urgent need for more laboratory space led to the construction of a chemistry building, the second structure on the campus, which opened in the fall of 1886. Additional teaching staff being also essential, Nicholson proposed Rachel Lloyd, whom he had known as a fellow student at Harvard Summer School in 1880 and 1883 (7). Although Lloyd was well-qualified (she had completed her doctoral studies early in 1887) the Nebraska faculty nominating committee hesitated to recommend "unconditionally" the hiring of a woman chemist, and so her initial appointment was a one-year position as acting associate professor of analytical chemistry (8). The need for a second chemist was quickly becoming even greater than the rapid expansion of the undergraduate chemistry classes dictated. With the passage by the federal government of the Hatch Act in 1888, moderate federal support for experimental undertakings at the state Agricultural Experiment Station became available. Consequently the work of the station, which was carried out by the university faculty members, was also increasing; Lloyd joined the staff as assistant chemist as soon as she arrived in Lincoln.

Who was this pioneer among early women chemists? She was born in the small community of Flushing, in eastern Ohio, January 26, 1839, the second daughter in the Quaker farming family of Robert and Abby (Taber) Holloway (9). The Holloways were of English ancestry. Of the four children, she was the only one who survived past infancy, and her childhood and youth were marked by one tragedy after another. Her mother died when she was five and her father when she was twelve, leaving only her step-mother, Deborah (Smart) Holloway. She acquired some early education at the Friends' school in Flushing, and in 1859, at the age of twenty, married Franklin Lloyd, a Philadelphian of Quaker background, who worked as a chemist with

the firm of Powers and Weightman. Little more than six years later Franklin Lloyd was dead. Their two children had pre-deceased him, both dying in infancy (10). Rachel Lloyd then spent some time in Europe and when she came back, turned to teaching as a way of earning a living. Her first position was at the Chestnut Street Female Seminary in Philadelphia (11).

She also continued her education: starting in 1875, she spent six of the following eight summers at Harvard Summer School, which had begun in 1874 and offered courses of intensive instruction in botany, chemistry, and geology tailored to the needs of college and high school teachers. Lloyd studied botany during two summers and chemistry all six (12), specializing in advanced analysis and organic chemistry; latterly she also collaborated with the course organizer, Charles Mabery, in a research project on the synthesis of substituted acrylic acids. The work was reported in three substantial joint papers in the *American Chemical Journal* (13). In 1883 she became professor of chemistry at the newly opened Louisville School of Pharmacy for Women in Louisville, Kentucky, and instructor at Hampton College, a small liberal arts college for women, established in Louisville in 1877 (14).

Lloyd's ambitions reached beyond teaching in a small college, however. In 1885 she resigned from her Louisville positions to continue her studies and went to the University of Zürich, which had been open to women since the 1860's. Thanks to her already considerable laboratory experience, she completed her dissertation research in two years (under the direction of Russian-born chemist Victor Merz) and received her degree in 1887 (15). She was then forty-eight. The spring and early summer of 1887 she spent in London, at the Royal College of Science (South Kensington) and the School of Mines. From there she accepted the Nebraska offer.

The work for which she became noted was her part in a systematic examination of the economic feasibility of the production of beet sugar in Nebraska (16), a multi-year research and development project carried out by the staff of the Agricultural Experiment Station. Preliminary trials of beet culture conducted by the station in 1873-74 had given discouraging results. Yields of beet per acre from a test plot on the university farm had been disappointing, and the State Board of Agriculture had decided against continuing the experiment, despite the more hopeful outlook of the university's professor of agriculture, S. R. Thompson (17).

By the late 1880s, however, Nebraska's farmers were becoming somewhat more prosperous; prospects for the introduction of new crops were more favorable, and a modest but dependable amount of federal funding

was available to help support experimental work on the project. Furthermore, Nicholson was especially interested in sugar beets. Obtaining a variety of seed from the U.S. Department of Agriculture (18), and from France and Germany, where the beet industry was already well established, he distributed it to farmers throughout the state who were willing to raise test plots while keeping records of the important variables; these included type of soil and seed, weather conditions, cultivation procedures and yields per acre. Lloyd, who had seen at first hand the success of the crop in Europe, shared Nicholson's enthusiasm for looking into the possibility of beet culture in Nebraska. She undertook responsibility for the laboratory work the project entailed—the determination of the sugar content of the raw product. For this she was provided with some student assistance, but she carried out much of the laborious analytical work herself (19). Preliminary tests on the 1888 crop gave encouraging results, and by the end of the following year the data she had accumulated provided a convincing demonstration of the potential of the industry in Nebraska. Cultivation costs and yields per acre were reasonably satisfactory, and despite the difficulties caused by inexperience and periods of unfavorable weather, a number of farmers began to take a serious interest in sugar beets. Steps were taken to scale up the operation and establish a sugar factory. Enterprising citizens of the Grand Island community guaranteed a certain acreage of beets, and the first refinery was established there in 1890 by the Oxnard brothers, sugar technologists with experience in both France and the United States (20). Encouraged by a bounty offered by the state for Nebraska-produced sugar, the Oxnards opened a second factory a year later in Norfolk (21). In 1892 the university started a Sugar School, one of only two in the country and the only one dealing with beet sugar technology. The instruction offered included a course in elementary chemistry as well as special work in the chemical control of sugar factory operations (22).

Considerable pride was taken in the success of the Experiment Station's sugar beet work, the university catalog published in 1899 claiming that (23):

No state in the Union has made a more thorough research into the many questions relating to the growth of the sugar beet, and its manufacture into sugar than has Nebraska, and no small portion of the solution of these questions has been carried on under the provisions of the Experiment Station Act, and by means of the funds coming from the general government...

Three of Lloyd's reports on the project appeared as part of the Experimental Station's "Sugar Beet Series" (24).

In 1891, with her health beginning to fail, partly because of overwork, Lloyd gave up her position as assistant chemist at the station. She continued to carry a full teaching load at the university however; and, in 1892, while Nicholson had seven months' leave for an extensive tour of sugar factories and beet farms in Germany and France, she probably served as acting head of the chemistry department. Although she taught her share of more advanced courses (25), she frequently conducted both lecture and laboratory sections of the large, lower-level classes, and so had contact with most of the students who came through her department (26). She took pains to meet the undergraduates in less formal settings as well, being an active member of the Camera Club and one of four faculty who were members of the popular Scientific Club (27).

During the 1890s and the following decade a remarkable number of women chemists joined the Nebraska Section of the American Chemical Society. Indeed, women were much more prominent in that section than in any other local section in the country. Lloyd herself joined the national society in 1891, being the first woman member admitted (except for Rachel Bodley who was given her largely honorary membership at the formation of the society in 1874). The second was Nebraska graduate student and chemistry instructor Rosa Bouton, who joined in 1893 (28). Lloyd's presence on the Nebraska faculty can hardly have failed to be a major source of encouragement for the women chemistry students.

Following her resignation in 1894 she returned to the Philadelphia area, where she still had Lloyd relatives. She died six years later at the age of sixty-one, March 7, 1900, in Beverly, New Jersey.

Although she came to the work late (at the age of forty-eight), and had to leave after only seven years, Lloyd occupied a senior faculty post in what was soon to become an important educational institution at a key period in its development. Manley gives a picture of the Lincoln campus at the time that is especially interesting, because, along with other early faculty who were well known and long remembered in Nebraska, Rachel Lloyd is mentioned by name (29). Noting that the decade of the nineties is in many ways the most interesting period in the history of the University of Nebraska, those years having seen its transformation from a small frontier college into a major institution, Manley goes on:

...visitors to the campus were impressed by the earnest attitude of students and faculty. An air of purpose permeated the buildings, and the ornate iron fence which surrounded the campus after 1891

seemed to proclaim that no outside distractions would be permitted to intrude upon those laboring within. University Hall and the newer buildings were thronged with students pursuing a wide range of academic and practical courses. Professor H. H. Nicholson and a brilliant woman professor, Rachel Lloyd, who had joined the faculty in 1888 [sic], presided over the Chemical Laboratory. Newly built Grant Hall symbolized the land-grant university's devotion to the citizen soldier-scholar. And in Nebraska Hall, the home of the Industrial College, labored "the four busy B's — Bessey, Bruner, Brace and Barbour, whose names are household words in Nebraska."

At least three special advantages helped Lloyd get her position: first, she brought exceptional academic qualifications (as well as considerable teaching experience) to the job market in 1887, seven years before the first woman received a Ph.D. in chemistry from an American university (30); secondly, she had a close personal and professional contact with Nicholson, made during her summers at Harvard in the early 1880s, and he was in a position to make a strong case in her favor (31); thirdly, she joined the Nebraska faculty just when there opened a window of opportunity, at a time of expansion but before the growing importance of the institution made the promotion of a woman chemist to a senior faculty position less likely (32).

Lloyd's character had been formed in a hard school; rather than bending under the misfortunes of her youth, however, she seems to have developed remarkable inner strength and fortitude. Her friend and teacher Charles Mabery remarked in an obituary on her great force of character and attractive personality as well as her energy and the breadth of her cultural interests (33). These were important qualities, perhaps essential, for a woman "outsider" making her way into nineteenth century academic science. Lloyd became a leader in several ways — in taking the initiative of going to Europe for doctoral training as early as 1885 (34), in securing a senior appointment on the chemistry faculty of a state university in 1887, and in taking a major role in an extensive and far-reaching agricultural research and development project before the turn of the century. Like her fellow chemist Ellen Swallow Richards of MIT (35), Lloyd holds a special place in the history of women chemists in America.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. *The Hesperian*, 1894, No. 27, 9 June, 2. The writer was Willa Cather, later to become famous for her novels of pioneer life in Nebraska. She was then an undergraduate at Lincoln and managing editor of the student newspaper.
2. The university received its charter from the state legislature in 1869, only two years after Nebraska became a state. Although endowed by the Morrill Land-Grant College Act of 1862, its establishment was not greeted with unanimous approval, certain factions in the state being of the opinion that Nebraska at that time needed a university "about as much as a cat needs two tails." Instruction was first offered in 1871 (see Robert N. Manley, *Centennial History of the University of Nebraska*, vol. 1, University of Nebraska Press, Lincoln, 1969, especially p. 14-17, quotation from p. 17).
3. Reference 2, p. 29, 91-92. The total enrollment figure for the first year was 130, but 110 were students in the preparatory department.
4. *Who Was Who in America*, vol. 1., A. N. Marquis Co., Chicago, 1943, p. 897. Information about Aughey came from reference 2, p. 23, 42-43.
5. H. H. Nicholson, quoted by Manley, reference 2, p. 82.
6. *Ibid.*, p. 82.
7. General Catalogue, "Summer Courses of Instruction in Chemistry, Botany and Geology." Harvard University, 1880, p. 221, 1883, p. 245.
8. Board of Regents Papers, February-April 1892, University of Nebraska archives. Lloyd became full professor the following year.
9. Olin E. Holloway, *Genealogy of the Holloway Families*, [n.p.], Knightstown, IN, 1927, p. 215-216; William Wade Hinshaw, *Encyclopedia of American Quaker Genealogy*, compiled by T. W. Marshall, Ann Arbor, Michigan, 1936—, vol. 4, p. 533.

10. Richard Louis Lloyd, "A Record of the Descendants of the Immigrant Robert Lloyd of Merion," [n.p.], ca. 1947 (excerpts provided by the Friends Historical Library of Swarthmore College).
11. This school was founded in 1850 by Mary L. Bonney and Harriet L. Dillaye, themselves graduates of Emma Willard's Troy Female Seminary in Troy, New York. By 1882 it was one of the oldest girls' finishing schools in America and was attended by girls from all over the country. After relocation in the Ogontz mansion in 1883, it became the Ogontz School for Young Ladies (information from Terrie Smith, University Relations, Ogontz Campus, Pennsylvania State University, Abington, PA).
12. Reference 7, student lists for 1875-77, '79, '81, and '83.
13. R. Lloyd and C. F. Mabery, "On the diiodobromacrylic and chlorbromacrylic acids," *Am. Chem. J.*, **1881-82**, *3*, 124-129; "Dibromiodacrylic and chlorbromiodacrylic acids," *ibid.*, **1882-83**, *4*, 92-100; "On ?- and ?-chlorbromacrylic acids," *ibid.*, **1884-85**, *6*, 157-165.
14. Catalogue, 1883-84, Louisville School of Pharmacy for Women (Filson Club: Historical Society, Louisville, Kentucky); 1885 Louisville City Directory (Caron's). Hampton College was founded by Lydia D. Hampton, a graduate of the New Jersey State Normal School, Trenton, New Jersey, who was a fellow student of Lloyd's at Harvard in the summer of 1880 (see John William Leonard, Ed., *Woman's Who's Who of America*, 1914-1915, The American Commonwealth Co., New York, 1914, p. 210, entry for Lydia Hampton Cowling).
15. Lloyd's dissertation research on the conversion of phenols to amines appeared in *Ber. Dtsch. Chem. Ges.*, **1887**, *20*, 1254-1265 ("Ueber die Umwandlung höherer Homologen des Benzolphenols in primäre und sekundäre Amine").
16. See Ann T. Tarbell and D. Stanley Tarbell, "Dr. Rachel Lloyd (1839-1900): American Chemist," *J. Chem. Educ.*, **1982**, *59*, 743-744; reference 2, p. 140; Glenda Peterson, "Rachel Lloyd made Beet Crop Success," *Sunday Journal and Star*, Lincoln, 1982, 24 October.
17. Robert Platt Crawford, "These Fifty Years" (Circular 26 of the Agricultural Experiment Station, University of Nebraska), University of Nebraska Press, Lincoln, 1925, p. 24-25.
18. Harvey W. Wiley, chief chemist at the U.S. Department of Agriculture from 1874 until 1913, strongly supported efforts to introduce the sugar beets into the United States, making seed available and assisting in analytical work as well (see "The Beet Sugar Story," United States Beet Sugar Association, Washington, D.C., 1959, p. 17).
19. Methods for sugar analysis were already fairly standardized by the 1880's. The procedure which Lloyd most likely would have followed was outlined by Tarbell and Tarbell (reference 16): a sample of finely divided, well-mixed beet pulp was digested with aqueous lead acetate solution, the resulting mixture filtered, and the optical activity of the filtrate, a measure of the sucrose content, determined by polarimetry. Reducing sugar content would also have been estimated (by reduction of Fehling's solution) as well as the percentage of sugar in the total solids, or coefficient of purity, the factor which indicated the overall ease with which white sugar could be produced (see R. A. McGinnis, ed., *Beet Sugar Technology*, Reinhold Publishing Corp., New York, 1951, p. 95-98).
20. Reference 17, p. 102. The Grand Island, Nebraska, factory was the third successful beet sugar factory in the U.S.
21. Soil and climatic conditions in the Norfolk district proved unfavorable for the production of beets with a high sugar content, and in 1905 this factory was closed and the equipment moved to Lamar, Colorado (reference 19, p. 16).
22. Reference 17, p. 102-103.
23. Anon., quoted by Crawford, reference 17, p. 101. In 1888, 100 years after Lloyd carried out her preliminary analytical work, the Nebraska sugar beet crop was valued at almost \$57 million (U.S. Department of Agriculture, Agricultural Statistics, 1990, U.S. Government Printing Office, Washington, D.C., 1990).
24. Rachel Lloyd, "Experiments in the Culture of Sugar Beet in Nebraska," 1890 (1 April), 1891 (15 April), 1892 (1 March) (University of Nebraska archives).
25. She also offered direction in research projects, as did Nicholson.
26. For example, in Nicholson's Department Report for the year ending 7 June 1893, Lloyd is listed as teaching eighty-eight students in Chemistry I and III during the first semester, and seventy-nine in Chemistry II and IV during the second. The only classes larger than hers were those in the preparatory division (Board of Regents Papers, 1893, University of Nebraska archives).
27. *Sombrero* [University of Nebraska Year Book], 1892, p. 165, 169. The Scientific Club, organized in 1890, had no fewer than ninety-seven members by 1892.
28. See the membership lists in the *Journal of the American Chemical Society*, Proceedings, for 1891 to 1910. As well as Lloyd and Bouton, Nebraska women chemists active in the local section included Mary Louise Fossler (B.S., 1894, A.M., 1898), Mariel Gere (B.S., 1895, A.M., 1899), Mariette Gray (B.S., 1895) and Rachel Corr (B.S., 1898, A.M., 1906); they were followed a few years later by Mabel Hartzell, Mildred Parks, and Mamie Short.
29. Reference 2, p. 111-112.
30. Charlotte Roberts (Yale, 1894) and Fanny Hitchcock (University of Pennsylvania, 1894) were the first women to receive doctorates in chemistry from American universities (see Walter Crosby Eells, "Earned Doctorates for Women in the Nineteenth Century," *Bulletin, American Association of University Professors*, 1956, *42*, No. 33, 644-651).
31. Lloyd's warm friendship with Nicholson, eleven years her junior, and his wife Jennie is made clear by the fact that the Nicholsons named their third child Rachel Lloyd.
32. Lloyd's appointment to the Nebraska faculty was probably early enough to avoid the full impact of the general reaction to the perceived threat of "feminization" of the

sciences, a reaction which set in during the 1880s and 1890s (see Margaret W. Rossiter, *Women Scientists in America. Struggles and Strategies to 1940*, The Johns Hopkins University Press, Baltimore, 1982, Introduction, p. xvii). Two other women chemists, Rosa Bouton and Mary Fossler, followed Lloyd on the early Nebraska faculty. Bouton, however, after seven years of teaching in the chemistry department (1891-98), was asked to take on the task of establishing the university's School of Home Economics; Mary Fossler became an instructor in the chemistry department in 1899 and was promoted to assistant professor of chemistry and associate professor of physiological chemistry nine years later. She held these positions until she moved to the University of Southern California in 1919. Admittedly, both Bouton and Fossler had A.M. degrees rather than Ph.Ds., and although lack of a doctorate was not a major barrier for men (Nicholson had an A.M.) it probably spelled a greater disadvantage for women.

33. C. F. Mabery, "Professor Rachel Lloyd, Ph.D., Zürich," *J. Am. Chem. Soc.*, **1901**, 23, 84.

34. A number of American women scientists took doctoral degrees in Germany and Switzerland in the 1890's, but except for the botanist Emily L. Gregory (later of Barnard College), who received a Ph.D. from the University of Zürich in 1886, Lloyd would appear to have been the first American woman scientist (excluding physicians) to take a European doctorate.
35. Richards was instructor of sanitary chemistry at MIT from about 1883 until her death in 1911.

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BAYER'S PROCESS FOR ALUMINA PRODUCTION: A HISTORICAL PERSPECTIVE

Fathi Habashi, Laval University, Quebec City

The Bayer Process (for alumina) as we know it today involves two steps:

- The pressure leaching of bauxite with NaOH solution to obtain sodium aluminate solution.
- The precipitation of pure aluminum hydroxide from this solution by seeding with fine crystals of $\text{Al}(\text{OH})_3$.

The leaching step was invented five years after the precipitation step (Table 1), and the precipitation step was an improvement to the Le Chatelier Process (1), namely replacing CO_2 by the seed (Fig. 1).

In 1888 a British Patent entitled "A Process for the Production of Aluminum Hydroxide" was issued

Chatelier (1850-1936) is best known for the thermodynamic principle which bears his name.

Bayer (2) was born in Bielitz, a few kilometers southwest of Cracow in Silesia, at that time a Province of the Austrian Empire, now in Poland. The map of Europe at that time was quite different from what we know it today. It was the age of empires: the British, French, German, Russian, Ottoman, and Austrian empires. The Austrian Empire was composed of a vast territory encompassing the present day Austria, northern Italy, Bohemia, and Moravia which are parts of present-day Czechoslovakia, Hungary, Transylvania (a part of present-day Romania), Croatia, Dalmatia and Bosnia

Table: Bayer's Patents

Contents	Country Granted	Number	Year
Precipitation of pure $\text{Al}(\text{OH})_3$ from sodium aluminate solution by seeding	Britain	10,093	1888
	USA	382,505	1888
	Germany	43,977	1888
The pressure leaching of bauxite with NaOH to obtain sodium aluminate solution	Britain	5,296	1892
	USA	515,895	1892
	Germany	65,604	1892

to the Austrian chemist Karl Josef Bayer (Fig 2, 3) who, at that time, was living in Saint Petersburg in Russia (known as Leningrad from 1924 to 1991)(Table 1). The process immediately achieved industrial success, displacing the thermal process known as the Le Chatelier process that had been used until that time to produce alumina from bauxite. The thermal route was invented by Louis Le Chatelier (1815-1873), the Chief Inspector of Mines in France, whose son the chemist Henri Le

Herzegovina (parts of present-day Yugoslavia), and Silesia and Galicia in southern Poland. While the official language was German, many other languages were spoken, e.g., Hungarian, Romanian, Czech, Polish, Ruthenian (an old name for Ukrainian), Slovak, Slovenian, Serbo-Croatian, and Italian. The multitude of nationalities and languages caused many revolts and political unrest, but music and the arts were flourishing. This was the time of Johann Strauss and his waltzes and

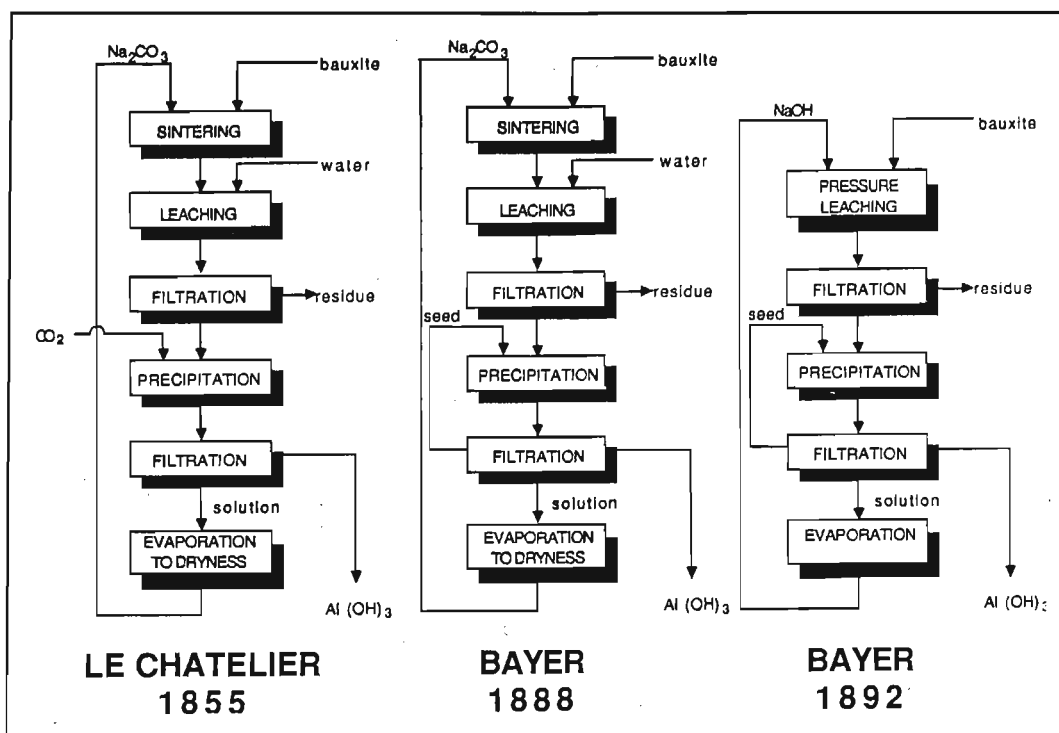


Figure 1 The development of Bayer's process for alumina production

Gustav Mahler and his symphonies. Bayer attended school in his home town and at the wish of his father, who was an architect, started to study architecture.

Later Bayer switched over to science and went to Wiesbaden in Germany to work in the laboratory of the famous chemist Remigius Fresenius (1818-1897), then in a steel factory in Charleroi, Belgium. In 1869 he enrolled at the University of Heidelberg where he worked under Professor Robert Bunsen (1811-1879) for three years. At that time Bunsen's laboratory was visited by many chemists who became famous later on. Among those were Dimitri Mendeleev, Friedrich Beilstein, Henry Roscoe, Auer von Welsbach, Lothar Meyer, Victor Meyer, and many others. Bunsen's reputation stems from his discovery, together with the physicist Gustav Kirchhof (1824-1887), of the spectroscopic method of analysis and the discovery of the two metals rubidium and cesium by this new tool in 1860-61. Bunsen is also famous for the burner known by his name and now found in every chemical laboratory. In Heidelberg, Bayer earned the doctorate at the age of 24 after submitting a thesis entitled, "A Contribution to the Chemistry of Indium." Indium had been discovered few years earlier by the two German chemists, Ferdinand Reich (1790-1882) and Theodor Richter (1824-1989) utilizing Bunsen's spectroscope.

In the same year Bayer obtained his doctorate, Europe was undergoing tremendous changes. There was the war between France and Prussia; the French were defeated at Sedan, Napoleon the Third surrendered, and the Republic was proclaimed. Also, Germany was proclaimed a united empire: the victorious Prussian King Wilhelm the First was named Emperor of Germany at Versailles, near the defeated French capital. Italy, like Germany, also became one nation in the hands of Garibaldi.

After obtaining his doctorate, Bayer returned to his home country Austria where he was appointed a lecturer at the University of Technology at Brunn, a few kilometers northeast of Vienna in the Moravian Province of the empire (now in Czechoslovakia). He left the University in 1873 to establish a research and consulting laboratory in Brunn.

However, he later gave up this venture and moved in 1885 to St. Petersburg, the capital of Russia. Russia at that time was open to all foreigners with technical and artistic skills but was suffering from the reign of terror of Alexander the Third after the assassination of his father, Alexander the Second, in 1881. In Russia, Bayer grew his beard the way the Russians did (Fig. 2). He was a contemporary to such famous personalities as



Figure 2 Bayer in Saint Petersburg, Russia

Tchaikovsky, Rimsky-Korsakov, Pavlov, and Mendeleev.

Bayer's years in Russia were his most fruitful and creative years. He joined the Tentelev Chemical Plant near Saint Petersburg to work on problems of production of pure aluminum hydroxide for the dyeing of fabrics. The plant, presently known as "Red Chemist Plant," was using the Le Chatelier Process to produce aluminum hydroxide which was used as a mordant for dyeing cotton, wool, and silk. Mordant dyeing was described by Pliny in Roman times when naturally occurring alum (aluminum sulfate) had been used. The textiles to be dyed were soaked in a solution of the hydroxide dissolved in a weak acid, then squeezed, dried and steamed whereupon the hydroxide precipitated on the fibers. Thus treated, the textiles could be immersed in a dye solution to form a colored "lake." This was a standard method of dyeing at that time. For example, Turkey red, a popular red color, was prepared by dyeing with alizarine on aluminum hydroxide mordant.

While in Tentelev Bayer, at the age of 41, made the discovery that aluminum hydroxide could be precipitated from sodium aluminate solution if a seed of a freshly precipitated aluminum hydroxide were agitated

vigorously in the cold solution. The pure product could be collected by filtration and washed. The process was soon adopted by the Tentelev Plant. This was the subject of his first British Patent of 1887 and the German Patent of 1888 (Table 1). Four years later he made his second discovery that alumina contained in bauxite could be dissolved selectively by heating with a solution of sodium hydroxide under pressure in an autoclave to form sodium aluminate solution. He found also that the alkaline mother liquor obtained after the precipitation of aluminum hydroxide could be used.

At the age of 45, after firmly establishing his professional career and his social status, Bayer married the niece of the Russian statesman, Count Sergei von Witte, who was of German origin and who served briefly as prime minister after the 1905 Revolution during the reign of the last Russian Tsar Nicolai the Second.

After seven years in Saint Petersburg, Bayer then moved to another chemical plant at Yelabuga on the Kama River, 200 kilometers east of Kazan in the Tatar region not far from Urals, to build the second plant for alumina manufacture by his process. Coloring matters were used by man from ancient times, but these were all naturally occurring: for example, indigo and alizarine were mainly extracted from plants and insects and were imported to Europe from distant countries. At Bayer's time synthetic dyestuffs were produced for the first time on a commercial scale, and it was in this industry that high pressure reactors were first applied. Organic intermediates which were needed to manufacture the synthetic dyestuffs were produced in heated agitated reactors that were able to withstand the pressure required for reactions such as sulfonation, nitration, reduction, etc.

Bayer remained only two years in Yelabuga. During this period he received numerous contracts from foreign countries to build alumina factories. The aluminum industry in Russia started only many years after the revolution; bauxite was first mined there in 1926 at a location called Bocksitogorsk (which means bauxite city) and is 150 kilometers east of Saint Petersburg. The reduction plant was constructed in 1932 at Volkhov not far from the deposits.

Bayer then returned to Austria, apparently with the intention of developing the aluminum industry in his own country. He settled in Rietzdorf in southern Styria and devoted some time to scientific research (Fig 3). During this period he developed a method for the manufacture of synthetic cryolite which is used as an electrolyte in the aluminum industry. He then developed the first bauxite deposit in Austria and built a plant to produce Al_2O_3 by his process. However, he was unable to



Figure 3 Bayer in Rietzdorf, Austria

raise enough capital, and thus his plans failed. Bayer, although an average scientist, was an inventor and had a great sense of enterprise. He published only one paper entitled "Studies on the Winning of Pure Aluminum Oxide" but his patents were of great importance. He died suddenly at the age of 57; his widow survived to the age of 94. The foreign companies (except two) who were applying his patents stopped paying royalties after his death. It was difficult at that time to sue them, and consequently his house and laboratory had to pay for his debts. In 1906 his family moved to Graz.

Bayer and his wife raised five sons and a daughter. His home in Rietzdorf was a meeting center for many famous industrialists, among whom were Paul Heroult (1863-1914), and Charles Martin Hall (1863-1914) the discoverers of the electrolytic process for aluminum. He loved music and the arts; he himself was a talented artist. He spoke six languages: German, French, English, Russian, Italian, and Slovak. He had an excellent collection of minerals which he displayed at the Chicago exhibition in 1890.

Bayer's process involving both pressure leaching and precipitation by seeding is used today in practically the same way as when it was discovered one hundred years ago. However, marked improvements in the engineering aspects have taken place and these are responsible for decreasing the cost. The economy in energy is due to two factors: an increased heat recovery and the use of large autoclaves. Heat exchangers and flash tanks are now extensively used to economize energy. Flash tanks serve the additional purpose of the evaporation of solutions. The larger the reactor the less will be the heat losses. Construction of such equipment that can be used reliably is due to improvements in engineering design and manufacturing. Along with autoclaves, precipitation tanks have increased in size correspondingly. Furthermore, steam is now used for heating and agitation and autoclaves are connected in series to permit continuous operation. This allows automation and decreasing manpower.

The use of tube or pipeline autoclaves began simultaneously in Germany and in Czechoslovakia in 1967 for the leaching of bauxite by a modified Bayer Process. In this process a temperature of 300°C is used, resulting in a vapor pressure in the system of about 13000 kPa. Because of the high temperature, a reaction time of only 2-3 minutes instead of 4-6 hours is sufficient to extract the aluminum. The continuous process has a high thermal efficiency because of the effective heat exchange system.

A new importance was given to the Bayer Process when gallium was needed by the semiconducting indus-



Figure 4 Medal in honor of Bayer awarded at the International Light Metals Congress

try and its recovery from process solution became desirable. Gallium was first discovered in zinc blende and its first production was from this source. When it was discovered in bauxite in 1896, however, this new source

became the major supplier although its average concentration is less than 0.01%. Alusuisse, a major aluminum manufacturer in Switzerland, commenced industrial production of gallium from bauxite in 1955. Gallium follows aluminum in the Bayer Process being recovered from the aluminate solution. The present world production of gallium is about 50 tons/years.

Bayer is honored in his native country Austria by the medal bearing his name and awarded every six years to a distinguished researcher in the field of aluminum. (Fig. 4) The award ceremony takes place during the International Light Metals Congress, which is held in Leoben and in Vienna. Bayer's first name appears in the Germanized spelling as "Karl" in his patents but in the Latin form as "Carl" on his medal (Fig. 4).

The first medal was awarded at the Fourth Congress in 1961 to the Swiss metallurgist Prof. Alfred von Zeerleder of the Eidgenössische Hochschule in Zürich for his work on aluminum alloys. The second medal was awarded at the Fifth Congress in 1968 to the German Chemist Professor Hans Ginsberg of the Technische Hochschule in Clausthal for his two volume book on "Bauxite and Aluminum." The third medal was awarded to the Austrian metallurgist Professor Roland Mitsche of the Montan Universität in Leoben for organizing the Light Metals Congresses and for his book "Angewandte Metallographie." In 1981 two medals were awarded: one to the German chemist Dieter Altempohl, Head of Research Department at Alusuisse in Switzerland and author of "Aluminum and Aluminum Alloys;" the other to the American chemist Allen Russell, Vice-President of Alcoa who developed the Alcoa Chloride Process.

In 1987 two medals were again awarded: one to the German chemist Dr. Klaus Bielfeldt, Director of Research of Vereinigte Aluminiumwerke in Bonn where he developed the pipeline reactor for bauxite digestion and the fluidized bed aluminium hydroxide calciner; the other to the Norwegian chemist Professor Kai Grjotheim of Oslo University, who contributed extensively to the chemistry of fused salts and particularly aluminum production. He coauthored "Aluminum Electrolysis. Fundamentals of the Hall-Heroult Process" and "Aluminum Smelter Technology. A Pure and Applied Approach."

Bayer's invention to satisfy the need of the Russian textile manufacturers soon turned out to become the most important invention for supplying the need of the growing electrolytic aluminum industry that was discovered four years earlier by Hall and Heroult. The Hungarian aluminum industry issued in 1987 a medal in Bayer's honor to commemorate the hundred years' anniversary of depositing his first patent.

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ALEKSANDR MIKHAILOVICH ZAITSEV (1841-1910)

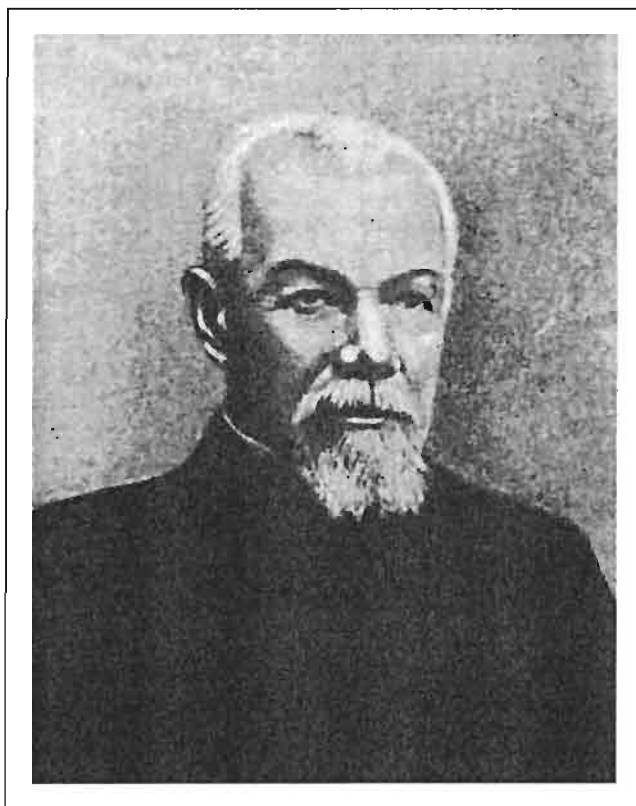
Markovnikov's Conservative Contemporary

David E. Lewis, South Dakota State University

Most students in organic chemistry today are familiar with Saytzeff's Rule for elimination reactions, although few, if any are aware of the Russian chemist, Aleksandr Mikhailovich Zaitsev (1841-1910), for whom it is named. In part, this may be due to the lack of western sources concerning his life. All the biographical material available on Zaitsev is in Russian (1, 2) with the exception of two German sources—the brief death notice in *Berichte* (3a) and the minimal information in *Poggendorffs* biographical bibliography (3b)—and two brief surveys of his work in English—the recent thesis by Brooks (3c) and a survey paper in *J. Chem. Educ.* (3d).

Zaitsev was born in Kazan' to a mercantile family that had lived in the region since the time of Ivan the Terrible (1533-1584), and there is evidence that the Zaitsev family had been agents of commerce between the Russian Empire and the Orient since that time. His father, Mikhail Savvich Zaitsev, had two sons by his first wife and three sons, of whom Aleksandr was the middle one, by his second wife, Natalie Vasil'evna Lyapunova. A merchant with control over the tea and sugar trade, Mikhail Savvich Zaitsev resolved early that his son should join the mercantile guilds and follow in his footsteps. However, Zaitsev's maternal uncle, the astronomer Mikhail Vasil'evich Lyapunov (later Professor of Astronomy at Kazan' University), persuaded his brother-in-law that young Aleksandr should attend the university, instead. Accordingly, Aleksandr was enrolled in the Gymnasium.

Founded in 1804, Kazan' University was the easternmost outpost of Russian higher education during the nineteenth century, and yet by the middle of the nineteenth century it had assumed a pre-eminent position in



A. M. Zaitsev

Russian organic chemistry despite its provincial location and status. This ascendancy of the chemistry department of Kazan' University was achieved under the guidance of such luminaries as Nikolai Nikolaevich Zinin (1812-1880), Karl Karlovich Klaus (1796-1864), and Aleksandr Mikhailovich Butlerov (1828-1886), and it was maintained under such renowned chemists as

Vladimir Vasil'evich Markovnikov (1838-1904), Zaitsev himself, and Aleksandr Erminingel'dovich Arbutov (1877-1968).

In 1858, following his graduation from the Gymnasium, Zaitsev entered Kazan' University as a student in economic science in the Faculty of Law. At that time, all students entering the Faculty of Law were required to pass a qualifying examination in Latin. Because there were no classes in Latin at the Gymnasium, Lyapunov himself had taught the young Aleksandr the Latin which he needed to pass the entrance examinations. At that time, also, all students in the Faculty of Law were required to pass two years of chemistry in order to graduate. It was while taking these required chemistry courses that the young Zaitsev came under the influence of one of the greatest organic chemists produced by Russia — Aleksandr Mikhailovich Butlerov. By the time that he had graduated, Zaitsev was no longer an economist, but a committed chemist. Zaitsev graduated with his degree in economic science in 1862.

Up to this time Russian tradition prescribed a fairly rigid course of action following graduation.

The most immediate concern for most students was to remain in Russia to write the dissertation for the degree of Kandidat, without which one could not obtain a salaried position as a laboratory assistant. Today, the degree of Kandidat at most Russian universities is the approximate equivalent of the Ph.D.; in the nineteenth century, however, it was somewhere between a modern master's degree and a modern Ph.D. Following graduation with the degree of Kandidat, most students studied abroad for two to three years, then returned to Russia to submit a dissertation for the degree of Master of Chemistry (the minimum qualification for obtaining a teaching post at a university). In order to obtain the rank of Professor at a university, one needed the degree of Doctor of Chemistry, which necessitated

the submission and defense of a dissertation, as well as passing an examination over every area of chemistry.

For whatever reason, whether from impatience and a desire to study under the best in Europe or simply because he did not think ahead about his financial security on his return to Russia, Zaitsev chose to ignore these traditions; this very nearly proved to be a fatal mistake. Immediately after his graduation from Kazan' University he left for Germany, where he entered the laboratory of Hermann Kolbe at the University of Marburg. In 1863, after his first year with Kolbe, Zaitsev submitted a dissertation to Kazan' University for the degree of

Kandidat. This 76-page hand-written dissertation was entitled, "The Theoretical Views of Kolbe on the Rational Constitution of Organic Compounds and Their Relationship with Inorganic Compounds." It contained an overview of Kolbe's version of structural theory (Kolbe viewed the term "chemical structure" as specious, and he eschewed it in favor of "rational constitution") that had led him to predict the ex-



Химическая лаборатория Казанского университета.

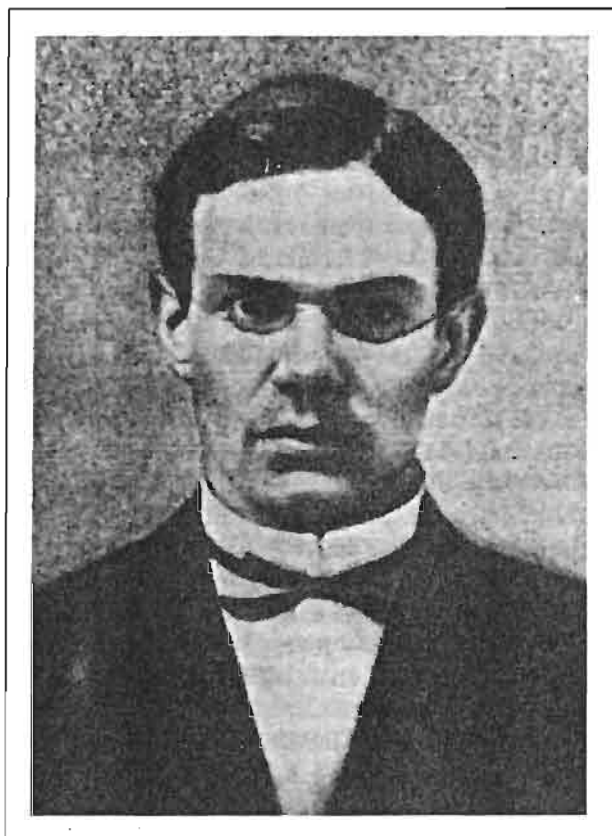
Kazan University Chemical Laboratory in Zaitsev's time

istence of, among other compounds, the tertiary alcohols. Ironically, it was Butlerov who was the primary examiner of this dissertation. As one of the developers of the modern structural theory of organic chemistry, and as the chemist who first synthesized *tert*-butyl alcohol (4), thus confirming Kolbe's predictions, Butlerov was intimately acquainted with Kolbe's views (and opposed to them). Unfortunately for Zaitsev, the dissertation was neither well written nor novel — Butlerov characterized it as "a poor rendering of the German" — and the degree was not awarded.

Zaitsev's studies continued uninterrupted at Marburg until August, 1864. At Marburg, he studied the chemistry of organic sulfur compounds. He made the first of his major discoveries — the sulfoxides, whose

existence and formation he reported in a series of papers (5) during the last half of the 1860's — while studying the oxidation of organic sulfides by nitric acid. During the 1864-1865 academic year (August 1864-April 1865), Zaitsev moved to Paris, where he studied under Charles Adolphe Wurtz at the Université de Paris. His work at Paris, primarily concerned with the reactions of carboxylic acid derivatives (6, 7), was subsequently the basis of his successful dissertation for the degree of Kandidat (8).

In May, 1865, Zaitsev returned to Marburg to be greeted by the news that Kolbe had accepted the Chair



Zaitsev as Laboratory Assistant (1871)

of Chemistry at the University of Leipzig. Choosing not to follow his mentor to his new post, Zaitsev returned to Russia. Here he was unable to work as a salaried laboratory assistant because he lacked the degree of Kandidat. This did not deter Zaitsev, who immediately offered his services "as a private individual" — an unpaid, unofficial laboratory assistant — to Butlerov. He quickly impressed his mentor, who urged him to write his dissertation for the degree of Kandidat. In 1865, he submitted his dissertation, "Concerning Diamidosalicic Acid," based on the results of his two semesters of work in Wurtz' laboratory. The papers de-

scribing this work appeared in both French and German the same year (6). The degree was awarded and, thanks to the support of Butlerov, Zaitsev obtained a position as laboratory assistant in agronomy in 1866. The university also committed the direction of the laboratories in agronomic chemistry to him.

In order to teach at Kazan', Zaitsev needed a degree beyond the Kandidat. The expected degree was the Master of Chemistry degree, but it would require two years of study beyond the Kandidat before he could submit a Master's dissertation. Therefore, once again in defiance of Russian tradition, he wrote up the results of his Marburg work and sent them to Kolbe at Leipzig in the form of a Ph.D. dissertation (9). In 1866 he was granted the degree of Ph.D. by the University of Leipzig (one may speculate on the extent to which Kolbe's influence affected this outcome). Herein may also lie some of the origins of the disdain of Markovnikov, Butlerov's student and successor at Kazan', towards Zaitsev. When Zaitsev submitted his Ph.D. dissertation to the University of Leipzig, Markovnikov, who was an ardently nationalistic Russian, was a senior student in Kolbe's laboratories, and probably privy to the fact that Zaitsev had once again flouted Russian tradition by applying for a doctoral degree from a foreign university.

The work for which Zaitsev was awarded the Ph.D. by Leipzig appeared the same year as a paper in *Liebigs Annalen* with the same title, "Ueber eine neue Reihe organischer Schwefelverbindungen." He completed his dissertation for the degree of Master of Chemistry, "On the Action of Nitric Acid on Certain Organic Compounds of Divalent Sulfur and on a New Series of Organic Sulfur Compounds Obtained from this Reaction," in the first half of 1867 (10). Initially, several members of the faculty of the University did not want to permit Zaitsev to submit the dissertation because he already held a doctoral degree from a foreign university (despite the fact that foreign doctoral degrees were not recognized in Russia at the time); it was only because of Butlerov's intervention that he was permitted to do so. He successfully defended the dissertation in October, 1868, and was awarded the degree that December.

In May, 1868, Butlerov accepted the chair of Chemistry at St. Petersburg University. However, he asked for and received permission to delay his departure from Kazan' until January, 1869, to permit a smooth transition of the chair to his successor and student, Markovnikov. This delay proved to be critical for Zaitsev's career. Since its earliest days, Kazan' University had two chairs, one in chemistry and one in chemical technology. In the 1840's these two chairs were occupied by Zinin, who discovered the first method for the reduction of nitrobenzene to aniline,

and Klaus, the discoverer of ruthenium; when Zinin moved to St. Petersburg, his chair remained vacant. When Klaus also left Kazan', Butlerov was appointed as his sole successor.

Of course, when Butlerov announced that he was to become the Professor of Chemistry at St. Petersburg, Markovnikov (who had already substituted for his mentor while Butlerov was abroad defending his claims of priority in developing the structural theory of organic chemistry) quite rightly expected that he would become the sole Professor of Chemistry at Kazan'. However, Markovnikov was an irascible and prickly individual whose politically progressive ideas did not sit well with a conservative administration. Consequently, the administration delayed his inevitable appointment to the Chair of Chemistry as long as possible. Indeed, there was sufficient opposition to Markovnikov's appointment as Butlerov's sole successor that the University decided that both chairs of chemistry should be filled when Butlerov left. Their first choice for the second chair was another Butlerov student, Aleksandr Nikolaevich Popov (1840-1881), who had written a brilliant master's dissertation on structural theory under Markovnikov's direction. The university administration may have viewed Popov's friendship with Markovnikov as a potential buffer between themselves and Markovnikov. In 1869, however, Popov accepted the Chair of Chemistry at the University of Warsaw and moved to Bonn for advanced study under Kekulé in preparation to take up his new post. This may actually have been fortunate for Kazan' University for Popov's health was not robust, and he died before achieving anything further of note (or for which he was given the appropriate recognition, at least, as we shall see later).

This left Zaitsev, for whom Markovnikov had little regard, as the next logical choice. As a political conservative, Zaitsev had the support of the dean and the administration, especially in the light of the very strong recommendation which Butlerov wrote for him. In January, 1869, Zaitsev was elected unanimously to the Council of Docents and appointed to the second chair of chemistry. Following his appointment, Zaitsev taught the public courses in organic and inorganic chemistry, and the practicum in organic and analytical chemistry. Markovnikov taught the special course in organic chemistry and the analytical and organic chemistry practicum to his students.

Zaitsev quickly gathered a number of laboratory assistants (although never as many as Markovnikov). In September, 1870, he defended his doctoral dissertation, a two-part study entitled, "A New Method for Converting a Fatty Acid into its Corresponding Alcohol. Normal Butyl Alcohol (Propyl Carbinol) and its Conversion to Secondary Butyl Alcohol (Methyl Ethyl

Carbinol) (11)." Markovnikov—who had defended his own dissertation in April, 1869, and had been appointed Extraordinary (May, 1869) and then Ordinary (spring, 1870) Professor of Chemistry—was the primary reviewer of the dissertation. Overtly positive, albeit with a very condescending tone towards the author, Markovnikov's review of Zaitsev's dissertation was meant to be read between the lines. This is in marked contrast to Zaitsev's review of Markovnikov's own dissertation, which contained high praise. Fortunately, the faculty was aware of Markovnikov's antipathy towards Zaitsev and of Butlerov's high opinion of him; so, Markovnikov notwithstanding, Zaitsev was awarded the doctor's degree and was appointed Extraordinary Professor of Chemistry in November, 1870. One year later, the dean nominated Zaitsev as a candidate for the rank of Ordinary Professor of Chemistry, a post to which he was elected in November, 1871, in a 19-12 split vote.

It is very possible that Zaitsev's appointment as professor—which Markovnikov had tried to prevent—was one of the precipitating factors that led to Markovnikov's rancorous departure from Kazan' University less than six weeks later. Certainly, Zaitsev's 1869 appointment as his colleague had infuriated Markovnikov, who refused to speak to his new colleague (in October, 1869, he wrote to Butlerov, "With the departure of Popov I am determined to speak to nobody. I see Zaitsev only before his lectures...") (12). After Markovnikov's departure, Zaitsev assumed the direction of the chemistry laboratories at Kazan' as Professor of Chemistry. It was not until 1884 that Zaitsev obtained a colleague with Professorial rank, when Flavian Mikhailovich Flavitskii (1848-1917)—another Butlerov student—was appointed to the vacant second chair of chemistry at Kazan' as Professor of Inorganic Chemistry.

Most of Zaitsev's independent scientific work is characterized by the extension of and continued development of the ideas of his mentors, especially Butlerov; and his career is usually associated with the continued development of the Butlerov school at Kazan'. His earliest independent work, however, owed more to the influence of Kolbe on his professional development. It was a continuation of the work he had begun while a student at Marburg, where he had discovered the sulfoxides during his studies of the oxidation of thioethers. Had the usefulness and versatility of these sulfur compounds as synthetic intermediates been recognized during the nineteenth century, Zaitsev's reputation may well have flowered like that of Markovnikov, but it was to be nearly 100 years before the full potential of sulfoxides and sulfonium salts in organic synthesis was realized. Today it is difficult to imagine modern organic synthesis without methods based on the chemistry of the sul-

foxides and sulfur ylides that have been developed since the 1960's (13).

It is clear from Butlerov's writings that he rated Zaitsev's graduate research in sulfur chemistry far above the work he had done in Paris, and it was the papers describing the work that Zaitsev had carried out in Kolbe's laboratories that Butlerov cited in several glowing recommendation letters that he wrote for him. Indeed, it is not inconceivable that Butlerov himself may have advised his protégé to continue his work in this area. Whatever the underlying reasons, Zaitsev continued to study the chemistry of organic sulfur compounds after his return to Russia, at least until after his appointment as Professor of Chemistry at Kazan'.

By the early 1870's, Zaitsev had begun to publish papers describing the synthesis and transformations of alcohols, and by far the majority of his scientific papers are concerned with this field of study, where he did much to further Butlerov's influence on the development of Russian organic chemistry. His first independent contribution was the discovery that carboxylic acid chlorides could be reduced cleanly to the corresponding primary alcohols with 3% sodium amalgam in dry ether with acetic acid as a buffering agent and hydrogen source (14). Zaitsev applied this reaction to several acid chlorides, including succinyl chloride. During the reduction of succinyl chloride with sodium amalgam he discovered a new product whose analysis agreed with its formulation as succinaldehyde, and which would thus provide evidence of aldehydes as intermediates in his acid chloride reduction; with further work, however, he proved the structure to be that of γ -butyrolactone; this constituted the first synthesis of this compound (15).

Butlerov's influence pervades most of Zaitsev's scientific work, but nowhere is it more apparent than in his work with dialkylzinc reagents. In 1864, Butlerov had prepared *tert*-butyl alcohol by the reaction between phosgene and dimethylzinc, a method he subsequently extended to the reaction between acid chlorides, in general, and a dialkylzinc (4). The report of this result confirmed the existence of tertiary alcohols, a possibility that had been predicted from a theoretical standpoint four years earlier by Kolbe. As a Butlerov student working under Kolbe's direction when the synthesis of *tert*-butyl alcohol was reported, Zaitsev must have been under intense pressure to acquire an interest in the synthesis of alcohols by means of dialkylzinc reagents. Certainly, Zaitsev's major contribution to organic synthesis was to extend the work of Butlerov in the applications of dialkylzinc reagents in organic synthesis. Zaitsev extended the Butlerov reaction to other carbonyl compounds, including ketones and other acid derivatives; he showed that the reaction between dimethylzinc or

diethylzinc and an ester or ketone would afford the tertiary alcohol (16). At this time, also, his brother and student, Mikhail Mikhailovich, showed that the reaction between a dialkylzinc and an anhydride would give a ketone (17). Zaitsev also showed that the reaction between a dialkylzinc reagent and a ketone may, like the Grignard reaction, give reduction rather than addition: the reaction between 4-heptanone and dipropylzinc fails to give the tertiary alcohol, and the secondary alcohol obtained by reduction of the ketone is the major product of this reaction (18). In many ways, it was Zaitsev rather than his mentor who pioneered the use of dialkylzinc reagents for the synthesis of alcohols.

In addition to his own work, Zaitsev further influenced the development of organic chemistry—especially organozinc chemistry—through his students, several of whom founded their own schools. One of the most brilliant and highly regarded of Zaitsev's students was Egor Egorevich Vagner (or Wagner) (1849-1903), later Professor of Chemistry at the University of Warsaw. As a student under Zaitsev between 1870 and 1875, Vagner developed the first general synthesis of secondary alcohols by the reaction between dialkylzincs and



E. E. Vagner

ethyl formate (19), a reaction which he later extended to the reaction between dialkylzinc reagents and aldehydes (20). Until the advent of the Grignard reaction some thirty years later, this route was the method of choice for the formation of secondary alcohols. It is also interesting to note that the Grignard reaction itself was developed in an effort to improve the yield of the Zaitsev-Vagner synthesis by replacing the zinc atom with a more reactive divalent metal. The Zaitsev-Vagner synthesis of alcohols was rapidly eclipsed by the Grignard synthesis, which was simpler to carry out, and within twelve months the Zaitsev-Vagner synthesis had been relegated to a position of historical interest only. However, the advent of asymmetric synthesis has added a touch of irony to the story: whereas the Grignard addition reaction has proved to be difficult to carry out with high levels of asymmetric induction, Noyori (21) has found that the Zaitsev-Vagner addition is amenable to chiral catalysis to give very high levels of asymmetric induction in the adduct.

Another of Zaitsev's students whose name is associated with synthetic applications of organozinc reagents is Sergei Nikolaevich Reformatskii (Reformatsky) (1860-1934), later Professor of Chemistry at the Uni-



S. N. Reformatskii

versity of Kiev. In his own work, Zaitsev had shown that allylzinc reagents are particularly easy to prepare, and the extension of the concept to α -halocarbonyl compounds must have been a logical one. Certainly, it was Zaitsev who suggested to Reformatskii that he should study the formation and addition reactions of organozinc reagents from α -bromocarboxylic esters. The reaction was first carried out at Kazan' in 1887, so the reaction now known under Reformatskii's name (22) was actually discovered in Zaitsev's laboratory. Until the development of the strong lithium amide bases in the 1970's made preformed lithium enolates routinely available, and the subsequent resurgence of the aldol addition reaction as a method for carbon-carbon bond formation (23), the Reformatskii reaction was the only major synthetic method which could be used to prepare β -hydroxycarbonyl compounds from aldehydes and ketones without significant dehydration.

Zaitsev's master's dissertation described the oxidation of sulfides, and during his doctoral work he began to study the oxidation of unsaturated organic compounds. His interest in oxidation reactions continued for many years after his doctoral studies, and he pioneered the use of alkaline potassium permanganate for the oxidation of fatty acids (24). However, it remained for his student Vagner to realize that this reaction could be applied generally to the oxidation of unsaturated compounds to the corresponding 1,2-diols (25), thus providing a method for fixing the location of double bonds in a molecule. In this form the reaction was widely applied to structural problems in terpene chemistry as the Wagner oxidation.

The third of Zaitsev's students to have a significant impact on the development of modern organic chemistry was Aleksandr Erminingel'dovich Arbuzov, who succeeded his mentor as Professor of Chemistry at Kazan'. Arbuzov was to achieve eminence as an organophosphorus chemist, and he carried out pioneering research into the chemistry of organic phosphorus compounds. As a graduate student under Zaitsev, Arbuzov had begun his studies by carrying out the synthesis of allyl methyl phenyl carbinol, which was published in Russian in 1901 (26). However, the advent of Grignard reagents quickly rendered Arbuzov's initial studies rather moot; the Grignard reagents were easier to make and handle, and the Grignard reaction gave higher yields. For his master's dissertation, he submitted a thesis on phosphorous acid (27), on the chemistry of which he built an eminent career. Arbuzov's impact on modern synthetic organic chemistry is somewhat indirect: the phosphonate esters produced by the Arbuzov-Michaelis rearrangement (28) are the source of the phosphonate anions that are the key reagents in the Wadsworth-Emmons olefination reaction (29).



A. E. Arbuzov

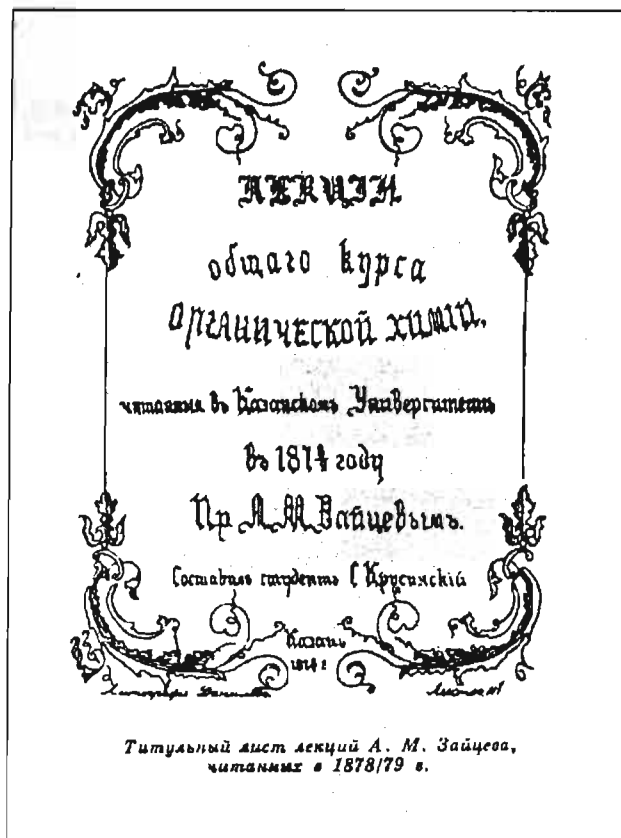
The paper for which Zaitsev's name is included in most organic chemistry textbooks—the paper in which he first expounded the empirical rule for elimination reactions now associated with his name—appeared in *Liebigs Annalen der Chemie und Pharmazie* in 1875 (30). Oddly enough, this paper was often quoted during the ensuing century, but it was not until the 1960's that Zaitsev's name was attached to his rule in most undergraduate textbooks. Even more diagnostic of the changing emphases in organic chemistry: although undergraduate organic chemistry textbooks published during the 1990's still include extensive discussion of the Saytzeff Rule and the underlying reasons for Saytzeff orientation in elimination reactions, they now specify his discovery of the sulfoxides as Zaitsev's major contribution to the development of modern organic chemistry.

Much of the impetus behind the work that led to the Saytzeff Rule, as it is usually spelled in textbooks, was provided by Markovnikov's doctoral dissertation, where it was implied that elimination should be the opposite of addition: that elimination should follow what we now call the Hofmann route instead of the Zaitsev route. It is fairly clear that Zaitsev formulated

his rule largely on the basis of published data, as well as those of his students Grabovskii and Vagner, and that it was published strictly as an empirical rule for predicting the regiochemistry of the dehydrohalogenation reactions of alkyl iodides. What has not been well publicized, however, is the fact that Popov (then a student in Kekulé's laboratory in Bonn) had proposed the possibility of a similar empirical rule in December, 1871, in a letter describing his proposed scheme for the oxidation of *tert*-amyl alcohol to his mentor, Butlerov. In 1872 Popov published a paper on the oxidation of ketones with chromic acid, in which he raised the possibility of the elimination of 3-methyl-2-butanol to the trisubstituted alkene as a possible first step in the cleavage reaction to acetone and acetic acid (31). In 1873, he presented the same view of elimination, illustrating it with the same oxidation reactions, at a chemical conference in Kazan'. In this presentation, he also postulated that proposals made for dehydration reactions might equally be extended to dehydrohalogenation reactions (32). Although it is likely that Zaitsev was unaware of Popov's letter to Butlerov, he was certainly aware of Popov's views on oxidation reactions: in his first paper with Vagner (19) he cites Popov's paper in *Liebigs Annalen*. Nevertheless, in the paper describing Zaitsev's Rule, he gives credit only to Vagner and Grabovskii. The reasons for this are not clear, but after a reading of Popov's *Annalen* paper it is difficult to see just how this work, at least, would have impacted Zaitsev's thinking in more than a peripheral way (certainly, this author would not have felt obligated to quote the Popov paper had he been writing Zaitsev's paper).

Zaitsev spent his entire academic career at Kazan' University, teaching and carrying out research in the tradition of Butlerov before him. In 1878, he wrote a 477-page textbook of organic chemistry (with a 42-page preface); in 1890 it was superseded by a larger, 873-page edition which was used until 1902. Although not a founding member, Zaitsev was among the first to join the Russian Physical Chemical Society, serving as its president in 1905, 1908, and 1909 and as its Vice-President in 1903 and 1910. In 1885 he was appointed a corresponding member of the Academy of Sciences, and in 1903 he was made an honorary member of Kiev University. As a teacher, Zaitsev followed the traditions of his own mentors, Butlerov and Kolbe. Like his mentors, Zaitsev was a "hands-on" teacher, known for his frequent appearances in the laboratory, and he inspired both respect and loyalty in his students.

When viewed as a body, Zaitsev's seventy-five scientific papers are characterized by the same empiricism that pervades most nineteenth-century organic chemistry: Zaitsev's Rule is an empirical statement which was couched in empirical terms; many of his observations



Title Page of 1878/1879 Text by Zaitsev

of the reactivity of dialkylzinc reagents with carbonyl compounds are couched in empirical terms. In none of his papers do we find any of the mechanistic discussions which characterize more modern papers. Nevertheless, when viewed from the perspective of the last decade of the twentieth century, Zaitsev's contributions were widespread and seminal. Unfortunately for Zaitsev, however, much of their importance was not recognized until many decades after his death.

In many ways, Zaitsev was fortunate to live at the time he did. During his lifetime, Russian organic chemistry was characterized by an inventiveness and a vibrancy which it has seldom achieved since, with the frontiers of the science being thrust forward by such luminaries as Butlerov, Vagner, Favorskii, Zelinskii, and Markovnikov. Perhaps it was his misfortune, also. In the absence of such company, perhaps his own contributions to the science would have been recognized earlier, and his own star would have shone more brightly.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the help of Dr. Nathan M. Brooks of New Mexico State University through

several telephone conversations during the preparation of this manuscript. *Credit:* The photographs of Zaitsev (1867), the Kazan' Chemical Laboratory, and the title page of Zaitsev's text are taken from the biography by Klyucheich and Bykov, Ref. 2b.

REFERENCES AND NOTES

- Zaitsev's name is generally spelled two ways in this manuscript: In the references to journal articles in German and French his name is spelled exactly as it appears in the journal (Saytzeff), and it is transliterated from the Cyrillic as Zaitsev for journal articles in Russian. The same treatment has been applied to the journal articles of other Russian chemists. Russian-language sources are indicated by [Russ.] after the complete citation. Most of Zaitsev's papers appeared in both Russian (in *Zh. Russ. Phys.-Khim. Obshch.* quoted below as *J. Russ. Phys. Chem. Soc.*, or in *Zh. Russ. Khim. Obshch.*, quoted as *J. Russ. Chem. Soc.*), and German or French. Because of the limited accessibility of the Russian sources, the German or French references are quoted in the list below wherever possible.
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FRITZ FEIGL (1891-1971)

The Centennial of a Researcher

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Mario Abrantes da Silva Pinto, CONSULTEC, and
Claudio Costa Neto, Universidade Federal do Rio de Janeiro*

Fritz Feigl would have celebrated his 100th birthday on May 15, 1991. It was quite unfortunate he passed away on January 23, 1971, from a cerebral thrombosis. This article, representing the gratitude and admiration of his friends and former coworkers from the Laboratório da Produção Mineral, Rio de Janeiro, Brazil (where he worked from 1940 until his death) is intended to document and analyze the importance of his work. It is divided into three sections: first, an overall view of his life and personality are presented, based, in part, on data extracted from publications celebrating his 70th birthday and memorial lectures (1-7), but mostly from recollections of the authors. This is followed by a critical appraisal of his scientific production. Finally, the response of the scientific world to his discoveries and their ramifications is presented.

Early Life in Europe

Feigl was born in Vienna, then the Austro-Hungarian capital. He descended from a well-to-do Israeli bourgeois family of good cultural background. As a Kohen—a descendent of the priests from the time of the temple of Jerusalem—he was named Efraim ben Shemuel Hakohen. As a member of the highest priestly class, he had the right to bless the Israeli people and to serve in the Temple of Jerusalem (7).

Educated in Vienna, he developed a fine taste in literature and classical music. He liked outdoor activities; when he lived in Europe, he used to climb mountains, ski, and walk in the Wienerwald. The habit of strolling he maintained in Rio, where he used to go on foot daily (ca. five kilometers) along the shores of Ipanema and Copacabana, to his laboratory, located in Praia Vermelha.

After finishing his humanities studies, he graduated in Chemical Engineering from the Technische Hochschule in 1914, the year when the First World War started. He served as an officer in the Austro-Hungarian Army during World War I; was wounded in battle on the Russian front, and returned as captain with a bronze and a silver medal and the Military Service Cross. When the war ended, he resumed studies at the University of Vienna, obtaining his doctorate in chemistry on 1 April 1920, under Prof. Spath, with a thesis entitled "Über die Verwendung von Tüpfelreaktionen in der qualitativen Analyse."

His vocation was dedicated to the academic world; he soon joined the faculty of the University of Vienna as Assistant Professor (1920); became Dozent in 1927, Professor of Inorganic Analytical Chemistry in 1935, Full Professor in 1937, staying until 1938. His teaching extended to the Volkshochschule in Vienna, a School created by the republican government of Austria to give opportunity for study at the university level to those who, returning from war, had to maintain daytime occupations. There he taught undergraduate courses in chemistry for no fee, three times a week, from 6-9 pm, for many years, until his exile in 1938.

At the University of Vienna, G. Hirsch (1921), F. Rappaport (1923), S. Taubes (1924), E. Chargaff (1929), K. Weissberg (1930), H. Kapulitzas (1930), L. Weidenfeld (1930), E. Rajman (1936), V. Anger (1936), V. Demant (1937), among others, worked under his supervision (8).

Early in his life he met Regine Freier, a seventeen-year-old Israeli girl, who came to Vienna in 1914, as a refugee from Kolomyia, in the Carpathian Mountains, East Oriental Galicia Poland, fleeing from the Russian troops. In Vienna, she initially studied accounting; later,

in 1919, she started chemistry, working under Feigl's supervision, to graduate with a thesis on sulfuric acid. In 1924 Feigl married Regine (she had previously been married to an Austrian banker).

She bore him a son, Hans Ernest, who came to Brazil at an early age and did all his studies through the university in this country. Graduated in chemistry, he became his father's coworker, with some published papers. Hans received a Ph.D. in Chemistry at the University of Zürich, under Paul Karrer, with a thesis entitled "Neuere Arbeiten über syntetische Pterine;" his post-doctorate was terminated abruptly by his death from cancer in 1954; according to his wishes, he was buried in Rio de Janeiro, Brazil.

Regine Feigl had an important role in Feigl's life; she had a strong personality, was a brilliant business woman, and contributed significantly to establish the family's fortune. She would always mention how proud she was of her husband's scientific success.

In 1938, as a consequence of the Anschluss in Austria, the Feigl family emigrated from Vienna to Switzerland, and then to Belgium, where they started their lives again (Feigl had already been, for a long time, a techni-

him as a Jew. Due recognition must be made that the 2nd. English edition of his book *Qualitative Analysis by Spot Tests* (1939) carries, in the preface, a dedication to his honored colleagues of the University of St. Andrews, as gratitude for their liberal attitude.

The Move to Brazil

In 1940, Belgium was invaded by the Nazis. As a Jew, Feigl was soon transferred to a concentration camp near Perpignan. Mrs. Feigl, away on that occasion, only later was informed of Feigl's destiny. Regine and Hans moved to Toulouse, near the camp. There she had the opportunity to contact the Brazilian Ambassador in Vichy, Luiz de Souza Dantas, who obtained the necessary visas for them to enter Brazil. They left for Andorra, in the East Pyrenees, and from there went to Portugal; in Lisbon, they embarked to Brazil aboard the ship *Serpa Pinto*, arriving in Rio de Janeiro on 29 November 1940, as a refugee family. Feigl, then 49 years old, settled permanently in Rio.

After the end of World War II, when scientific exchanges were taken up again, Feigl received many invitations to work in other parts of the world, mainly from the United States and England. As gratitude for his and his family's reception in Brazil, as well as for the intervention of Brazilian authorities to rescue Mrs. Feigl's two brothers who were also in a concentration camp in France, they never left Brazil. Within five years, in avowed recognition of his contribution to science, he was granted Brazilian citizenship.

How did Feigl come to settle in the Laboratório de Produção Mineral (LPM), in Rio de Janeiro? A professor of the Escola Nacional de Agronomia of the Universidade do Brasil, Coriolano Pereira Jose da Silva, learning of Feigl's arrival in Rio, informed Mario da Silva Pinto, then Director of the LPM, who, understanding the importance of obtaining the cooperation of such a researcher, immediately alerted his superiors, the General Director of the Departamento Nacional de Produção Mineral (DNPM), Jacques de Moraes, as well as the Minister of Agriculture, Fernando Costa. He insisted on the advantages of having Feigl settle in Brazil and establish a research center in microchemistry. It would also be possible to assign him work on a number of relevant technological problems. Within two weeks Feigl was contracted at the LPM and, at the end of 1940, he took up his post as a researcher, which he maintained for over twenty years until his formal retirement in 1961, although he continued working to the end of his days. At the LPM, a small laboratory was set up for him; during



Figure 1 Feigl and son, Hans Ernest

cal consultant on photographic emulsions to Gevaert, in Antwerp). There he carried on research in an industrial laboratory, as well as university teaching in Ghent.

While in Belgium, he received an invitation from the University of St. Andrews, in Scotland, to continue his research at that university; the opportunity to leave Belgium did not materialize, because, as a consequence of Austria's annexation to Germany, his passport became a German one, carrying a capital letter "J" identifying



Figure 2 C. P. Ferreira, D. Goldstein, F. Feigl, I. M. Kolthoff, A. Espinola, O. R. Gottlieb (Rio Airport, 1956)

the period of its installation, he went to work as a guest of Prof. Coriolano P.J. da Silva and his assistant Alcides Caldas, in their analytical chemistry laboratory, at the Escola Nacional de Agronomia which was then next to LPM.

At the LPM, Feigl created a new research line. He started with four Brazilian LPM chemists as assistants: G.F. Dacorso, P.E.F. Barbosa, L.I. Miranda and N. Braile; a short course on "Spot Tests" was taught at the end of 1941. His dedication to work was extraordinary; he was the first to arrive at the laboratory in the morning and the last one to leave in the evening. Research papers immediately started appearing, and within one year the Bulletin was published with the title "Microchemical Investigations," a reporting of the work developed in the period May-December 1941. This publication was followed by five other LPM Bulletins on similar subjects. These were followed, in 1943, by two other publications, "A Laboratory Manual of Spot Tests" and "The Spot Tests in Chemical Teaching," both in Portuguese.

Two technological problems were assigned by the Director of the LPM to Feigl: the first one, on caffeine, a scarce but valuable chemical at that time, and the second on the phosphate deposits at Gurupi. He and A. Schaeffer, from the Brazilian Military Technical School, developed a process to extract caffeine from coffee by sublimation at reduced pressure. The process gave excellent results on a bench-scale, but, when it came to scale-up, was unsuccessful. Feigl, then, in a short period devised another process employing the abundant

and inexpensive solvent kerosene to extract caffeine from concentrated coffee water extracts, which turned out to be highly efficient. Because Brazil was overproducing coffee, part of this excess was then used to produce caffeine. A quantity of 500 tons of the product was obtained at the Companhia de Produtos Quimicos Alka, in Santo Andre (Sao Paulo), from the expandable quota of the National Coffee Department. About 48,000 tons of coffee were processed instead of being dumped into the sea or incinerated; and the highly valued product which resulted was marketed domestically and exported.

The Companhia de Produtos Quimicos Alka, which had been founded with contributions of shareholders, had Mrs. Feigl as Technical Director, Mario A. da Silva Pinto as Technical Consultant, and Ciro Lustosa as Industrial Manager, who was also responsible for running the plant. This lasted for three years; as the war ended, foreign markets were reopened, and all coffee production became negotiable; as a consequence, the necessary raw material was no longer available. The three years of operation made feasible the start of the Feigl family fortune, which later became considerable, due mainly to Mrs. Feigl's extraordinary business competence.

In 1946 another technical problem was assigned to Feigl: the solubilization of the phosphate contained in the phosphorus bauxite of Gurupi; this is an aluminum phosphate, which occurs in this region of Maranhao, Brazil. The process developed was ingenious: a molecular disorder was thermally induced in order to allow the phosphate to become soluble in ammonium citrate. The mined bauxite, after fragmentation, was thermally treated in a rotary furnace. An experimental field test of the practical utilization of the invention was then prepared and put under the responsibility of Alvaro Barcelos Fagundes, at that time Director of the Instituto de Pesquisas Agronomicas. The fertilizer was tested in several experimental stations, but unfortunately this developmental study did not result in any commercial operation although a patent was granted to LPM.

Upon his arrival in Rio, it was not easy for Herr Prof. Dr. Eng. Fritz Feigl, accustomed to the formal environment of the European universities, to adapt to the atmosphere of freedom and informality of the new world,

more so that of Rio de Janeiro. But he soon learned to enjoy the tropics; all Feigl's homes in Rio were located right on the shore of the most famous beaches, first in Ipanema, later in Copacabana. He just had to walk across the street to the white sand and swim in the warm waters of the Atlantic Ocean. In the long walks from home to his laboratory, his skin acquired a beautiful tanned look, for which he received the kind nickname of "baiano" (native of the state of Bahia).

When Feigl immigrated to Brazil, he already had experience at a university as well as a research career: he had been Full Professor at the University of Vienna, where he published one hundred and sixty papers, three German editions of his book *Qualitative Analyse mit Hilfe von Tüpfelreaktionen* and two English editions of this same book, under the title of *Qualitative Analysis by Spot Tests*. In Brazil, where he directed a large number of competent collaborators, he revealed his incomparable capacity of starting up again without losing his courage, idealism, or confidence in humanity. In this new environment, he encountered a number of young chemists who understood the privilege of working with such a notable man of science; many of them came from abroad, from different countries to his laboratory in LPM: Phillip W. West (Louisiana State Univ.), Hans A. Sutter (Celanese Chemical Co.), and F. L. Chan from the United States; Y. Hashimoto from Kyoto, Japan; E. Jungreis from Israel; and Ramon Rossel from Argentina.

Thirty five Brazilians may be counted as his disciples. Whenever he had an opportunity, he used to exalt the intellectual capacity and the dexterity of his Brazilian coworkers, whom he considered of the same high level as those he had in Vienna. To the competent and studious chemists at LPM the opportunity was given to spend some time in Feigl's laboratory, returning, afterwards, to their regular activities.

Recognition and Honors

Feigl's work found wide recognition in Brazil and abroad. For his outstanding achievements in analytical chemistry, many honors were bestowed on him, which attest to his tireless efforts in internationally promoting interest in spot tests. While still living in Vienna, he received the Heitiger Prize of Chemistry and the Pregl Prize of Microchemistry, from the Austrian Academy of Sciences; later, he was awarded the Weizmann Prize for Natural Exact Sciences of the City of Tel-Aviv, the Hexler Prize of Vienna, the Great Prize of Science and Culture of Austria; the Emisch Medal of the Austrian Academy of Microchemistry; the Gold Medal of the City

of Vienna (the Ehrenmedall der Bundeshauptstadt-Wien, 1967), the Wilhelm Exner Medal, of the Austrian Industrial Society; the Talanta Medal, of the Pergamon Press. In Russia in 1962, he received the Lomonosov Medal of the Academy of Sciences of Moscow.

In Brazil, he received the Order of Rio Branco, from the Brazilian government, the Albert Einstein Prize of the Brazilian Academy of Sciences, and the Moinho Santista gold medal Prize from the Moinho Santista Society. He also received many university titles and memorabilia: Doctor Honoris Causa of the Universidade do Brazil (now Universidade Federal do Rio de Janeiro),

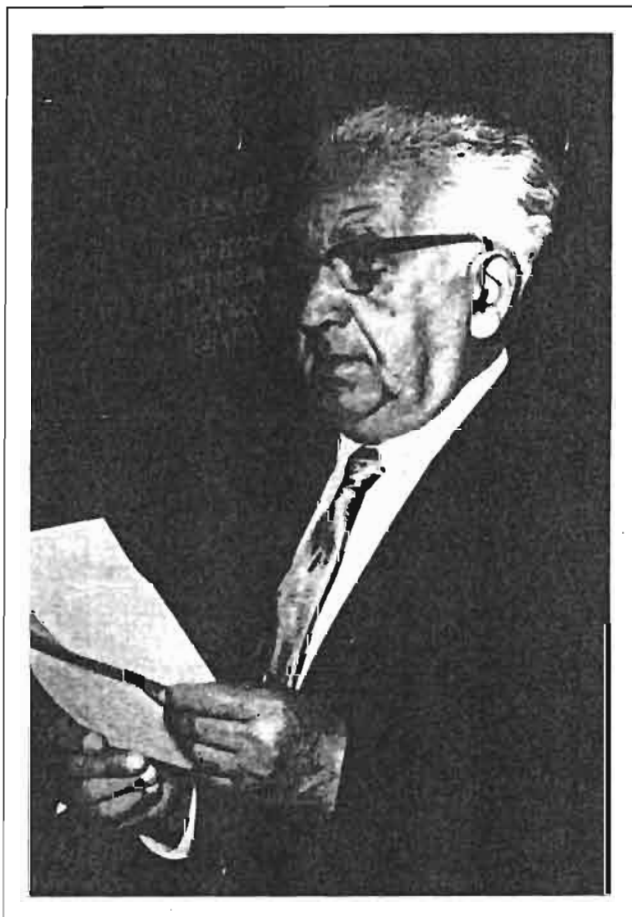


Figure 3 Fritz Feigl, Feigl Symposium, Rio de Janeiro, November, 1962

the Universidade de Sao Paulo, the Pontificia Universidade Catolica do Rio de Janeiro, Technische Hochschule of Vienna and the University of Jerusalem. In 1958, he was made Emeritus Professor of the University of Tokyo, receiving a medal and a bronze sculpture from the Pharmacological Society of Japan. He was Governor of the Hebrew University of Jerusalem and belonged to the Board of Governors of the Weizmann

Institute in Rehovot, Israel. He was made honorary citizen of the State of Guanabara, Brazil, and of the city of Baton Rouge, in the USA.

Feigl was a corresponding member of the Austrian Academy of Sciences and Fellow of the Academies of Science of Gothenburg and of New York. He was a Full Member of the Swedish Academy of Sciences and of the Brazilian Academy of Sciences. He was also a member of the Austrian Society of Microchemistry, the Austrian Association of Chemistry, the Midland Section of the Society for Analytical Chemistry, the Society for Analytical Chemistry (London), the Japanese Society for Analytical Chemistry, the Japanese Society for Pharmaceutical Chemistry and of the Brazilian Pharmaceutical Association. On 10 April 1970, he was elected Member of the Pontifical Academy of Sciences of the Vatican, in chair number 54.

Laboratories were named in his honor: his laboratory in the LPM, as well as one in the Weizmann Institute and another at the University of Recife (Brazil).

His 70th birthday was extensively celebrated. The Chemical Society of Midland sponsored a symposium in Birmingham, from 9-12 April 1952, which was attended by nearly 500 scientists from 24 countries. All plenary sessions were related to spot tests. The proceedings of this symposium characterized Feigl by saying that "His incomparable knowledge of chemical reactions and his ability to explore them for analytical purposes qualify him as one of the greatest analytical chemists of all times." Commemoration of his 70th birthday in Brazil included the placement of an engraved bronze plate in his laboratory at the LPM and the "Feigl's Symposium," which was held by the Brazilian Academy of Sciences from 16-23 of November, 1962, in Rio de Janeiro. This symposium was sponsored by the Academy, the Brazilian Research Council, the University of Brazil, the University Sao Paulo, the Pontifical University of Rio de Janeiro, and the Brazilian Chemical Society. Papers were presented by the most representative members of the Brazilian chemical community, and several foreign researchers participated: R. Belcher (U. of Birmingham, UK), P. W. West (Louisiana State U., Baton Rouge, USA), H. Malissa (Institut für analytische Chemie, der Technische Hochschule, Wien, Austria), D. L. Rucknagel (Univ. of Michigan, Ann Arbor, USA), H. J. McDonald (Stricht School of Medicine of the Loyola Univ., Chicago, USA), C. Djerassi (Stanford Univ., Calif., USA), A. Bondi (Agricultural Research Station, Rehovot, Israel), H. Weiss (Chemisches Institut der Universität Freiburg, Germany) (9).

Feigl was proud of the capacity of the Jews to revive, reestablish, become active and flourish again, after persecutions and losses. He was proud of the reconstruction of the State of Israel and contributed to the grandeur of the University of Jerusalem. Regine Feigl, a Jew, was also a good friend of Catholics; in Galicia, Poland, she studied in an Ursuline school because of the good quality of education provided. The Feigl family was very interested in the Jewish community of Rio, his name appearing in all new organizations, such as the Federation of Israeli Societies of Rio de Janeiro and the Israeli Confederation of Brazil; Feigl was the Chairman of the Brazilian Israeli Society. Good benefactors, they contributed with substantial donations to the Pontificia Universidade Catolica do Rio de Janeiro and to universities and research centers in Israel, to causes for poor students, providing them with scholarships.

Feigl died when he was almost 80 years of age. He maintained his interest in chemistry and in research for ten years after his retirement from LPM; his mind was clear until October, 1969, when a thrombosis incapacitated him until January 23, 1971, the date of his death. In the words of Dr. Henrique Lemle, Grao-Rabino of the Israeli Religious Association of Rio de Janeiro, at Feigl's funeral, "All three crowns - the Tora (of knowledge), the Kehuma (of the priesthood), and the Kalkhut (of the kingdom) characterize in a special form the life of Fritz Feigl (7)."

Everybody who worked with Fritz Feigl held the conviction that he was a great scientist and admired him for his intuition, his knowledge of chemical reactions, and his incredible ability to develop new spot tests. His strength in dealing with adversities, contagious enthusiasm, happiness, and satisfaction with work can never be forgotten by his LPM colleagues. He is sadly missed by his many disciples everywhere.

His Work

Feigl was a very productive scientist. It is to be noted that he started publishing in 1919 and maintained a considerable level of creativity except in the period 1940-1941, during his persecution by the Nazis and his move to Brazil.

His productivity in Europe, up to 1939, totaled 160 papers; as a grand total, he published 436 articles, according to a complete list of his original papers presented by Anger (10). A list of his twenty books can be found in the 1971 *Almanac of the Austrian Academy of Sciences* (11) and in *Analytica Chimica Acta* (10). The present authors raise this number to 24, by including

the Portuguese publication *Reacoes de Toque no Ensino da Quimica*, (Boletim n. 12 do Laboratorio da Producao Mineral, Rio de Janeiro, Brasil, 1943, 112 pp); two translations in Russian of the *Spot Tests in Inorganic Analysis* (12) and a Japanese version of *Spot Tests in Organic Analysis*, 5th edition.

His first book, *Qualitative Analyze mit Hilfe von Tüpfelreaktionen*, Academische Verlag-schaften, Leipzig, 1931, with 387 pages, appeared in several editions and translations into English and other languages, each new edition being enlarged and improved, containing a considerable number of new tests, improvements to known ones and updated explanations of the chemistry of the reactions on the basis of new concepts. These books reflect his personal experience since most of the tests were developed either by himself or under his direction.

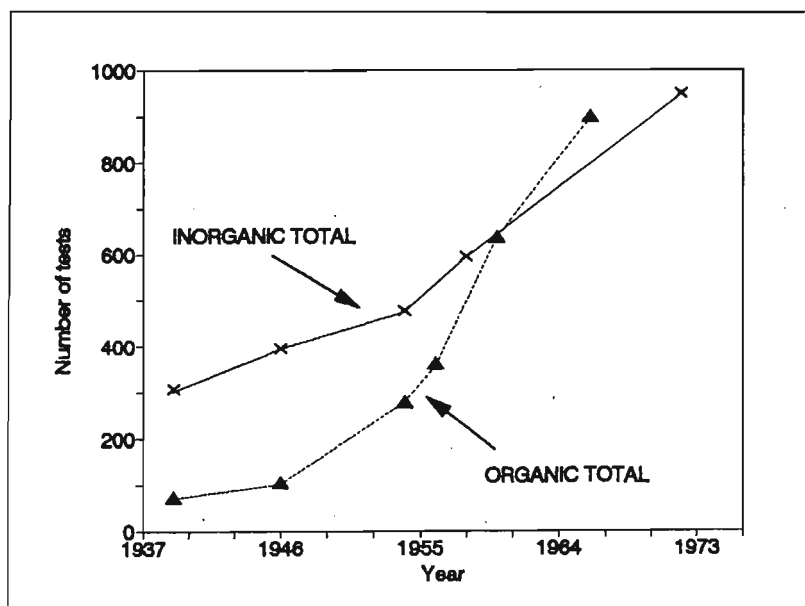


Figure 4 Number of Spot tests in Editions of Feigl's Texts

The progression of the number of new tests presented in the various editions of the *Spot Tests* is shown in Fig. 4 (13). The dramatic increase of organic tests in each new edition is particularly striking.

His Brazilian research production was larger than that of the European epoch. Out of his total of 436 articles, 276 were written in Brazil, in collaboration with Brazilian chemists. His masterpiece, *The Chemistry of Specific, Selective and Sensitive Reactions* was entirely written in Brazil (13).

His Legacy

Although Feigl was the great developer of spot tests, the earliest "spot test" registered in the literature was Hugo Schiff's detection of uric acid in 1859 (14): a drop of an aqueous solution of this acid placed on filter paper impregnated with silver carbonate resulted in a gray or black fleck of finely divided silver. This finding coincided with the first studies of Christian Friedrich Schönberg and Friedrich Goppelsröder on capillary analysis. It can be said that Feigl's work was based on these pioneering ideas. His early association with Friedrich Emich was also of great influence to his work; as a researcher in microchemistry, he followed F. Emich and F. Pregl, already well known researchers in this field. In the period 1917-1923 he introduced new methodology for the characterization of inorganic species, exploring the combination with organic reagents, which led to intensely colored products. This gave rise to the technique of spot tests ("Tüpfelanalyse" in German, "Analyse de Touche" in French, "Analyse de Toque" in Portuguese).

The spot test method allowed for the detection of as little as one nanogram of the substrate in a drop of solution, corresponding to a dilution of 1:5,000 - 1:500,000,000. The important concepts of "Limit of Identification" and "Dilution Limit" (or its reciprocal, the "Concentration Limit") all defined by numerical values, were developed by Feigl to deal with these levels of detection of the substances. As important as these concepts for analytical chemistry was the differentiation between "specific" and "selective" reactions (and reagents), accepted and recommended by IUPAC (16, 17) as an "official" jargon for analytical reactions.

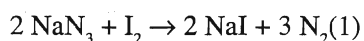
Organic reagents exhibited a special suitability for spot tests. A systematic study of the use of organic reagents in chemical analysis led Feigl to pioneer a relationship between selective and specific properties of reagents and certain structural factors, the reactive groups. In 1936 he authored the first analytical and interpretative presentation in English on the use of organic reagents in inorganic analysis (18). This was followed by another article (19) and by his major literary production in book form, *Chemistry of Specific, Selective and Sensitive Reactions* (15). The search for new spot reactions or the improvement of the selectivity for the ones already known had a definite role in stimulating the preparation of new organic compounds. The sys-

tematic study of the use of organic reagents in chemical analysis led Feigl to pioneer a relationship between selective and specific properties of reagents and certain structural factors, the reactive groups. In 1936 he authored the first analytical and interpretative presentation in English on the use of organic reagents in inorganic analysis (18). This was followed by another article (19) and by his major literary production in book form, *Chemistry of Specific, Selective and Sensitive Reactions* (15). The search for new spot reactions or the improvement of the selectivity for the ones already known had a definite role in stimulating the preparation of new organic compounds. The sys-

tematization of relationships between atomic groupings in organic compounds and selective action on metal ions enriched the chemistry of coordination compounds, leading to the isolation of new complex organometallic compounds. This happened in his own laboratory with Goldstein's discovery of glyoxal bis(2-hydroxyanil) as a reagent for calcium (20). Feigl's research extended the ways in which chemical reactions can be employed in analysis: the widespread use of organic compounds as precipitation, color, and masking agents; the utilization of catalyzed and induced reactions; solid-phase reactions at elevated temperatures and reactions in the gas phase through contact with suitable solid or dissolved partners (21); pyroreactions, as pyrohydrolyses and pyroammonolyses; reactions yielding fluorescent products or those that quench fluorescence; interfacial effects such as the adsorption of dyestuffs on metal oxides or hydroxides, producing colored lakes, in which chelate bonding is fundamental. Last but not least should be mentioned the importance of conditioning of tests to enhance sensitivity or selectivity; he emphasized that it is not correct to speak of the sensitivity of a reaction without reference to the conditions under which the test is performed.

Results from other fields were introduced by Feigl in spot tests. The use of induced and catalytic effects was entirely new in analytical chemistry at the time he published his first paper on the subject. Some outstanding examples of contributions are given below.

- Test by catalytic acceleration of the iodine-azide reaction (22). The redox reaction



is very slow. Nevertheless, it can be catalyzed by inorganic sulfides, thiosulfates and thiocyanates, and also traces of solid or dissolved organic compounds containing the C=S or C-SH groups. A very sensitive detection procedure for these groups was accomplished by spot tests, with extraordinary limits of identification, as, for example, 0.0003 γ for thioacetic acid at a dilution limit of 1:100,000,000.

- Test by catalytic acceleration of the formaldehyde-o-dinitrobenzene reaction (23). The reduction of o-dinitrobenzene by formaldehyde proceeds very slowly in alkaline carbonate solution, but 1-2-dioxo compounds catalytically accelerate this reaction to such an extent as to effect a very sensitive test for α -diketones, p- and o-quinones. The sensitivity is extraordinary for the following dioxo compounds: 0.05 γ diacetyl; 0.05 γ anthraquinone; 0.002 γ phenanthraquinone; 0.01 γ 2-me-

thyl-1-4-naphthoquinone (vitamin K₃); 0.002 γ 3-nitrophenanthraquinone.

- Test for basic compounds with nickel dimethylglyoxime or zinc 8-hydroxyquinoline solutions (24). The reagent is the saturated nickel dimethylglyoxime (water-alcohol) equilibrium solution containing Ni²⁺ and H⁺ ions. As basic materials such as ethylenediamine, diethanolamine, benzidine, etc., remove H⁺ ions, black nickel dimethylglyoxime precipitates. The sensitivity of this test is 5 γ ethylenediamine, 20 γ diethanolamine, 2 γ α -naphthylamine, 15 γ p-phenylenediamine, 10 γ benzidine, and 15 γ tetrabase (4). Inorganic analysis also benefitted from spot tests. Relevant examples of very sensitive inorganic spot tests are shown in Table 1 (23).

Despite the sophistication of modern instrumental analyses, spot tests find large-scale application in areas in which it is important to obtain a quick response, with a simple, rapid, and inexpensive technique. These are, for instance, "screening tests" in clinical analysis; control of the quality of air; food analysis, water analysis; soil tests; geochemical prospection; forensic tests. Some of the most frequently performed tests routinely applied are described by Jungreis, who published a descriptive book with details and methodology of some hundreds of applications of spot tests to these various fields (26). Many companies in the US and Europe manufacture compact systems ("kits") based on spot tests applied to clinical analyses (26). Such kits are produced either in the form of tablets or as plastic strips ("dipsticks") with eight or nine separate reagent areas affixed, which may be interpreted visually or, preferably, with a reflectance scanning instrument. These "dipsticks" allow for measuring of glucose, protein, ketones, occult blood, nitrite, bilirubin, and urobilinogen at different concentrations of each substance.

The Spot Tests philosophy applied by Costa Neto has led in other directions, as, for example, that in the analysis of geochemicals (bitumes, kerogen, oil, etc.) and other complex mixtures such as plant extracts, beverages, etc. (27). This approach, now called "Solid Phase Functional Group Analysis," comprises three main methods: the Solid Phase Extraction (a separation method used to fractionate complex mixtures according to its functional group content); the Solid Phase Functional Reagents (functional group reagents, leading to colored products, bound to a solid matrix, used to analyze trace amounts of compounds in dark materials like bitumes etc.) and the Functional Marker Method, used to analyze functional groups in solid materials (as kerogen, for instance).

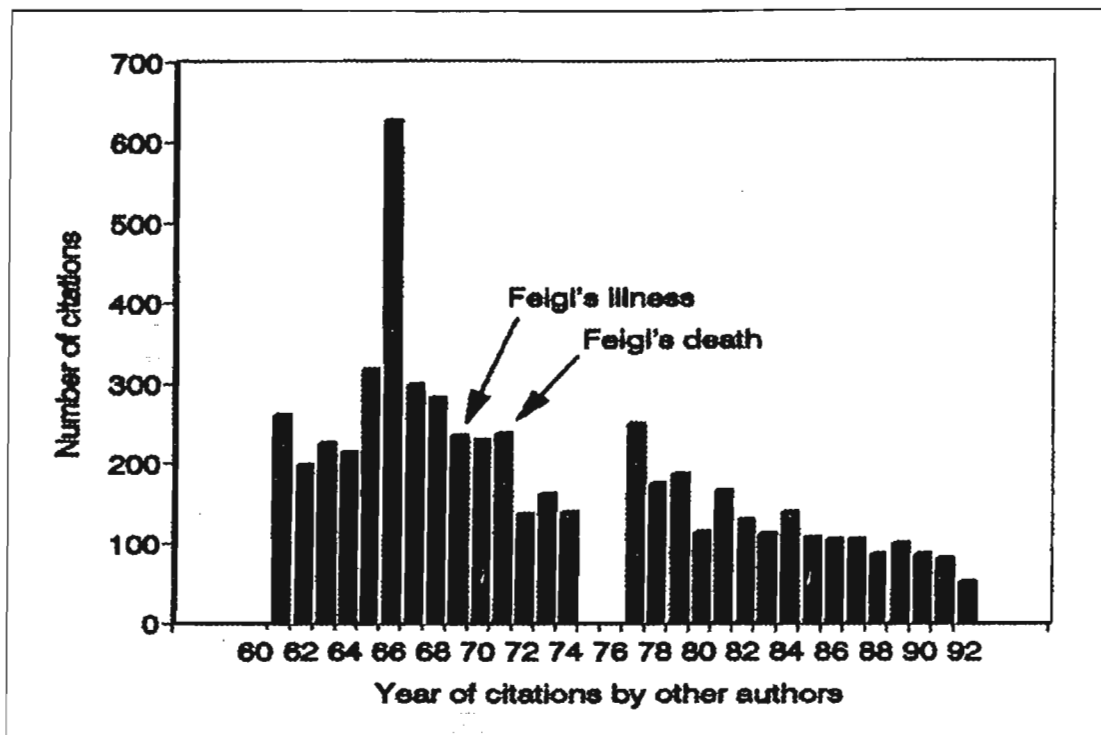


Figure 5 Citation of Feigl's Publications (*Science Citation Index*)

The development of reactions and methods of analyses based on Feigl's discoveries is impressive. Figure 5 shows the data between the period 1961 to the present for 3,560 references to his work, recorded in *Science Citation Index* (28). More impressive still is the existence of 52 references to his work in 1992, twenty-one years after his death. It is estimated that Feigl's work has been cited 5,000 times since 1961.

Feigl was not a man of only hands-on work at the laboratory bench, but also a philosopher of chemistry. As he used to say, "Chemical equations don't translate all changes in a reaction system; they convey the chemical fate of the reactant system." This is also referred to in one of his articles in Portuguese (29) as well as in Chap. XI of one of his books (15), when he says: "If the formation of materials by chemical means involved nothing beyond the mere reaction, then, the chemical process which is accomplished in accord with its stoichiometric formulation would invariably lead to products of the same form, species, color, solubility, etc. Experience has repeatedly demonstrated that this is not always true. Although an equation represents the most important part of a chemical event, nevertheless, it cannot portray everything that happens in the course of the formulation of a material."

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**EUGENE GARFIELD
POSTDOCTORAL FELLOWSHIP
IN THE
HISTORY OF SCIENTIFIC
INFORMATION**

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THREE HUNDRED YEARS OF ASSAYING AMERICAN IRON AND IRON ORES

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It can reasonably be argued that of all of the industries that made the modern world possible, iron and steel making holds a pivotal place. Without ferrous metals technology, much of the modern world simply would not exist. As the American iron industry grew from the isolated iron plantations of the colonial era to the complex steel mills of today, the science of assaying played a critical role. The assayer gave the iron maker valuable guidance in the quest for ever improving quality and by 1900 had laid down a theoretical foundation for the triumphs of steel in our own century.

Yet little is known about the assayer and how his abilities were used by industry. Much has been written about the ironmaster and the furnace workers. Docents in period dress host historic ironmaking sites and interpret the lives of housewives, miners, molders, clerks, teamsters, and hostlers. The assayer goes unrecognized. Part of the reason for this is that the assayer did not become an integral part of the works until after the Civil War. Hard won empirical knowledge guided the operation of furnaces and any need for detailed analyses could be provided by outsiders. Finally, a better understanding of metallurgical chemistry, combined with increasing process sophistication, more demanding industrial applications, and rising production costs made on-site laboratories both practical and desirable.

Between the early colonial period and the end of the nineteenth century, American iron production progressed from a tradition based, empirically directed enterprise to a scientifically managed industry. The assayer played an important role throughout this process. Even though assaying was an established branch of metallurgy by the mid 1500's, laboratories were not incorporated into most ironworks until after the 1860's. A number of

factors were behind this development; increased process sophistication, a better understanding of how impurities affected iron quality, increased capital costs, and a generation of chemically trained metallurgists entering the industry. This paper describes the major advances in analytical development. It also describes how the 19th century iron industry serves as a model for the way an expanding industry comes to rely on analytical data for process control.

1500's to 1800

By the mid 1500's the operating principles of assay laboratories were understood and set forth in the metallurgical literature. Agricola's *De Re Metallica* (1556), Biringuccio's *Pirrotechnia* (1540), and the *Probierebüchlein* (Assaying Booklet, anon. 1510) all describe assaying techniques. (1, 2, 3) The use of cupels, fluxes, acids and quantitative analysis were understood and applied even though it would be several hundred years before a theoretical framework was available to the practicing assayer (1).

Agricola and Biringuccio both believed in direct observation and had a modern appreciation of practical experience. Both men assured their readers that if the assay were done carefully, the orebody's yield could be accurately predicted. Agricola went on to say that great care must be taken because a small error will be multiplied many times in bulk processing. He recommended two or three determinations and averaging the results (1). Biringuccio admonished the assayer to trust no one and weigh everything (2).

Although these works describe the analysis of precious metals in great detail, their instructions for iron

analysis seem rudimentary. Biringuccio states that since tin, lead, copper, and iron could be smelted to determine purity, less care is required than with the more valuable precious metals. None the less, he does give directions for evaluating iron ores. A sample of ore is soaked in a strong solution of lye. Afterwards, it is placed on a well burning fire and develops the color of the "fumositities" (volatile impurities?) which issue from it. The assayer can employ a small bellows or blowpipe after soaking in order to study the bubbles which form. They are an indication of the "evilness" (2).

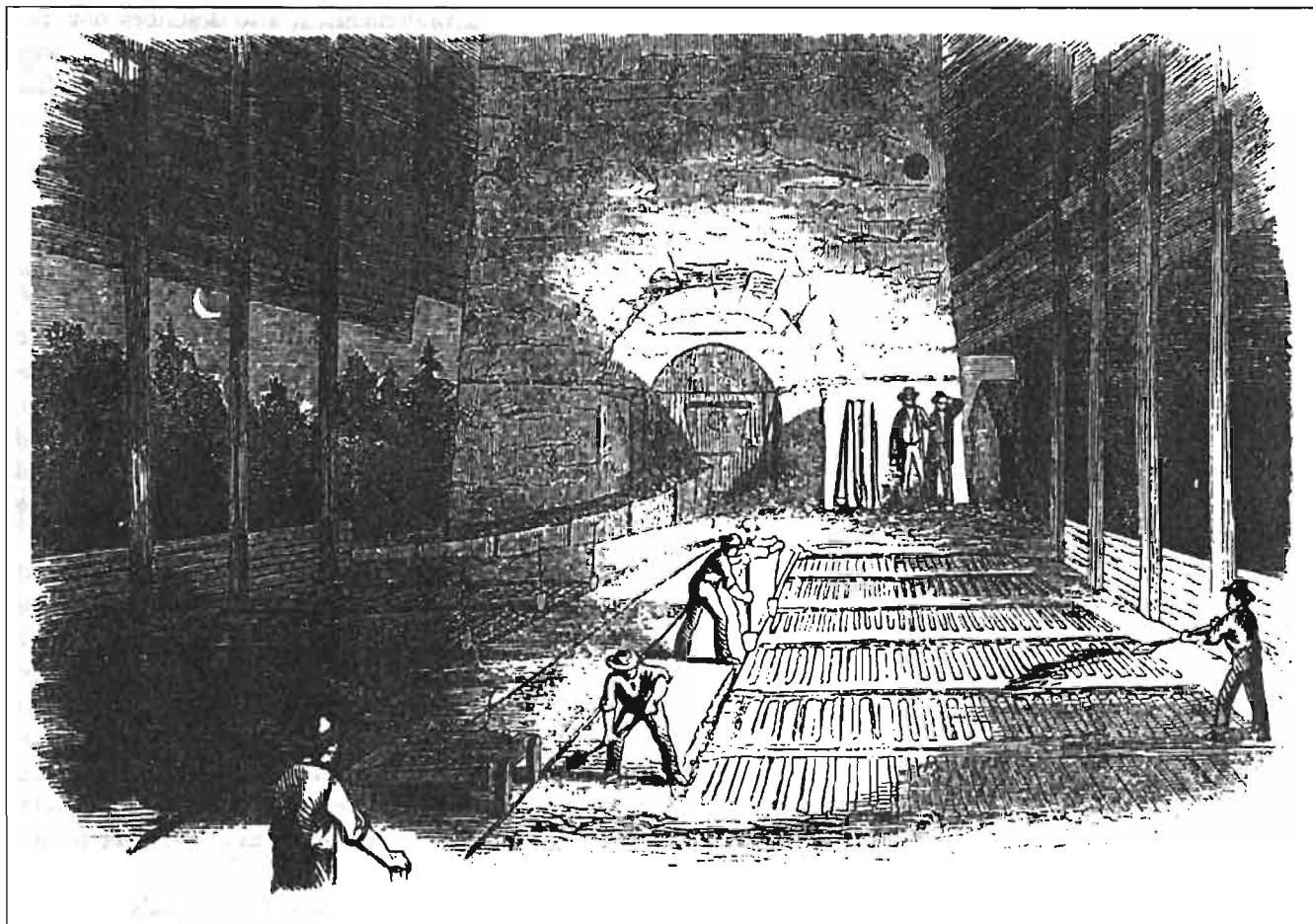
Biringuccio's discussions of iron include visual descriptions intended to help the miner select good ores. Color, porosity, foreign inclusions, and texture are described (2). Agricola takes Biringuccio's idea of smelting ores to obtain their metallic content one step further by giving detailed instructions for iron. They are worth noting since they will be essentially unchanged for another three hundred years. The ore is first burnt. Then it is crushed, washed and dried. The assayer then uses a magnet to concentrate the iron-rich particles and sweeps

them into a crucible with a small brush. Saltpetre is added to the crucible which is then heated until only pure iron remains. The whole operation can be performed in a blacksmith's forge (1).

Such was the state of the art when the English began to explore North America in the late 1500's. Assayers often accompanied early expeditions to America. A German assayer, as well as "mineral men and refiners," accompanied the 1583 expedition to Newfoundland. We may never know exactly what was discovered because both samples and scientists were lost in a shipwreck (4).

The first recorded trial of North American iron ores by an English assayer was in 1585, during a reconnaissance prior to the establishment of the Roanoke Island Colony. According to Thomas Hariot, colony historian and servant of Sir Walter Raleigh (5),

..in two places of the country specially one about four score and the other six score miles from the fort or place where we dwelt, wee found near the water side



Interior of Blast Furnace from "Among the Nail-Makers," *Harpers*, June, 1860.

the ground to be rockie, which, by trial of a mineral man, was founde to hold iron richly. It is founde in manie places of the countrey else. I know nothing to the contrarie but that it maie bee allowed, for a good marchantable commoditie...

The mineral man was Jacob Ganz, a Czechoslovakian Jew who emigrated to England (6). The orebody was located on the main land of present-day North Carolina.

In noting the numerous false starts and errors made by her explorers, historian James Mullholland speculates the arts of prospecting and assaying were particularly backward in 16th century England (4). Recent archaeological discoveries may tell a different story. Excavations carried out by the National Geographic Society and Colonial Williamsburg Foundation have uncovered a 16th century assay laboratory at the Roanoke Island Colony. Records show that several assayers, including Jacob Ganz, accompanied the colonists. Remains of a small wooden shed were excavated and the artificial evidence shows that the laboratory appears to have been well equipped. Archaeologists have not completed the final report on the site (7). No doubt it will shed much light on 16th century analytical chemistry. The Roanoke Island assay laboratory vanished with the rest of the lost colony. With the exception of this facility, assaying as recognized by a modern chemist seems to be almost nonexistent in Colonial America. Whether it was unrealistic optimism on the part of mine promoters, difficulty in inducing skilled assayers to emigrate, or some other factor, the reasons that America lagged behind Europe deserve additional study.

A few years later, in 1608, Captain John Smith sent two lots of iron ore samples back to England for evaluation. The first consisted of two barrels of stones described as "such as I take to be good iron ore at the least." He also sent along notes describing the location of the stones. His comment prompts one to wonder whether he was sending back rocks with no clue as to what they were and hoping for the best. Later in the year, a shipment of ore sent for trial yielded 16 or 17 tons of iron (8).

For most of the colonial era, small scale laboratory assays seem to have been rare. Visual examinations and simple tests probably were the best way to judge ore quality. The only really certain evaluation would be to produce test batches of bar stock in a bloomery or furnace. The Saugus Iron Works in eastern Massachusetts provides a good example. These works operated during the mid to late 1600's. According to the records, John Winthrop the Younger, who managed the works, constantly searched the nearby bogs for good quality ores.

In his book on the works, *Iron Works on the Saugus*, Hartley mentions several techniques that could have been used during the period. These include measuring the specific gravity, judging by appearance, magnetic attraction, or crushing followed by magnetic separation. A touchstone method was also available. A streak was made on a piece of black marble or other stone with the ore, the color of which was indicative of the ore type. Bog ore or limonite leaves a yellowish/brown streak (9). Although these techniques were identified as being available, none of them was identified as being used. Winthrop's correspondence indicates that at least at Saugus, metallurgy had not yet outgrown alchemy (9).

No formal analysis of Saugus ores was made until the 1950's (10). Despite this, Winthrop's search for good ores was successful as archaeological specimens typically tested between 35 and 55% (9). Hartley claims that ores were tried by Winthrop's "finer" (9). Normally used to remelt pig iron, a finery could also have been used to smelt small pilot batches of ore by the bloomery process (11).

It is worth pausing here to examine this process in some detail. A bloomery is a small scale-plant to smelt iron ores. Although it was frequently mentioned as the principal method of evaluating a new orebody prior to the mid 1800's, it should not be thought of only in that context. With capital scarce, many iron producers began with a bloomery and built a blast furnace afterwards. This was often the only practical way to earn revenues in the early stages of an iron enterprise. The bloomery was usually constructed as a block of brick, about 3 or 4 feet high and at least as deep and wide. At the back, a large bellows fed air through a tube set in the brickwork. Also at the back end, the outermost courses of brick were carried upwards to make a tall wall that shielded the bellows. A hearth was set into the center of the top. Layers of charcoal and ore were stacked there and the coal ignited. As the ore became soft, it was taken out of the fire and hammered, usually by a water-powered trip hammer. This process consolidated the metal and squeezed out slag. Reduction of the iron was accomplished by the reaction of carbon monoxide, a by-product of incomplete fuel combustion, and the oxygen contained in the ore (11).

The bloomery process has one important advantage over the blast furnace. Because the metal is worked at sub-melting point temperatures, it does not absorb appreciable amounts of carbon from the fuel. Consequently, the final product is a low carbon, highly malleable wrought iron. The iron was so malleable that, until the late 1800's, it remained competitive with blast

furnace iron whenever ductility was desired (12). As an assaying technique, the bloomery process had the advantage of being cheap, easy and familiar. While the operating conditions did not accurately reflect those in a blast furnace, any malignant impurities would still manifest themselves (12).

At about the same time that Winthrop was producing iron at Saugus, Dutch settlers were prospecting in present day New York and New Jersey. In 1644 Henrick van der Capellen reported the discovery of copper, iron, and lead. Samples were sent to the Netherlands but proved worthless once assayed (4). This sort of oversight was not unique; reports of "mines" often did not even indicate what sort of orebody was being explored (13).

The English entrepreneur Peter Hasenclever undertook an ambitious program of industrial development in the 1760's and 1770's. Smitten with the potentialities of the new world, he founded the American Company with extensive iron and agricultural lands. Before taking ship for the New World, Hasenclever purchased several thousand acres in Northern New Jersey and Southern New York. His agents went to Germany to recruit experienced miners and iron workers (14). The company immediately launched a dramatic construction program, building five furnaces, several forges, roads and reservoirs. Miners opened 53 workings. Some of what happened next is recounted in Hasenclever's own memorandum (14):

Heaps of fine iron-ore lay on the surface of the earth, and there never was a finer prospect for success. But after the Miners had worked a while, some of the mines which produced excellent ore vanished, other mines turned sulphurous, copperish, coldshear, full of mundic and arsenical matters, so that the ore could not be made use of. These circumstances might appear incredible if the places could not be shown. In short, the appearance was so certain that we began to build a dam for a great reservoir and some log houses, we cut coal wood and made an expensive road, which after all, we were obliged to abandon...

Hasenclever seems to have understood the importance of having pure ores, but he never seems to have made any kind of preliminary testing. Perhaps he relied on a visual inspection to locate his mines. Of the 53 original mines, all but 7 were eventually abandoned. Hasenclever cannot be judged too harshly, for the situation was not at all uncommon. Exposed portions of an orebody, washed by rain and snow, are often much purer than deeper portions (14). (Variations of assay data over time are frequently attributed to this phenomenon.) Know-

ing what he did about ore quality, Hasenclever would have certainly overcome that problem. The record shows that his enterprise was defeated by incompetent middle managers, tremendous capital demands, and a shortage of skilled workers.

Hasenclever recognized that education was vital to the industry's growth. Before leaving Europe, he collected specimens of ores (including South American silver ores) along with books about mines and metals. In America he added to the collection, intending to present it to a college in New York or Philadelphia. Financial troubles forced his return to London and much of the collection was lost en route. Fortunately, the American specimens were lent to a London friend and eventually found their way to the British Museum (14).

The case of the Rocky Hill Copper Mine may also prove instructive. The mine, located in the hills of Northern New Jersey, was originally explored in 1744. Samples were taken from all parts of the mine and sent to London for assaying. Once the relative values were determined for different parts of the orebody, all subsequent shipments were classified by their exact origins in the mine. Because of restrictive trade laws, the mine shipped unprocessed ore to England for smelting. As excavations progressed, ore quality deteriorated. Finally, transportation costs exceeded the value of the refined copper. Unfortunately, this was not discovered until worthless ores began arriving at the smelter (13). Had even rudimentary assaying been a regular practice, this might not have happened.

One of the few first-hand descriptions of an iron trial during the colonial period came from Jarad Eliot, a Connecticut clergyman and physician. Eliot was a true renaissance man and a firm believer in the scientific method. He is principally remembered for extensive agricultural experiments but he also dabbled in iron making. Eliot was aware of the extensive deposits of black, iron-rich sands along the Long Island Sound and New England coasts. He determined to test their suitability as a source of raw materials for an iron works owned by his son; but he was also keenly interested in the sand's geological origins and much of his manuscript is devoted to his ideas on the subject (15). He began by collecting from a nearby beach some forty pounds of the sand which was carried home in saddlebags.

The iron particles were first separated with a hand magnet. Eliot assured his readers that if this had proved impractical, he would not have given up because he knew that not all ores are magnetic. Once separated, the metallic iron would have had to be reduced. For this purpose, the actual trial was carried out by the bloomery

process (15). Eliot took the iron particles to a local forge. Upon presenting the fine sands to the founder, Eliot was told, one, the founder was forge man, not a bloomer and two, that it probably wouldn't work anyway. Being both an idealistic and practical man, Eliot countered with a compliment and a bribe. The forge man was told that he was very skillful in his art. It could be supposed that the differences between a forge man's and a bloomer's work were not so great that a talented worker could not overcome them. The bribe was a bottle, offered if the process could be made to yield good iron and in the full knowledge that a sober and judicious man would not abuse the gift. For several hours the assembled company waited for the iron to melt. Then a bar was thrust into the hearth and when it was withdrawn, small amounts of metallic iron were sticking to it. Later a pasty mass of iron was produced, taken from the fire and hammered into a bar that weighed 52.5 pounds. A blacksmith tried the bar and pronounced it to be the equal of the best Swedish iron.

Eliot continued both his experiments and geological observations. In another experiment he mixed the iron sands and a poor quality bog ore. The mixture produced a "tolerable" quality bar stock. Despite encouraging results, large-scale utilization of the sands was impractical because they contained 1/3 common grit. It made the material hard to flux and produced only glass. After a cartload full sat overnight in a rain storm, the grit was washed away. This discovery not only gave Eliot a practical method of purification, but it caused him to revise his geological theories on the sand's movement and origins. His hopes were high for the widespread use of iron sands in blast furnaces. Working iron sands ultimately proved impractical because they took longer to smelt than other ore sources. His record of the trial clearly illustrates the scientific application of assay techniques (15).

In evaluating finished iron for quality, colonial iron masters often employed fracture analysis. In this procedure, a bar of wrought iron is mechanically fractured and the metal's quality judged by grain size. Directions for fracture analysis appear in a 1741 assaying book (9). This method is still in use today (12).

During the 1700's, a number of talented chemists turned their attention to ferrous metallurgy. Among the first was the French chemist Reaumur. He published a scientific textbook in 1722, describing his experiments with iron and steel. In his experiments he described how different refining operations produced varying amounts of slag. Reaumur knew that different types of iron had different amounts of "earthy matter" (silicon)

and how the addition of sulfur affected the quality of the iron (16).

In 1781, Torben Bergman published "Dissertatio Chemica de Analysi Ferri." The work was prefatory to a doctoral defense by his student Johann Gadolin at Sweden's Uppsala University. Bergman sought explanations for the different types of iron and steel in terms of the metal's chemical composition. He reasoned that only elements commonly found in the ore were responsible for the changes in the metal: sulfur, plumbago, arsenic, zinc, and manganese. His experiments, by wet chemical methods, were both quantitative and careful (17). Other Swedish chemists made significant advances in metallurgical and mineralogical analysis during the 1700's. Among their most notable achievements was the development of blowpipe analysis between 1746 and 1820. This technique was already in use in Germany by 1700, but the Swedes transformed it into a versatile tool for many types of chemical analysis. They used the blowpipe for thermal decomposition, oxidation, reduction, glass formation and colonies, as well as observing flame colors. Several treatises were published on their techniques, and the best practitioners were able to achieve good qualitative results (18).

Blowpipes were used in American laboratories in the 1800's (19). The technique declined in importance as spectroscopy became popular in the 1860's but continued to be an important tool for geologists and mineralogists. Textbooks on the subject were still being published even after the second world war (18).

The question naturally arises as to how much metallurgical literature crossed the Atlantic and was available to Americans. North Americans made every effort not to become an intellectual backwater. But the fact remains that many important books in this field were not available in English until the twentieth century.

Jarad Eliot conducted a single experiment on the role of sulfur in iron and he urged others to take up the task. We do not know whether he was influenced by any European examples (15).

During the American Revolution, the need for sulfur in gun powder manufacture caused the Continental Congress to authorize assays of iron pyrites. Several sources were examined in a search to find the highest sulfur content (20).

1800 to 1860

The first six decades of the 1800's were pivotal in the development of assaying facilities in the American iron industry. Technological, economic, and political forces all played important roles in this period. Both state and

national governments needed to identify and evaluate mineral resources. Many states established an assayer's office and/or a state geological survey. These offices were not only instrumental in advancing the science of assaying, they promoted much valuable geological research, fostered economic development, and left a chronicle of industrial development. At the federal level, government departments sought information on iron resources. The Navy in particular needed metal for ordnance and ship fittings. Civilian agencies also consumed iron for public buildings and other uses. In the academic community, metallurgical chemists were learning how impurities and chemical composition affected iron quality. Just as importantly, they were disseminating this information by means of technical journals, textbooks, and college-level courses for mining engineers, analytical chemists, and metallurgists.

As new sources of ore were discovered assayers were frequently employed to make preliminary evaluations. However, regular assaying over the life span of a mine was not a common practice until the end of the century. Occasionally an assay was performed for an established mine, such as those supplying Pennsylvania's Hopewell Furnace.

The principal testing methods employed during the first half of the 1800's fall into three not mutually exclusive categories. First was laboratory analysis. Second was the production of a pilot batch in either a bloomery or a blast furnace. Third was testing a small quantity of finished iron in some demanding application. For the most part, iron consumers relied on the reputation of the mine or furnace that supplied the metal and not on any extensive knowledge of the metal's chemical composition. Alternatively, the consumer might depend on the experience of an iron broker.

State and Federal Geological Surveys

The New Jersey State Geologists Office can serve as an example of this type of organization. It was established in 1835 to "provide a geological and mineralogical survey of the State of New Jersey". Throughout its history, the survey published information on New Jersey's mineral resources. Beginning in 1835, the survey proceeded by irregularly until 1868 as funding levels fluctuated. Only four "annual" reports were issued during these years (21). After an eight-year hiatus, funding was restored in 1864 and the survey placed on a statewide basis. The 1864 to 1867 reports culminated in the monumental 900-page *Geology of New Jersey*. After its publication, the State Legislature authorized an extensive program which continues uninterrupted to this day (21).

In 1910 the survey issued a comprehensive summary of all its data on the state's iron industry and resources, "Iron Mines and Mining in New Jersey." The volume contains assay data from both state and private laboratories. Not only was this data used to evaluate the economic value of the state's iron resources, it was also used as the basis for geochemical investigations into the origins of the orebodies (21).

Among the noted scientists working in the agency was Henry Wurtz, a chemist and mineralogist. His is most remembered for his contributions on iron ores and mining in the 1858 annual report (21). The widely distributed 1868 report of the New Jersey State Geologist contained hundreds of assays; most consisted of only five analyses: iron, silica and insoluble matter, sulfur, phosphoric acid, and magnetic iron ore. A much smaller number of more complete assays reported aluminum, magnesium alkalies, and water (23).

Writing in 1910, State Geologist W.S. Bayley felt that the earlier analyses done at the state laboratory were less trustworthy, especially with respect to titanium, phosphorus, and sulfur. Titanium was generally not analyzed until after 1879 (22). This was a serious oversight as titanium was a troublesome contaminant in many New Jersey ores (12).

As new orebodies were discovered in the Lake Superior Region, state assayers in Boston and Paris were called upon to evaluate the ores. Their reports reveal something about the assayers and the range of analyses available to them. The state assayer in Boston reported on 13 September 1856:

Peroxide of Iron	
(68.044% pure iron)	98.02%
Oxide of Manganese	1.28%
Silica	0.44%
Lime	0.32%
Total	100.06%

Also tested for, but not found were titanium, phosphorus, sulfur, arsenic, chrome or other "injurious substances." The ore was estimated to yield 69% metallic iron in a blast furnace. It is interesting to note that the report was signed C.T. Jackson M.D., Assayer, etc.. There is no mention of what the "etc." included (24).

The French state assayer's report from Paris was not dated but was issued from the School of Mines. It was signed by L.E. Rivot, Professor of Analytical Chemistry and Director of the Assay Office. The list of analytes included:

Metallic iron	Carbonic acid	Alkalies
Oxygen	Water-soluble silicates	Water
Magnesia	Phosphorus	Arsenic
Oxide of iron	Lime	Sulfur
Oxide of magnesia		Alumina
		Gangue

The last item, gangue, is a mix of quartz, alumina, iron oxides, lime, and alkalies (24).

The Federal Government was also interested in promoting the growth of the industry and inventorying the nation's iron resources. One early and ambitious project was undertaken in August, 1857. Concerned that iron being used in public buildings would rust, the Treasury Department began a nationwide search for iron with low oxidation rates. Congress appropriated \$2,500 for the study (25).

All iron manufacturers were asked to provide 2-3 small samples of both iron and ore from each mine being worked. Each would be tested for resistance to rust. They were also asked to provide the location of the mines and furnaces, extent of deposits, types of fuel used, distances from raw materials and markets, annual production statistics, the locations of rolling mills, and applications data (25). As the US Navy was one of the principal government iron consumers, it often evaluated samples of finished iron for strength and other physical properties.

By far the most important federal project on ore analysis was the 10th census. Published in 1886 by the Bureau of the Census, the final report was a complete study of America's mining industry, excluding only precious metal production (26).

In 1879, agents of the US Geological Survey were empowered to act as agents of the census bureau in order to collect data on the industry. There was at that time not even a preliminary list of mining concerns. Data would be collected by special agents working in the field and by correspondence. The agents were to be assigned areas where they were familiar with the mining operations. It was considered important that all data be as uniform as possible (26). Back in Washington, one chemist and six assistants analyzed 1,377 samples of ore for a total of more than 4,400 individual determinations.

Exploration and Assaying of New Orebodies

Perhaps the most engaging accounts in the metallurgical literature are those describing prospecting in remote and undeveloped areas. Some are widely reprinted and read by a general audience, such as the tales of early

geological surveys in the Adirondack Mountains. These accounts are among the earliest descriptions of hiking, climbing, and camping in the region. In the instances reported in this paper, and in several others, Native Americans are credited with knowing about the ore deposits and calling attention to them. The prospectors employed them afterwards as guides.

Many letters and documents survive from the Adirondack Iron Works near Lake Placid, NY. These documents illustrate the relationship between the discovery, evaluation, and exploitation of an orebody in the period prior to 1860. The proprietors first learned of the ore bed in October of 1826 while prospecting for silver. After a field examination, the ore was analyzed and found to be free of sulfur; no record is available to show how this was ascertained. By 1830 the company had secured title to the land and was making preliminary arrangements for development. Near the end of 1830 Archibald McIntyre, one of the owners, wrote that he anticipated good results from the ore trials and he was thinking ahead to appointing an ironmaster. In the winter of 1831 a test batch of six tons was extracted and sent for processing. The Adirondack snow proved too severe for the crude road haulage and the ore had to be abandoned and retrieved in the spring (27). It is not clear whether the tests proved entirely satisfactory. The ore was described as "found to make an excellent iron for every purpose, except that, requiring polishing..." (27). But in June 1833, McIntyre wrote that "I cannot avoid sometimes of having my fears. For the ore has not been tested, the roads are abominable and coal wood in the vicinity is very scarce" (27). The comment that the ore had not been tested may refer to a laboratory assay or perhaps to large scale production in either a furnace or bloomery. Later it was suggested that finished iron be sent to the New York Navy Yard for trial in actual applications. Earnest development began in 1832. Among the supplies sent to the works were two volumes of Cleaveland's *Mineralogy*, and one volume each of Bakewell's and Eaton's *Geologies* (27).

As mining began, several bloomers were hired to begin experimenting with reducing the ores. It was a long and arduous process. Although the quality was good, the production rate was slow. Both the bloomers and their employers were becoming discouraged. It was not until August of 1834 that good loops began emerging from the bloomery. It was then suggested that bloomers be brought up from New Jersey who would have experience with "mountain Ores". The bloomery was coming along so slowly that it was suggested in September, 1834 that the ore be shipped to a blast fur-

nace for trial. Other suggestions included abandoning the works (27). They were indeed abandoned. But when the State Geological Survey explored the area between 1837 and 1841 new impetus was given to reviving the works. The ore was again evaluated and again found to be of good quality. Finally, the company resumed operations in 1838 with a blast furnace (27). For all of the tests, evaluations, and reports of good quality, the ore continued to be extremely difficult to work. Finally in 1848 it was found to contain 10% titanium. Not finding it sooner was described in one letter as "a rather extensive oversight" (27). The bloomery struggled for three years to produce good iron and the blast furnace did not have much more success. Another furnace was built in 1844, and ten years later a still larger furnace was erected. It was hoped that the 1854 furnace would save the company but it came too late (28). There has always been some controversy about the exact cause of the company's troubles. One side maintained that the presence of titanium dioxide in the ore rendered it unworkable, and the other side countered that labor troubles, transportation difficulties, and the Adirondack winters were responsible (27, 28).

It was not until the 1890's that experiments were performed to discover a way of smelting the ore. The successor to the Adirondack Company was trying to sell the property, but the ore's titanium content discouraged many potential buyers. Company President James MacNaughton hired French metallurgist August Rossi, who tried the ores in both large and small furnaces and published favorable results (27). Despite the favorable press, negotiations dragged on; and it was not until 1914 that a dramatic trial was made to settle the issue once and for all. The company leased a furnace belonging to the Northern Iron Company at Port Henry, NY, hauled tons of ore out of the woods, built a magnetic concentrator, and began large-scale production. Favorable results were again reported at the October, 1914 meeting of the American Iron and Steel Institute (27). Many years later Bruce Seely would write that the persistence shown by the Adirondack Company was due in large part to optimism and a faith in science to solve problems, rather than to any real potential of the ores (28).

As mineralogical prospecting became more sophisticated, specialized professionals were utilized. Some 45 years after the discovery of ore deposits at Adirondack, chemistry professor Albert H. Chester was sent to northern Minnesota's Vermillion Lake in search of new iron deposits. The conditions under which the prospectors labored were just as rugged, but the level of organization was vastly improved. Charlemagne Tower,

a patent attorney, and his partner Alfred Munson, a wealthy iron manufacturer, decided to sponsor an investigation of this region. Albert H. Chester, professor of mineralogy, geology, and chemistry at Hamilton College of Clinton, New York, was hired to perform the field work. In addition, he would analyze the samples in the college laboratory. His salary was \$250 per month plus expenses (29). Chester arrived in Duluth early in the summer of 1875. He would be guided by George Stuntz. Stuntz, trained in mathematics, chemistry, and surveying had worked as a civil engineer and surveyor in the region before opening a successful trading post. His interest in the state's iron reserves dated from the mid 1860's. Tower's son-in-law, Richard Henry Lee, a competent surveyor with a rudimentary knowledge of chemistry, also accompanied the expedition (29). There was a total of eight men in the party who departed Duluth on July 13 for a ten-day canoe trip to the Ojibway Indian Agency on Vermillion Lake. They spent two days inspecting hematite exposures before moving southwards to the Mesabi Hills. They were charged with examining the ore and mapping suitable routes to bring it out of the hills (29). Field examination of the Mesabi samples revealed an iron content so low as to render them commercially unproductive. In an understandable oversight that would later return to haunt him, Chester dismissed the entire Mesabi Range. He had in fact only explored its leaner eastern end. The better quality ores lay farther to the south and west. He did however send two Ojibway Indians with Stuntz and John Mallmann, an experienced miner, back to Vermillion Lake (29). They sunk their first test pit near what is now known as Stuntz Bay. Three holes were drilled about 42 inches deep and filled with 18 inches of black powder. The resulting explosion opened a crack about 40 feet long and 4 to 5 feet deep. Working with sledge hammers and soap covered ash wood wedges, the crew exposed the ore and prepared for a second blast. This second blast, for which all their remaining powder was used, uncovered 60 tons of high grade ore (29). That fall, analysis of the ore samples back at Hamilton College revealed that the Vermillion Lake samples, in addition to being as high as 76.77% iron, were very low in phosphorus and thus well suited to the Bessemer process. Assays of the Mesabi ores confirmed the conclusions reached during the field examination (29).

Assaying and Iron Consumer, 1800-1860

Locating an orebody is only the first step in its exploitation. Depending on the time period and the resources available to the mine promoters, different kinds of "tests"

and "trials" followed. Generally a mine owner requested a formal assay early in the process and seldom followed it up with periodic rechecking of ore quality. Pilot batches of ore were also smelted and sent to potential customers. After the mine was established, iron consumers relied on its reputation to tell them whether the ore or metal made from the ore was suited to their needs. This was the case whether the iron consumer was a furnace, foundry, or manufacturer. The Adirondack iron mines serve as one excellent example of this process. Iron production began in the region about 1798, although local tradition places the date as early as 1776. By 1879, 23% of American total iron output came from the Adirondacks (30). Mineville or Port Henry ores were magnetically surveyed in 1810. The surveys confirmed the presence of large deposits and samples were taken for analysis. There is no record of what was done with the samples (30).

Andrew Williams, a founder of the Chateaugay Ore and Iron Company, had a background working at a local forge. He was noted for his constant efforts to locate good quality ores. Around mid century, he secured test lots of ore and processed them at his forge on the Saranac River. This was probably done by the bloomery process. He shipped the test batches to selected customers who in turn reported favorable results (30). By the end of the century, the Adirondack iron mines and furnaces had complete assay laboratories. The 1884 assayer's record book from the Witherbee-Sherman Company is now preserved in the Adirondack Center Museum. Just before the first world war, an extensive survey was made of the Chateaugay Ore Bodies. It included magnetic surveys, geological, diamond drill sampling, and chemical analysis as well as surveying and mapping of the existing workings (30).

In 1824 when James P. Allaire purchased an iron works near Freehold, New Jersey, one of his first steps was to contact Professor Silliman of Yale and send him four samples, two of the local bog ore and two of the bog soils. His decision to send the samples to Yale came as a result of an earlier visit. Allaire had noted that the geological specimen collection contained no bog ores. Silliman analyzed the ores and sent the results back to Allaire (31). Silliman tested for oxyd of iron, aluminum, manganese oxide, water, silica, and iron phosphate. Perhaps Allaire did not trust Silliman's favorable report. The first furnace charge contained ore from Milton, Delaware in addition to the ore from the local bog (32). Allaire was not the only 1820's furnace operator to turn to an academic for assistance in evaluating a new orebody. Two rival claimants for the Adirondack

company's ore beds took their samples to Union College for comparison with the college's geological specimens (27).

A number of private laboratories eventually began operating in conjunction with mining engineers or promoters. The Belvedere Iron Company's prospectus from 1865 survives and gives an example of the exploration and assaying practices at that time. The company employed Messrs. Partz and Buck, Practical Mining Engineers and Metallurgists (33). Partz and Buck mapped veins of Pipe Ore, a variety of hematite, and computed 900,000 tons were available. A few shallow pits were excavated but most of the initial reconnaissance was done on the surface and comparisons were made with nearby excavations. Chemical analyses were conducted at Partz and Buck's laboratory at 39 Nassau Street, NY (33):

Proto-peroxide of iron	95.56%
(yielding metallic iron	65.12%)
Silica	0.55%
Alumina	3.49%
Phosphoric acid	0.18%
Lime	0.22%

"Faint traces" of sulfur were also detected and it was reported that neither phosphoric acid nor sulfur was present in large enough quantities to be troublesome. The report also recommended more exploratory pits (33).

Mine promoters frequently made small batches of finished metals and then sent them to be tested. Franklinite from Sussex County, New Jersey was reduced in a bloomery. The finished iron was then sent to the National Forge in Paris. There it was tested in a hydraulic press and found to withstand pressures of 40kg/mm (34). Other tests were carried out at Washington's Navy Yard in 1859. Because Franklinite pig iron was found too hard to be cut, it was mixed with other iron samples and fused in a crucible. The mixture was subjected to tests of density and tensile strength. The work was carried out under the superintendence of Commander John A. Dahlgren, better known for his ordnance work during the Civil War (34). (A number of other furnace operators also sent samples to the Navy Yard for evaluation.) Another, less scientific evaluation, was to send some finished iron to a dock constructor who used it as an iron band on a pile driver. The contractor later offered a favorable testimonial (34).

Large manufacturers had the financial resources to buy either their own iron mines or at least a major interest in someone else's. In the period before regular as-

saying became part of the quality control routine, they thus insured a dependable supply of good iron. The Phoenix Bridge Company, a supplier of pre-fabricated truss bridges, was one of these. But the smaller concern did not have this luxury. In some cases they were able to make special arrangements with a specific furnace. In other cases, the manufacturer would stockpile selected iron, and still others relied on commission brokers to get the metal they needed.

The career of Dr. Charles Stewart, M.D., provides some examples of how manufacturers selected iron. He had received his medical degree from the University of Pennsylvania in 1853. But before he began practicing medicine, his father brought him into the firm of Rodenbaugh, Stewart and Company. The company originally set out in the mid-1830's to make cut nails. Within a few years, they diversified into making iron wire and, as nail prices fell, switched exclusively to wire production in 1845 (35). This proved to be an excellent decision: wire was needed for the telegraph, suspension bridges, wire ropes, hoopskirts and later, barbed wire. When Rodenbaugh withdrew from the partnership, Dr. Stewart took his place; it was the beginning of a fifty-year career (35). Charles Stewart was not only concerned with business affairs; he also was deeply involved in the technical aspects of production. The Stewart family kept adapting their operations to changing technology. As manager of the wire drawing works, Charles introduced many innovations and process improvements (35).

Because of its great ductility, bloomery iron was used for drawing wire. But Stewart often had trouble finding suitable stock. By studying the technical literature, he learned that ideally the stock should consist of "neutral iron," i.e., containing neither sulfur nor phosphorus. This metal would remain flexible over a wide temperature range. Flexibility was especially important in wire drawing since the stock had to be heated and cooled repeatedly (35). The company was buying iron from the Adirondacks via commission brokers in Troy and Albany. The company also bought iron from banks, which, by advancing money, came to own large accumulations of iron, ore, and even charcoal. In a departure from the usual practice, Stewart decided that he should visit the bloomeries and meet directly with their managers. He wanted personally to explain the specific requirements of his company and get a sense of which producers could meet them. His first step was to copy the trade marks from the bar stock on hand. When he had identified the makers, Stewart departed for the Adirondack mountains (35). On the train north, Stewart

met a Mr. Witherbee, a well known mine manager in the area. The two began talking over Stewart's plan and Witherbee enthusiastically endorsed it. Witherbee not only identified all of the maker's marks that Stewart had copied from the bar stock, he wrote out the chemical composition of most of the region's major ore beds. Stewart was thereby able to pinpoint exactly the suppliers that were best suited to his needs. His tour of the region was as eventful as it was productive. One of the bloomery managers with whom he met was delighted to learn first-hand about customer requirements because commission brokers in Albany and Troy had kept him in the dark about such things (35). In a separate incident, Stewart was asked by another wire manufacturer to testify in a lawsuit alleging that a certain bloomery was selling inferior metal. Years later Stewart would recall that he had previously hired a chemist to assay the metal, and a copy of the results was on file in Stewart's office. Stewart told the plaintiff that he was unprepared to testify against the supplier since both the assay results and his experience with the metal spoke eloquently for the defense (35).

Advances in Metallurgical Chemistry

Although Stewart and his company did not employ a full-time chemist, they were able to take advantage of a number of important developments in metallurgical chemistry. During the 1840's and 1850's several important discoveries were made about iron quality and its chemical composition. The two most common problems with iron produced in the 18th and 19th centuries were being either "cold short" or "hot short". Cold short iron is brittle at low temperatures and hot short iron is brittle at higher temperatures. These problems are the direct result of phosphorus and sulfur, respectively. In the case of hot short iron, iron sulfide crystals form on the grain boundaries within the metal. The crystals weaken the adhesive forces between the grains and fractures result (12). Perhaps sulfur was the first impurity recognized for its detrimental potential. The practice of washing and roasting ore to remove sulfur is an old one. Once sulfur and other impurities were recognized for the damage they caused, assay laboratories started looking for them. It is difficult to establish an exact date when this began. But in the 1840's, published studies began describing various impurities, their effect on ore quality, and techniques for detecting them.

In October, 1849, *Scientific American* reported on a paper presented to the British Scientific Association. Phosphorus was already known as a detrimental impu-

rity; now precise determinations were available to confirm its role in producing cold short iron. The analysis was highly labor intensive, involving two acid dissolutions/evaporations, smelting, and two filtering steps before calcium phosphate was precipitated by a calcium chloride/ammonia mixture (36). A few months later, another report appeared in *Scientific American*. It was taken from the *London Mining Journal* and related iron strength to composition. Strength was found to be the result of carbon content and freedom from other impurities. Arsenic was thought to give Berlin Iron its fluidity but also to make wrought iron hard and brittle. Manganese, when alloyed with iron, was found to close the grain and improve both iron and steel. In wrought iron, however, manganese produces a hot short effect. This report also reiterated phosphorus as being the cause of cold short iron (37). By the 1850's just about all assay reports listed at least iron, sulfur, phosphorus, and manganese. On or two others were often listed, usually alumina or silica.

The New Jersey Geological Survey's 1856 report announced plans to investigate the chemical changes occurring during the puddling process. Survey chemists had obtained samples of ore, furnace cinders, samples from the puddling process, and finished iron. In the puddling process, pig iron is converted to wrought iron by burning out the excess carbon. In the 1850's this process was not well understood, and this would have been one of the first efforts to study the phenomena scientifically. It is unclear whether this work was actually carried out. However, in 1857, English chemists working with Staffordshire Iron did publish results from a similar experiment (38). The importance of these experiments was that they shed light on the role of carbon in regulating iron strength. It was known in 1850 that strength was inversely proportional to the percentage of carbon. More work was needed to understand the underlying chemical mechanisms (39). This eluded metallurgists because strength is not merely dependent on the amount of carbon, but also on its form. By the end of the decade, it had been discovered that it was graphite that made cast iron brittle (39).

The availability of scientific assay data was no guarantee that the data would not be misapplied or misinterpreted, however. A well known case involved wheels for railroad cars. It was a demanding industrial application as well as a lucrative market. Beginning in the 1830's, American railroads adopted cast iron wheels with a chilled tread and flange. Although cast iron is more brittle than wrought iron, the chilled tread gave the wheel extraordinary durability. When being cast, the metal

rapidly cooled where it came into contact with the mold. Iron and carbon remained mixed and the resulting metal resembled steel with a 3.5% carbon content. In the center of the mold, the metal cooled slowly and the carbon separated to form graphite (40). Improving safety and durability meant employing the best metals available. Without a detailed knowledge of metallurgy, wheel foundries were forced to rely on the reputation of the pig iron, such as from the Carwheel Mine in New Jersey. In the 1830's and 40's, this usually meant a mix of Baltimore and New Jersey ores. Wheel makers typically selected material free of sulfur and phosphorus, but these elements were effective in producing a good chill. On the other hand, silicon had a detrimental effect (40). By the 1880's wheel foundries kept stockpiles of different types of ores and mixed them for obtaining the best metal. Samples were pulled daily from the furnace and tested for strength and chilling properties (40).

By far the single most important metallurgical discovery that led to the widespread adaptation of assay laboratories was the Bessemer Converter. Prior to the introduction of the Bessemer process, steel was manufactured in relatively small lots by the crucible process. Although a great advance in steel production, it was discovered almost immediately that the method did not work if the ore contained any phosphorus. The original, or Acid Bessemer Process, made use of a silica-based furnace lining. Later, the Basic Bessemer Process was developed. It used a limestone furnace lining that reacted with the phosphorus and carried it off in the slag (11).

In May of 1868 the Freedom Iron Company of Greenwood, PA opened the 4th Bessemer steel plant in the United States. Proceeding without a preliminary assay, the company spent a year trying unsuccessfully to manufacture steel. According to later sources, a \$50-analysis would have revealed the phosphorus. The company's problems were not solely attributable to ore quality. A labor force untrained in steel making and a poorly designed physical plant were also to blame. The need for assaying as a preliminary to steel making did not originate with the Bessemer process. In 1852, Frederick Overman advised that in selecting iron for conversion to steel, "color, strength, and hardness are not unerring guides." The material may contain "more than one-two thousandth part of silex or silicon, phosphorus, sulfur, calcium, copper, lime tin, or arsenic and will never make first rate steel." Overman advised that a professional assay was needed and even included the address of a Philadelphia academic who would be will-

ing to do the work. Conversely, a pilot batch, while the surest way of ascertaining suitability, required six to ten tons of iron (41). In August, 1860 the Cambria Iron Works established what was claimed to be the first assay laboratory as an integral part of an iron works. Robert Woolston Hunt was employed for \$20 a month. Although the Civil War interrupted operations, it was re-established in May, 1866. The Cambria Works eventually produced the first commercially rolled steel rails and it was for this effort that the laboratory was established (42).

1870's and 1880's

By the 1870's and 1880's assay laboratories were becoming common at both iron mines and furnaces. By this time, not only were there significant advances in metallurgy, thermodynamics, and metal processing technology, but a communications infrastructure was available to disseminate information on these topics. But the overriding reason for the development of the laboratories was economic. Iron consumers, whether they were buying ore or finished metal, would typically continue to use the same sources until something went wrong; only then would an assay be called for. The problem, of course, was to anticipate changes within an ore bed and make adjustments before lots of inferior metal were being sent to customers. The only way that this could be done was to test each shipment of ore leaving the mine or arriving at the furnace (43). At first only the larger producers could afford the facilities to do this. For instance, in the New Jersey Geological Survey's 1910 report, most of the data from furnace and mine laboratories consisted of magnetite analyses. Regarding these, Bayley states that they were mostly from stockpiles or shipments, and therefore they represented only the quality of ore that could be obtained at prevailing prices. Few "complete" magnetite analyses were available, but many partial analyses contained all those elements of interest to furnace operators (19). Earlier analyses from blast furnace laboratories were generally poor, often including no mention of sulfur, although it did show up in later reports. Bayley does go on to say that as a rule, these laboratories managed to get accurate numbers for iron, sulfur, and phosphorus (22).

By the last decades of the century, many mines and furnaces made regular assaying a normal practice. Over a 12-year period, 1892-1904, the Thomas Iron Company tested every shipment of ore from their Richard Mine for iron, phosphorus, silica, lime, and alumina (22). The company also tracked the iron content of each shipment from the Little Mine and was able to determine that in a

375-carload shipment, the average was 53.34%. The highest shipment was 25 carloads in July, 1891, at 62.25% and the lowest was 37.94%. Over a two-year period, June, 1891 to October, 1893, 531 carloads were sampled and the company reported average figures for iron 56.29%, silica 7.94% and phosphorus 0.103% (22). Among other New Jersey and Pennsylvania mines and furnaces that had regular assaying regimen were Empire Iron and Steel, Durham Iron Works, and the Wharton Furnace (22).

Modern chemists would no doubt find much that is familiar as well as unfamiliar in a late nineteenth century assay laboratory. Although many types of instrumentation were still decades away, precise quantitative work was done by wet chemical methods. De Konick and E. Dietz in their 1873 book, *Analysis and Assaying of Iron and Its Ores*, give a number of directions for running an assay laboratory and performing analyses. Originally published in Europe, the book gives an insight into what the daily routine and working conditions were like for a chemist of that period (44). To begin with, there were a number of skills that the assayer and his assistants needed just to obtain supplies. Directions are given for drawing off and condensing steam from an engine as a source of distilled water. There were also a number of tests that had to be done on the water to establish its purity. The assayer and his assistants had to know how to generate and store their own hydrogen, oxygen, and chlorine. Like modern chemists they often prepared special solutions for work in the laboratory, but the solutions had to be tested for purity more frequently than would be done today. For example, bromine water had to be tested for sulfuric acid with a barium chloride spot test. Spot tests were used on solutions of iron, tin, zinc, and other cations that had been prepared by dissolving metal in acid. Acids also had to be tested for impurities; hydrochloric acid, for example, might contain traces of sulfuric acid. Sometimes acids were evaporated in a platinum crucible and the residues measured as a test for purity, acetic acid commonly being evaluated in this way. The assayer had to know which reagents could be purchased pure and which had to be recrystallized or be put through some other process of purification. Commercially available oxalic acid, for example, had to be recrystallized. Other reagents had to be prepared in the laboratory. The titration of iron with potassium bichromate required potassium ferricyanide, which was prepared by the reaction of chlorine and potassium ferrocyanide (44).

Today's visitor to a restored ironworks does not get an accurate idea of the noise, soot, and dust that charac-

terized the ironmaking process. When the furnace was in blast, the assayer needed to take special precautions to protect both laboratory and reagents from airborne contamination. It was suggested that, except under extraordinary conditions, the skylights be kept closed and all air entering the laboratory be passed through a screen made of copper gauze. Ideally the laboratory should be one story or at least a few feet off the ground to avoid rheumatic complaints from cold floors. In colder months the floors may be covered with cocoa-nut matting. Light should be from a skylight. Benches, if space permits, should be placed close to windows, especially when colors had to be compared and titration endpoints determined by color. North-facing windows were best. Although gas light could be used for illumination, the authors felt strongly that natural light was superior. Like most modern laboratories, there were the main work room, a balance room, another room for preparing and storing reagents, and a writing room, with desks and reference books (44). The laboratory needed several small furnaces, muffle furnaces for assay by cupellation and scorifying ores, assay melting furnaces, and a good "wind" melting furnace capable of melting wrought iron and holding a 6-inch crucible. The well equipped laboratory also had a large sand bath, 6- or 7-foot square, 3 feet high, and placed under a large iron hood. Aside from providing heating for experiments, it served several functions. One was to warm the room; glass shelving could be placed nearby for warming cold reagents, and a drying cabinet might be incorporated into the base. The fire that heated the sand bath also served more than one function. Ideally it was best to place the fire outside of the laboratory so as to avoid smoke and soot. The draft from the fire was directed up a tall chimney, and flues leading from the various benches, gas reaction apparatus, and ovens carried noxious fumes to the chimney. There were also small vents along the ceiling leading to the chimney to pull air out of the room. A large wrought iron plate, 5 or 6 feet long by 3 feet wide, could be placed next to the sand bath. This plate was for "combustions, small furnace operations, etc.", presumably smelting small amounts of metal in crucibles; ventilation led from this table to the main furnace flue. Opposite the sand bath and furnaces was a small enclosed chamber for gaseous reactions. Access was provided by a sliding glass door and tubes led below the laboratory floor to a gas generation room. Here "sulphuretted hydrogen" (hydrogen sulfide?), chlorine, and "carbonic anhydride" would be generated and kept under the pressure of two or three feet of water. Six or more rubber tubes would direct the gases into whatever

solutions were to be treated. Water in a cistern, mounted near the ceiling and connected by a pipe to a tank below floor level, provided sufficient pressure to force air from the lower tank through tubing into the work room. This provided the "wind" that enhanced combustion in the laboratory fires. The flow of water from the upper cistern to the lower tank also aspirated a partial vacuum used for filtration, bell jars, or room temperature evaporation dishes. Hoods might be sheet metal, zinc, or iron. Plaster over wooden lath construction was also employed, in which case the plaster would be treated with boiled linseed oil or simply whitewashed. The laboratory thus described was ideal for metallurgical work, and it is safe to say that all laboratories were not so generously outfitted. The authors freely admit that many iron producers failed to appreciate that good laboratory facilities were a sound investment. On this point they said (44):

...make-shift laboratories, like make-shift tools and machinery generally, are the most expensive in the end.

None of these developments would have been possible without trained men and intellectual tools. Many of the more prominent figures had careers that spanned the empirical to scientific eras of the industry. Three of these men are presented for the reader's consideration.

Robert Woolston Hunt (1838-1923), already mentioned, was the first chemist to be employed full-time at an ironworks (42). His career began in 1855 when he inherited his father's drugstore. Moving to Pottsville, PA in 1857, he went to work at the iron rolling mill of John Burnish and Company. His cousin was a senior partner and Hunt began as a puddler or roller. He subsequently took a course in analytical chemistry at the Philadelphia laboratory of Booth, Garret, and Reese. Hunt was hired by the Cambria Iron Company in August of 1860, to set up their assay laboratory at a salary of \$20 a month. When the Civil War broke out, Hunt enlisted in the Union Army. After the war, Hunt returned to Cambria but was sent to Wyandotte, MI to study the experimental Bessemer Converter. Hunt unexpectedly found himself in charge of the works after the resignation of several key individuals. When he returned to Cambria in May, 1866, Hunt was placed in charge of rolling the first batch of steel rails made commercially in the United States. In the course of a long career, Hunt developed new grades of Bessemer steel and devised and patented a successful rail mill feed table, a process for handling and rolling red hot blooms. He started a consulting engineering firm in Chicago in 1888;

eventually the firm had offices and laboratories in London, Mexico City, Canada, and several cities in the US. He was particularly interested in developing standards and in materials testing. He became president of the ASTM in 1912 and an officer in numerous engineering societies. He was also a frequent contributor to the technical literature.

Dr. B.F. Fackenthal, Jr. (1851-1939) was another chemist who was instrumental in placing the industry on a scientific basis. He began his 50-year career at the Durham Iron Works. He took a special course in chemistry at Lafayette College in 1874-1875. He was also a member of professional organizations such as the American Institute of Mining and Metallurgical Engineers, the ASTM, and both the British and American Iron and Steel Institutes. Between 1893 and 1913 he was President of the Thomas Iron Company (45). His interest in history combined with his knowledge of chemistry led to an unusual experiment. He took borings from stove antique cast iron firebacks and had them analyzed. By comparing the results with local ores, he had some success matching them to the sources of the iron (46).

Joseph Wharton (1825-1909) was trained as a chemist under Martin Boye of Philadelphia. Over a long career, his knowledge of chemistry allowed him to open up new markets and processes for many metals. After developmental work in the zinc, nickel, and lead industries, he began building a full-scale iron operation (47).

Dr. B.F. Fackenthal published a biographical volume of nineteenth and early twentieth century metallurgical chemists. The interested reader may wish to consult this study for more information about other chemists and their contributions to the industry.

Supplies for Laboratories and Training for Chemists

There were a number of textbooks available to assayers in the middle 1800's. The one most familiar to twentieth century scholars is probably Frederick Overman's *The Manufacture of Iron in All of Its Various Branches* (1854 and 1861) (19). Overman also wrote *The Manufacture of Steel* in 1852. The former book contained detailed assaying instructions which led the reader through a qualitative analysis scheme. Overman also gave detailed descriptions about ore types and how they reacted under blowpipe analysis. Overman's scheme is difficult for a modern chemist to follow. The author was left wondering how an untrained individual would have fared. There are no flow charts or "cookbook chemistry" instructions. There were no directions for sepa-

rating liquids and solids, although several of the procedures required it; nor is it clear whether separate samples should be prepared for different parts of the scheme (19). In *The Manufacture of Iron in all its Various Branches* (1854 and 1861) Overman wrote out a detailed wet analysis scheme for determining iron content, manganese, magnesium, phosphates, sulfur, lime, silicic acid, water, and carbonic acid. He said that, while a quantitative analysis is seldom insisted upon by most manufacturers and indeed seldom needed, qualitative analysis should be done in every case. The techniques are "easily effected" and should not be beyond the abilities of most managers. He gives directions for simple procedures (19).

The Henry Carey Baird Company of Philadelphia published a number of technical books in the nineteenth century. They described themselves as "Industrial Publishers, Booksellers, and Importers." Aside from Overman's *Manufacture of Iron...*, other titles included *The Practical Assayer Containing Easy Methods for the Assay of the Principal Metals and Alloys* (1879) and *The Practical Metal Worker's Assistant Comprising Metallurgical Chemistry, with the Art of Working all Metals and Alloys Including Malleable Iron Castings* (1879). Baird's 1979 catalog was 94 pages of "books for practical men" including works on economics, banking, machinery, textiles, metallurgy, chemistry, social science, politics, and "kindred subjects" (48).

In 1879 *Scientific American* began offering reprints of important papers as supplements. These cost about 10 cents and of 15 advertised, 11 were concerned with iron and steel. Although largely concerned with production, several did include sections devoted to the effects of impurities on iron quality (49). There are a number of cases when an isolated furnace operator obtained technical books for study. David Henderson at the Adirondack Works wrote in 1842 that he devoted many hours to metallurgical chemistry and had become "inoculated with a mania on that subject." He also wrote about making tests and experiments but information on what they were is not available (27). According to the historians currently restoring the Long Pond Ironworks in Ringwood, NJ, ironmaster and furnace owner Abram Hewitt was also known to have conducted extensive metallurgical chemistry experiments. His original notes are preserved in the New York's Cooper Union. In the late 1870's, Hewitt hired a Swedish metallurgist, trained at Uppsala University, to manage the works.

Urbanites had access to a number of technical libraries and college programs. The American Institute's 10,000 volume library was opened at New York City's

Cooper Union in 1859. Library privileges were extended to institute members. Volumes were available on agriculture, commerce, manufacturers, and the arts. Among these were the London edition of Mitchell's *Practical Assaying* and Leslie's *Iron Manufacturer's Guide* (50).

During the 1800's a number of technical colleges were established to provide professional education. Columbia University in New York City was well known for its mining and metallurgy programs. The college curricula followed by most 19th century practicing assayers deserve additional study.

Commercial laboratory supplies were also available in the urban areas. One interesting piece of apparatus was a laboratory-size hot blast furnace. The furnace was set on a flat table with a foot-operated bellows underneath. A crucible is placed inside a two-piece thick walled chamber and fuel packed around it. Air was heated before it entered the chamber. There were three adjustable "wind tubes" which could be pivoted or moved where needed. One of these fed the flame of a spirit lamp, which perhaps was used in blowpipe analysis. The furnace was sold by Barron and Brother of New York City. Their 1849 advertisement offered the furnace to assayers, chemists, dentists, and gold and silversmiths (51). Chemical ware was available from such suppliers as Moro Phillips of Philadelphia, who in 1857 offered "acid- and fire-proof ware of all kinds, up to 200 gallons, made to order, warranted to resist acids of all kinds and stand changes in temperatures from extreme heat to cold" (52). Dr. Lewis Feuchtwanger ran a chemical supply company at Maiden Lane in New York City. His 1859 advertisement listed metals and various reagents as well as "Best oils, cognac, rye, gin, rum." There was also a treatise on fermented liquors with copious directions (53).

Conclusions

Reviewing all of the hows and whys of the industry's gradual adoption of assaying, the reader may hear echoes of the present-day debate on national industrial policy and competitiveness. Many of today's proposals, particularly partnerships between academia, industry, and government have reflections in the 1800's. Some would point to the geological research conducted by the state surveys as an argument for increased funding for "basic" or "pure" research. And no one can downplay the role of education in bringing about this technological change—education that not only included technical colleges and the traditional academic structures, but the motivated furnace operator laboring through a self-di-

rected curriculum. Certainly no one factor or influence brought the modern industrial assay laboratory into being. More than anything else, this story should remind us that such profound changes are possible within an industry only when widely diverse individuals and institutions share their talents and resources.

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ABOUT THE AUTHOR

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BOOK NOTES

Chemical Sciences in the Modern World, Seymour H. Mauskopf, editor, University of Pennsylvania Press, Philadelphia, 1993, XXII + 417 pp. Bibliography (11 pp), Index (9 pp), 15 x 23 cm., hardbound, dust jacket, acid free paper, excellent printing and workmanship, \$39.95, ISBN D-8122-31 56-2.

Chemical Sciences in the Modern World (CSMW) is a collection of 18 essays by as many authors, varying in length from three to 58 pages (av. 21), which are based on talks given at a conference held in May, 1990, under the auspices of the Beckman Center for History of Chemistry. CSMW is the third book in a series, *The Chemical Sciences in Society*, published by the Chemical Heritage Foundation.

The 16 contributors for whom vitae are given include a museum administrator, an archivist/librarian, a corporate historian, a professor of the history of chemistry and chemical education, and 12 academic science historians.

In the first page or so of a 22-page introduction, the editor cites a few instances of how chemical products have transformed our lives and surroundings "for better or worse." Of the many problems, the one being addressed by these essays is the "invisibility of chemistry to the gaze of the modern historian." Specific objectives include 1) to make visible the best and most sophisticated scholarship in this field to the wider community of historians of science, technology, and medicine and to their students, 2) to serve the needs of historically interested chemical scientists and chemistry teachers, 3) to be useful to those concerned with promoting public understanding of science, 4) to be a valuable resource for those engaged in science policy studies, and 5) to stimulate greater interaction and communication with general historians, social scientists, and philosophers of science.

The 18 essays are grouped into four sections: Practice (5), Production (3), Public Interface (7), and Prospects (3). The first three are mostly analyses of comple-

mentary aspects of the chemical sciences and process industries. The fourth considers the future.

The subject matter is well researched and documented and, individually, each essay adds to the stock of historical knowledge and perspective. The wording of a few of the essays is so ponderous that I had to re-read many paragraphs several times before I thought I understood them. One excellent feature is that authors were able to modify their texts before publication, as a result of new insights gleaned from others at the conference. Since the book is relatively inexpensive, it should be in the hands of every serious student of the history of the chemical sciences.

As a collection, however, the essays were disappointing to me because they failed to represent clearly the status of the chemical sciences in the modern world. Perhaps I was led to expect something different. The illustration on the dust jacket is a reproduction of the frontispiece from A. Cressy Morrison's (b. 1864) 1937 book, *Man in A Chemical World*, which is entitled "Chemical Industry, Upheld by Pure Science, Sustains the Production of Man's Necessities." Therefore, from the dust jacket I inferred that CSMW would continue Morrison's theme but update it by half a century to correct for Morrison's myopia and one-sidedness. Writing as he did at the depth of the great depression and at the height of what historian Williams Haynes called "The Chemical Age", in Morrison's eyes chemistry and its industries could do no wrong, but beckoned all to share in a cornucopia of inexhaustible blessings flowing out of the nation's research laboratories.

Therefore, I expected CSMW not only to tell of the profession's and the industry's achievements during the past fifty years, but to point out what went wrong and to suggest ways in which mistakes can be corrected so that a tarnished public image may regain its luster. Although the chemical industry and the chemical sciences are widely depicted as a public enemy, the phrase is often heard, "There is good chemistry between us." I wanted the essayists to deal with this public ambivalence and to

consider how history can bring economic, political, and social perspective to corporate downsizing, reductions in fundamental research, pollution, superfunds, government red tape, globalization, maturation of glamour industries into makers of commodity products, and the ill preparation of some college graduates to enter the workplace (assuming jobs are available).

By contrast to these essayists, most of whom are far removed from the lab bench, reaction vessel, and business world, Morrison was a captain of industry. Associated with Union Carbide Corporation from 1906 until his retirement in 1930, he had held leadership roles in countless associations, councils, societies, and government agencies. His book, sponsored by the American Chemical Society, was to celebrate 300 years of chemical achievement in America. It was to be written in simple language so as to give the reader "a better understanding of the part that applied chemical science has had in raising the plane of living to a higher level than that enjoyed by any previous generation."

In CSMW, the section on Public Interface came nearest to meeting my expectations. Here, Helen Samuels and Joan Warner-Blewett show the increasing complexity of preserving the record of our chemical past. W. B. Jensen forcefully deals with the barriers to communication between chemist-historians and professional historians. Robert Bud discusses the problems museums

face in capturing the attention of the viewing public long enough to enhance its understanding of science. Christopher Hamlin shows how the study of past environmental disputes makes it quite difficult to see contemporary disputes in terms of "good guys and bad guys." Suzanne White traces the intricacies of regulating chemicals in food in a rapidly changing society since World War II and the resulting conflicts between large and small processed food manufacturers, regulatory bodies, and public advocates for nature's way. Finally, as a capstone, E. W. Brandt uses case histories to show how history can help industry communicate with the public, particularly in times of crisis.

I believe that most people in the chemical professions are very much aware of the widening gulf that lies between a vast and often hostile public on one side and relatively small numbers of chemical scientists and engineers, historians of science and technology, and industrialists on the other. Since bridging that gulf is going to be primarily the responsibility of those of us on the chemical side, an imperative first step will be to find better ways to communicate with each other and to meld our individual strengths in science, history, engineering, education, communication, and business into a workable, cooperative whole. *Herbert T. Pratt, 23 Colesbery Dr., Newark, DE 19720-3201*

Ideas in Chemistry. A History of the Science. David Knight, Rutgers University Press, New Brunswick, NJ, 1992. vi + 213 pp. Paper (Typeset), \$18.00.

Don't judge a book by its cover or its title. The adrenalin-stimulating cover blurb says: "In this unconventional history of chemistry, David Knight takes the refreshing view that the science has 'its glorious future behind it.' Today chemistry is primarily a service science." Refreshing? A cold beer on a hot day is refreshing: this provocative view of contemporary chemistry is anything but refreshing to a chemist and chemistry teacher. We are eternally young and vigorous, and we refuse to listen to anyone who says we are middle-aged. We must put aside our defensive attitude and listen to David Knight, who has many interesting things to tell us about history and chemistry.

As for the title, Derek Davenport, in his review in *Chemical and Engineering News* (May 24, 1993, p. 32),

says that "it takes considerable chutzpah to title a book of 200 or so pages 'Ideas in Chemistry' and even more to subtitle it 'A History of the Science'." Knight discusses the aim of the book in the first chapter and contrasts this book with other histories:

All these (other) writings will nevertheless give us a history of chemical ideas, whereas this book is about ideas in chemistry, where they are realized not merely in scientific books and papers, but also in apparatus, in laboratories and institutions, and in dyes. This is not a blow by blow account of the progress of chemistry, which it would be foolish to attempt in one small volume, but rather an attempt to pick instructive episodes in a more or less chronological order to see what roles chemistry has played over its long history.

The difference between "chemical ideas" and "ideas in chemistry" is, unfortunately, extremely subtle; and a better title would be "A Biography of Chemistry", which

is in fact the title of the introductory chapter. History as biography is not novel; Spengler said in *The Decline of the West*, "For everything organic the notions of birth, death, youth, age, lifetime are fundamentals." But Knight has concluded that chemistry has aged to the point where the biography is pretty much complete, with little anticipated for its future. This point is certain to be the one that attracts the most interest (better, scorn), but there is a fundamental chronological problem in treating the history of chemistry as a biography. A biography of Washington, for example, might be divided according to the various roles he played, with chapters entitled, "The Surveyor," "The Farmer," "The Soldier," "The President," arranged in chronological order. Knight's biography of chemistry is divided into chapters named for particular roles that chemistry has played, as noted in the passage above, for example, "A Useful Science" or "A Deductive Science." Knight connects these roles to certain historical periods, and one might mistakenly conclude that the period when chemistry was a deductive science was different from the time when it was an experimental science. As Knight says in the first chapter, "Naturally at no time was chemistry simply inductive or deductive, and it has always been experimental." In the following list I have given Knight's choice of chapter titles followed by a short description in parentheses of the content and/or chemists that are discussed. As can be seen, some chapters really involve unique historical periods and others do not. Thus, for example, one could write as well about the experimental science in the 18th or 20th centuries as the early 19th, as Knight has done:

1. Introduction
2. An Occult Science (alchemy)
3. A Mechanical Science (Boyle; Newton)
4. An Independent Science (Priestley, Black, Lavoisier)
5. The Fundamental Science (vitalism, electricity and chemistry)
6. A Revolutionary or an Inductive Science? (Dalton, Davy)
7. The Experimental Science (Davy, Wollaston, Faraday, Berzelius)
8. A Useful Science (Davy, Liebig, Playfair, Perkin)
9. A Deductive Science (chemical structure: Dalton, Kekulé, van't Hoff)
10. A Descriptive, Classifying Science (Davy, Avogadro, Mendeleev, Rayleigh, Ramsay)
11. A Teachable Science (chemical education)
12. A Reduced Science (Ostwald, Crookes, the Braggs, Moseley)
13. A Service Science (late 20th century)

If we only criticize the title or the way that Knight characterizes historical periods, emphasizing some aspect of the period and ignoring others, then we overlook the worth of this stimulating and informative book. I believe that the way to appreciate the book is to read each chapter as a separate essay on an aspect of chemistry and to ignore chronology. Each chapter begins with a short discussion of the topic at hand—science education, or deduction in science, or the nature of a revolution in science—and then proceeds to illustrate the topic with examples from the history of chemistry. Now, more examples may be cited from other periods, but that does not vitiate the value of Knight's examples. The chapters (essays) are well written, informative and interesting. Along with scientific aspects of chemistry are discussions of religion, philosophy, sociology, political history, as well as other sciences. The changing nature of the scientific profession, the development of scientific societies, the publication of scientific journals, the availability of specialized apparatus are discussed along with the major theoretical chemical developments: atoms, structural formulas, periodic law, etc.

Chapters 2, 5 and 6 are particularly rewarding. I have noticed a peculiar quantitative effect when I try to understand alchemy. If I read too little I feel ignorant; too much and I feel lost. Knight seems to have a good sense of proportion and gives us insight into the "chemical philosophy," as well as the practical discoveries of the alchemists. His discussion of chemistry as the fundamental science (Chapter 5) involves a period in which topics such as heat and electricity, as well as some biological theories, were considered to be part of chemistry, and I found this essay to be especially enlightening. The discussion of the chemical revolution in Chapter 6, adapted from a conference paper of 1988, raises several interesting points about continuity and discontinuity in chemical ideas and suggests that there is much more to explore besides the end of phlogiston and the new nomenclature.

The essay on chemistry as a useful science does not fit well with the time period which Knight assigns to it. He begins with a discussion of pure and applied science, and how gentlemen in England avoided things connected with "trade;" but he overlooks the experience in other nations in earlier times (practical investigations by Glauber, Boerhaave, Lavoisier) and the flourishing of industrial chemistry in later times. Knight tells us more than I care to know about Davy's investigations

of leather tanning but omits the important story of LeBlanc's process for soda production and its effect on the developing textile industry in Britain. Indeed, this may be the first commercial synthesis of a natural product, and the entire topic of synthesis of useful materials is virtually absent from the book. The agricultural research of Liebig and others mentioned in Chapter 8 ultimately led to the work of Haber in the laboratory and Bosch in the factory and the industrial synthesis of ammonia, which is ignored. Similarly, the lack of a synthetic dye industry in Britain after Perkin is discussed briefly, but the triumphs of synthetic organic chemists in the laboratory and the factory, leading to dyes, medicines, and plastics are not recorded.

The last two chapters concern the present century and reflect Knight's opinion that we are on the descending side of chemistry's trajectory. In the early days of the century, chemistry lost its position of importance in science to physics, as the physicists' explanations of chemical phenomena were adopted. Thus chemistry is "a reduced science" to Knight, meaning not quite as fundamental as before. Modern biology is based on organic chemistry and physical chemistry. In many instances, research could be classified as biochemistry or molecular biology. (See the recent discussion by P. G. Abir-Am, "The Politics of Macromolecules: Molecular Biologists, Biochemists, and Rhetoric," *Osiris*, 1992, 7, 164-191, on the power struggles between these disciplines.) Following Knight, should biology be considered a "reduced science?" Or should chemistry and biology be called "enhanced sciences" because they have been strengthened by contributions from other disciplines?

Further, Knight believes that chemistry has become "a service science" because other scientists have to know some chemistry, but the other sciences (e.g., biology, astronomy) are producing brilliant new discoveries while chemistry has become "not a senile science but a middle-aged one perhaps." I believe that one could look at the same evidence and call chemistry, as the American Chemical Society sometimes does, "the central science," sounding important, vigorous, fundamental, challenging. Chemistry now encompasses a vastly wider area of investigation and application. A colleague in my chemistry department publishes his research results in physics journals, and another publishes in ecology journals; they both call themselves chemists.

The importance of the question, "Is chemistry a service science or the central science?" depends on your professional outlook. The American Chemical Society is not likely to publish literature which urges students to become service scientists, nor to urge Congress to

fund more service research. Every scientist must be on the cutting edge, pushing back frontiers, creating potential technological employment. A social scientist who can look at the question "objectively" should conclude, I think, that modern chemistry is a complex enterprise involving many people and interests, and that any short label must be an inadequate and misleading descriptor.

Knight recognizes that "any book is personal, and its structure may seem implausible or misleading," and invites us to do our own research and form our own history of chemistry. In his short epilogue he urges us to learn what historians have said recently, as well as to read the original scientific literature. He sees the history of science as a fresh and open field of study, comparable to early 19th century science, and much more exciting than his view of modern chemistry.

Knight's writing is lively and interesting, though occasional ultra-SAT words like "inosculated" and "rebarbative" appear. Indeed, the spelling is often "rebarbative," with numerous omitted ("eighteenth"), inserted ("Lavoilsier") and changed ("chanded") letters, as well as missing and added words. The notes are extensive and useful, the index short and idiosyncratic. For example, there are index entries for "Failure", "Fashion" and "Fraud", but it would be difficult to find the discussion about the discovery of the "noble gases" on page 139, because there are no entries for argon, helium, inert gas, nitrogen, noble gas, or Rayleigh.

I also noticed a few factual errors. The claim that coal gas was a valuable by-product of the making of coke (p.104) might be modified; in the U.S., coal gas and coal tar were burned as they formed, and water gas was used for lighting. G. N. Lewis's definition of an acid (p.169) is an electron-pair acceptor, not a proton donor.

Publishers invariably overstate the audience for a book, and the tradition is upheld here. The recommendation of the book to "a general reader" is unjustified because of the necessary scientific jargon ("Pauling's theory of resonance giving way to the study of molecular orbitals") which makes much of the book inaccessible; "a student" might do better if she or he knew some chemistry, but the book is not really a useful textbook for the history of chemistry. The readers who will derive the most from the book are the "scientist" and "historian of science," who will bring their own knowledge of chemistry and history to interact with Knight's novel presentation of the subject—a presentation which, as the cover blurb says, will "engage the attention of anyone interested in the interplay of science and ideas." *Martin R. Feldman, Department of Chemistry, Howard University, Washington, DC 20059.*

My 32 Semesters of Chemistry Studies. Vladimir Prelog, American Chemical Society, Washington, D.C., 1991. xxiv + 120 pp. Cloth (Typeset), \$ 24.95.

The intriguing autobiography by Vladimir Prelog serves as an excellent companion to Barton's *Some Recollections of Gap Jumping* and Havinga's *Enjoying Organic Chemistry, 1927-1987* in that all three of these highly creative scientists were repeatedly able to weave a thread of stereochemistry throughout their research efforts. Indeed, the recognition of novel stereochemical principles was a primary reason why both Prelog and Barton were awarded Nobel Prizes.

The title of Prelog's book conveys useful background information. As a committed scientist who was highly motivated to remain at the frontier of chemical truth, Prelog was in a serious quandary as to how he might deal with retirement. With the ending of his formal career on the faculty in 1976, the most workable ploy by which Prelog might remain an active member of the ETH community was to accept the position of "postdoctoral researcher." Thereby, Prelog may have succeeded in becoming the only postdoc in the history of science who had previously won a Nobel Prize!

Like many chemists of his generation, Prelog conducted an extensive series of studies involving natural products. As a testament to his courage, intelligence, and versatility, his research in this area, especially in the 1940's, was of enormous breadth encompassing steroids, indole alkaloids, and quinine. By a careful reanalysis of earlier publications and a small number of inspired experiments, he was able to show that the published structure of strychnine was in error and then to propose a more accurate, alternative structure. In his classical investigation of the macrolide narbomycin, he isolated a simpler degradation product that since has become known as the Prelog-Djerassi lactone, a molecule of such importance that it has been prepared synthetically numerous times since 1975. As Prelog notes with some sense of irony, obtention and identification of this relatively simple by-product probably led to more fame than any of his other research projects at ETH. Yet many of his natural product studies led to real insight into major compound classes. This is exemplified by his work on nonactin, with its marvelous stereochemical peculiarities, and by his extensive investigations of the iron-containing ferrioxamines.

Relatively early in his career, Prelog was intrigued by conformational questions involving medium- and large-ring alicycles. Under the maxim that "necessity is the mother of invention," he independently developed the utility of the acyloin condensation as an entry into the heretofore rare medium-ring systems. From this "purely" synthetic research emerged marvelous forays into transannular chemical phenomena, an interest in large-ring compounds that was maintained with his now classical macrolide antibiotic studies, and an ever-expanding desire to raise sophisticated questions involving apparently arcane stereochemical issues. Yet from the latter came a re-exploration of the foundations of asymmetric synthesis that ultimately led to a much deeper understanding of the nature of stereoselectivity in enzymatic processes. As Prelog considered even such "simple" issues as which face of a molecule is prone to attack by an asymmetric reagent, questions of specific nomenclature arose as a natural consequence. The asymmetric component of enzyme catalysis is slowly losing its mystery as an affectionate marriage occurs between formal mechanistic electron flow arrow-pushing descriptions and fundamental stereochemical concepts. How intriguing that the "secret of life" still might actually be held by the distinguishable shape of our left and right hands, a perspective of reverse anthropomorphism probably first grasped by Pasteur! From the coming together of several key individuals to work out the specifics of such questions, we now have in place the extremely important Cahn-Ingold-Prelog (CIP) specification that has had a major impact on communication between organic chemists. Furthermore, adoption of this system and consideration of its implications have inevitably forced considerably greater sophistication in stereochemical thinking among virtually all contemporary organic chemists and biochemists.

The natural development of Prelog's research interests has often led him into very unusual stereochemical areas. Noting how the modern explosion of supramolecular organic chemistry emerged from the seemingly esoteric work of Cram, Lehn, and others, Prelog, through his current emphasis on geometric enantiomerism, vespirenes, enantioselective ion-specific electrodes, and oligomeric crown ethers, may be giving us an intriguing glimpse into the future of this discipline. What appeals to the curiosity of a very experienced scientist such as Prelog could well constitute "bread and butter" chemical studies for the next generation.

One of the most stimulating contributions made by Prelog was his rational synthesis of adamantane, a compound whose highly symmetrical structure is so aesthetically satisfying. Relating a fascinating anecdote, Prelog describes one of those incredibly rare intellectual leaps where intuition outperforms intellect. The Czech chemist Landa had isolated a hydrocarbon with molecular weight 136 and the unpredictably high melting point of 266 C! While Landa was repeating an elemental analysis, he noticed that this compound readily sublimed to afford tetrahedral crystals. When Landa showed these to Prelog's coworker Lukes, the latter walked to the blackboard and, within a few seconds, wrote the structure of "tetracarba-hexamethylenetetramine." To have this insight (and to be right) has to qualify as a rare instance in science where magic crossed the fog of ignorance—all before any modern instrumentation might assist in solving the structure. With a touch of sadness, Prelog confides that, because of wartime problems with his synthetic publications, many libraries are missing the critical papers and that this has given rise to the myth that he was only able to prepare traces of adamantane whereas in fact he made multi-gram quantities. The sharing of such sagas is an essential part of this series. The heroic players from the "golden age" of organic chemistry will soon pass on. This is the last time not only for them to share these wonderful adventures but also to clarify the facts behind some of the most intriguing intellectual advances of this century.

Besides containing an articulate, carefully crafted discussion of his many intellectual accomplishments, Prelog's autobiography abounds in wise observations regarding the "craft" of organic research. He notes, how, after a particularly long struggle to elucidate the correct structure for the antibiotic rifamycin, his final answer was at variance with a photograph that appeared in the publication documenting rifamycin's first successful X-ray structure. His anguish at making such a serious "blunder" was short-lived when he soon discovered that the model used for the published photograph had accidentally come apart during transport to the photographer and had been incorrectly reconstructed. From this incident comes his advice that chemists should be willing to have faith in their own wet chemical results when they have carefully taken pains to achieve internal consistency and should not be so willing automatically to capitulate in the face of the various modern structure-elucidation techniques. A second, much more tragic anecdote concerns the treatment of a graduate student by an advisor who became convinced that the particular student had somehow "cheated" on an important experi-

ment. In spite of the student's vehement protestations of innocence, the advisor publically condemned that student out of science. Even though later evidence demonstrated that the student's observations were probably correct, he had been denied a career in science. How sad that anyone else in science might also be able to commit such an injustice under conditions in which he or she strongly believed that they were "right." With all the current attention being paid to scientific fraud, perhaps we should be somewhat more willing also to give the benefit of doubt in cases where it is not absolutely certain that an unethical misdeed has transpired!

In reading these American Chemical Society autobiographies, one cannot help noticing that something very special sets these chemists apart from others. While these individuals are obviously gifted with extraordinary intellect, they also appear to have two special additional characteristics: a remarkable flair for choosing critical (and solvable) problems in organic chemistry and a driving force of will that allowed each of them to make a real difference in the development of their discipline. Whereas most of us in the daily practice of our profession consider ourselves fortunate if we uncover even a few publishable nuggets of new chemistry, these individuals shook the very fabric of their field and folded it into an entirely new form. There is evidence in each of their careers for a personal style that is unique. It may have been that, because they were so acutely original, they stood out from all the rest and thereby were able to attract the elite of their generation who, in turn, even further expanded an adventure newly begun. The special spark of creativity exhibited by individuals such as Prelog often kindles unique excitement in those with the intelligence and curiosity to perceive its presence and who also might wish to share in its warmth and illumination.

A key feature of Prelog's book shared in common with Barton's autobiography is the stark realization of just how important one or two key individuals can be in shaping the chemistry of their era and their continent. Chemists like Robert Robinson and R.B. Woodward appear over and over as lightning rods for the development of the careers of their junior colleagues. For example, the intellectual and spiritual debt of Barton to Woodward is made crystal clear in Barton's autobiography. For Prelog, the comparable individual was Ruzicka. The affection and esteem Prelog feels for Ruzicka is at once both endearing and educational. In a similar fashion to Barton, Prelog makes a great effort to point out how much his mentor influenced his career development. The leadership and stimulation of Ruzicka ranged from

the most simple task of securing entry visas for Prelog and his wife to more intangible aspects such as encouraging Prelog always to work up to his potential. Prelog makes the interesting and not generally known point that Ruzicka was an important backer of Woodward early in his career when many of his American contemporaries had not yet recognized Woodward's genius. While it might currently be fashionable to denigrate the possibly patronizing, career-shaping aspects of the old-fashioned scientific establishment, it is just as questionable whether a competitive "community" of vicious scientists is preferable. Perhaps all of us can learn a lesson in the importance of true encouragement and collegiality among pro-

fessionals. In my opinion, Prelog, in a subtle but effective fashion, is trying to communicate to the reader that the common enemy in the progress of science is our ignorance and should not be each other; and, furthermore, that positive, helpful individuals (such as Ruzicka), by rising to the occasion, can have an enormously constructive impact on their colleagues and institutions. One of the truly outstanding aspects of this series of books is the inclusion of these little homilies. Perhaps a cynic might find such comments by Prelog and others trite and inappropriate; but they might also just as easily be perceived as real food for thought. In the "Golden Age," the giants had class. *John Belletire, Ricerca Inc., Box 1000, Painesville, OH 44077-1000.*

The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry. Alan J. Rocke, University of California Press, Berkeley and Los Angeles; 1993, xiii + 501 pp. Cloth \$50.

Alan Rocke has masterfully combined in one volume the definitive study of the development of the structural theory of organic chemistry during the first six decades of the nineteenth century and the first full-length biography of Hermann Kolbe (1818-1884). Those who wish to obtain a more in-depth discussion as well as the latest scholarship concerning the development of structural theory will find Rocke's book a valuable companion to O. T. Benfey's classic *From Vital Force to Structural Formulas*, recently reprinted by the Chemical Heritage Foundation.

Herman Kolbe's many valuable contributions to the development of organic chemistry have been largely overlooked in this century. This is probably due to his self-destructive behavior in his latter years. Several of the newer introductory texts in organic chemistry reprint Kolbe's diatribe concerning van't Hoff's publication in 1874 of "The Arrangement of Atoms in Space." For most chemists today, knowledge of Kolbe extends to the reaction that bears his name for the synthesis of salicylic acid (1873), his electrochemical method of decarboxylation (1846), and his total synthesis from inorganic reagents of acetic acid (1844). However, Kolbe in his time was considered

to be one of the leading lights of German chemistry, being on the same plane as Liebig, Wöhler, Bunsen, Kekulé, and Hofmann. Among Kolbe's Ph.D. students were Griess, Clauss, Crum-Brown, Volhard, Graebe, Zaitsev, Menshutken, Markovnikov, Armstrong, E. von Meyer, Curtius, Schmidt, and Beckmann. Kolbe produced 156 solo papers and 20 co-authored publications; the students he supervised added another 287 over a period of 43 years. Students from Russia, Britain, and the United States came to Kolbe's laboratory in Marburg (1851-1865) and Leipzig (1865-1884) in large numbers and thus his influence extended well beyond the borders of Germany.

Kolbe's career spanned that most exciting period in the nineteenth century when the question of the structure of organic compounds was still in flux. Kolbe was the son of a Lutheran pastor and grew up in rustic simplicity in the villages of Elliehausen and Stockheim in the then Kingdom of Hannover in central Germany. He was very much influenced by his rural upbringing and his mentors Wöhler and Bunsen. Rocke summarizes the influence as follows:

Both chemists were enormously prolific, and moreover, extraordinarily skilled, inventive, and precise in laboratory operations...Wöhler and Bunsen were also alike in their brilliant teaching abilities, their predilection for experimental investigations, and their habitual avoidance of theory...But, significantly, both scientists left the discipline of organic

chemistry just when it began to explode theoretically in the early 1840s.

Kolbe never felt comfortable with the ideas of Dumas, Laurent, and Gerhardt and preferred to try to stem this rising tide of reform with inventive and polemics. However, by late 1855 Kolbe had realized that he was fighting a losing battle, especially after Wurtz's synthesis of both symmetrical and unsymmetrical hydrocarbons. These results showed that complete substitution of hydrogen by many elements was possible. Kolbe's most productive period now followed, as he used his own version of type theory. Rocke presents us with a detailed description of Kolbe's life and work at Marburg which was the most scientifically creative period in his life. Although poorly paid, his institute chronically underfunded and ill-equipped, he nevertheless managed to attract many students because of his brilliance.

In 1865 Kolbe was called to Leipzig. There he received an excellent salary while the best chemical institute in all of Germany was constructed for him. Just as he had accommodated himself to type theory, structural formulas were being almost universally accepted by German chemists. Rocke does a superb job of showing how Kekule developed his structural ideas based upon the reform of atomic weights and the concept of valence. Kekulé is portrayed as the diametrical opposite of Kolbe. Whereas Kolbe came from a humble background, Kekulé came from a prosperous family in Darmstadt, Hesse. Whereas Kolbe's education was very basic, Kekulé received a classical as well as scientific education at the Darmstadt Gymnasium. He is described by Rocke as "handsome, tall, strong, and athletic, an enthusiastic gymnast and dancer."

Kolbe could not and would not accept the idea of a carbon chain because structural theory excluded any electrical basis as the reason for bonding. Kolbe was an

early adherent of Berzelian dualism and never really felt comfortable with other views. From the pages of the *Journal für praktische Chemie*, of which Kolbe was editor from 1870, there appeared the most venomous ridicule of structural theory. Increasingly, Kolbe became isolated and alienated from the German chemical community, something which did not seem to bother Kolbe at all. Kolbe manifested the worst excesses of xenophobia, particularly anything French, and a virulent, almost pathological anti-Semitism. As Rocke states in his book:

Kolbe was nothing if not conservative in his theoretical preferences, and he began to view novel developments in chemistry as just another aspect of modernism. Somehow he began to associate structural formulas with sensualism and materialism, possibly even with irreligion. His whole life was devoted to the science of organic chemistry, and he saw that science almost in the personification of a pure virgin being seduced and destroyed by meretricious villains, by liberals, social democrats, traitors, atheists, Catholics, and Jews. In the 1850s and 1860s, he suffered periods of paranoia and severe depression, and after 1870 he appears to have had delusions of grandeur.

This is the Kolbe that most remember, rather than the man of many major scientific achievements. Rocke presents a balanced view of Kolbe with a level of scholarship, thoroughness, and documentation (83 pages of notes) that will please both the chemist and historian alike.

The Quiet Revolution will serve as an invaluable reference work on the development of organic chemistry in the nineteenth century and belongs on the chemist's bookshelf and in the library of every college and university with a chemistry program. *Martin D. Saltzman, Providence College, Providence, RI 02918.*

Issue 15/16, page 10: Credit for the portrait of Benjamin Silliman, Jr. to the Smithsonian.

Erratum

Issue 15/16, page 38: The structure of benzoic acid, the product in the last equation, should be:

