THE GENESIS OF ELECTROGRAVIMETRY

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In his Wolcott Gibbs Memorial Lecture, Frank W. Clarke, who had studied under Gibbs from 1865 to 1869, commented on the advances in analytical chemistry made by Gibbs and his students at the Lawrence Scientific School (1):

> But the most important of all was the electrolytic determination of copper, now universally used, which was first published from Gibbs' laboratory. It is true that a German chemist, Luckow, claimed to have used the method much earlier, but so far as I can discover, he failed to publish it. Gibbs, therefore, is entitled to full credit for a process which was the progenitor of many others.

As discussed later, C. Luckow published this claim soon after the appearance of Gibbs' account. A paper that marks the centenary of Gibbs' work on electrogravimetry does not mention Luckow, who may have originated the technique (2).

Oliver Wolcott Gibbs (1822-1908) - he dropped the first name, Oliver, early in his career - was a scientist of wide interests (1). Apart from his contributions to analytical chemistry, his work on the ammonia-cobalt compounds and on phosphotungstic and other complex inorganic acids occupied much of his career. He was very much a person-to-person teacher, keeping in close touch with his comparatively few students.

Results obtained by E. V. M'Candless, presumably one of Gibbs' students, form the basis of the 1864 announcement of the technique that later became known as electrogravimetry. Actually, the very brief announcement, "On the Electrolytic Precipitation of Copper and Nickel as a Method of Analysis", is the sixth and final section (pp. 334-36) of Gibbs' paper, which carries the general title "Contributions to Chemistry from the Laboratory of the Lawrence Scientific School" (3). The other sections deal with purely chemical separations, such as of chromium, manganese, cobalt, and uranium from various other metals.

The deposition of copper from solutions of the sulfate was carried out in a small platinum capsule connected to the negative pole of one or two Bunsen cells. The positive electrode was a stout platinum wire that dipped centrally into the solution. Completion of deposition, taking one to three hours, was checked by testing a drop of the liquid with hydrogen sulfide water. After washing and vacuum-drying over sulfuric acid, the copper-carrying capsule was reweighed. Six results with an average close to the theoretical value and a standard deviation of about 0.3% are quoted.

M'Candless then determined copper in copper-nickel coinage alloy. Four of his results were within 0.05% of the specified 87.50% of copper. Some abnormally high results were attributed to over-rapid deposition, resulting in a spongy deposit. This is difficult to wash free from impurities and also oxidizes easily.

Oliver Wolcott Gibbs

Two points made by Gibbs were that, after removal of copper, the solution contained any other constituents of the sample and that it was at least probable that nickel might be determined by electrolysis of an ammoniacal solution of its sulfate. In two determinations of nickel in a commercial sample, M'Candless obtained results of 91.36% and 91.60%. The metal deposit was bright and coherent, thus upholding Gibbs' prediction. What a pity that no nickel determinations were reported for the copper-free liquid from the coinage alloy experiments! Then we should have had the first example of an overall electrogravimetric analysis of a sample.

In 1865, C. Luckow, a chemist working for the Cologne-Mindener Railway, claimed that he had been determining copper and silver by electrolysis since 1860 (4,5). In view of subsequent events, there is no reason to doubt his claim. He entered his methodology in a competition organized by the Mansfeld Ober-berg und Hütten Direction in Eisleben. This company needed a rapid and reasonably accurate method for the determination of copper in ores, etc. The prize went to a Dr. A. Steinbeck for a method that involved titration in ammoniacal medium with potassium cyanide as a final step. However, Luckow also received an award. The details of both methods were published by the company in 1869 (6). Originally Luckow, like Gibbs, had used the rather slow deposition from sulfate medium; otherwise he might have won the competition. Progress by Luckow and by others soon increased the speed and versatility of electrogravimetry.

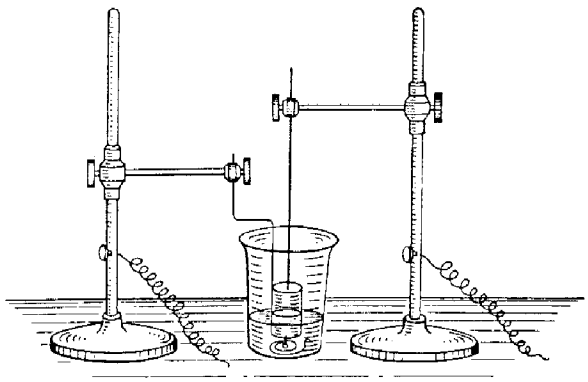
Two major advances made by Luckow were his discovery

that deposition of copper from dilute nitric acid medium was advantageous and his introduction of a separate cathode, i.e., one that was not also the solution container. He used a platinum foil that was about 2-1/2 in. long and 1-1/4 in. wide. This was bent into a cylinder and a stout platinum wire was attached. The anode, a flat platinum wire spiral of diameter to fit into the bottom electrolysis beaker, had a vertical extension to carry a binding post, and a stand with an arm carrying a screw connector held the cathode with its lower edge close to the anode.

Luckow also examined the electrolytic behavior of a number of other metals, especially those likely to accompany copper in technical samples (6). By suitable adjustment of the medium, he achieved simultaneous deposition of copper on the cathode and lead, as lead dioxide, on the anode.

Three years after the first communication from the Eisleben laboratories, another described some developments, including an improved platinum electrode system (7). The cathode, now of conical form, was slotted, so that oxygen arising from the anode could pass to the exterior of the cathode. In a sense, this was the ancestor of the gauze-type electrodes that permit free circulation of the solution. The actual aim was, however, to overcome a problem that occurred in the analysis of copper samples that contained much iron. With a simple cylindrical cathode a dark coloration, caused by reduction of iron along with the copper, appeared in the oxygen-starved region around the outside of the cathode. By the summer of 1869, the laboratory was able to determine copper in all samples that were free from antimony, arsenic and bismuth, which precipitate on the copper deposit and blacken it.

In 1880, Luckow wrote a partially-reminiscent paper concerning the use of the electric current in analytical chemistry (8). He recalled the accounts that he had published in 1865 (4) and pointed out the advantages of electrodeposition. One of these was that the process can run unattended, e.g., overnight. Following a survey of the electrochemical behavior of solutions of various acids and salts, Luckow referred to some of the then recent investigations by others. Examples included the determination of nickel (9-12), copper (9,10,12), cobalt (9,10,12), lead, zinc and manganese (11), and mercury (13). This last determination was described by Frank W. Clarke, the author of the Gibbs Memorial Lecture (1).



Luckow's electrode arrangement for electrodeposition

Some of the later developments that extended the scope and speed of electrogravimetry have recently been reviewed (14,15). One of these was the mercury cathode, developed by Edgar Fahs Smith and his students (14). The publication of Smith's book in 1890 (16) evoked a short note from Gibbs (17). This concerns a paper that Gibbs had read before the National Academy of Sciences in 1885. The note states that the experiments that he made on metal deposition on a mercury cathode were purely qualitative, and that Luckow subsequently applied the same process to the estimation of zinc (18).

References and Notes

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Hermann Kolbe

"BETWEEN TWO STOOLS": KOPP, KOLBE AND THE HISTORY OF CHEMISTRY

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Hermann Kopp (1817-1892) and Hermann Kolbe (1818-1884) were two outstanding German chemists during the period in which German chemistry rose to a position of prominence in Europe (1). Although I know of only five surviving letters from Kopp to Kolbe and only one letter draft from Kolbe to Kopp - a document which we reproduce below - they must have been well acquainted for four decades. They may have first gotten to know each other when Kolbe was working as a newly minted Ph.D. with Robert Bunsen (1811-1899) at Marburg, and Kopp was Privatdozent and then Ausserordentlicher Professor at nearby Giessen, during the years 1842-1845. After Kolbe became Bunsen's successor in 1851 (Bunsen having been called to Heidelberg), he maintained relations with all of the Giessen chemists and visited them not infrequently. Upon Justus Liebig's transfer to Munich in 1852, Kopp and Heinrich Will became Liebig's joint successors; the following year they divided up their duties, Will taking experimental chemistry and the directorship of the laboratory, with Kopp becoming professor of theoretical chemistry. In 1863 Kopp was called to Heidelberg, becoming a colleague of Bunsen; he remained there for the rest of his life.

Kopp's life work was investigating the relationships between physical and chemical properties of chemical compounds; he has rightly been regarded as one of the founders of the discipline of physical chemistry. But he was also active in a literary sense right from the beginning of his career - indeed, his first love as a student had been philology. His classic four-volume *Geschichte der Chemie* was complete by his 30th birthday. The first edition was quickly sold out, and he began immediately to work on revisions for a second edition; he died 45 years later, the revision still incomplete. When Liebig left Giessen, new literary duties were added - principal editor of Liebig's *Annalen der Chemie*, and, with Will, managing editor of the annual *Jahresbericht der Chemie*. He continued these duties even after his transfer to Heidelberg.

Shortly after his arrival in Heidelberg he was asked by the Bavarian Academy of Sciences to write a history of modern chemistry in Germany, as part of a project to commission two dozen disciplinary histories in a series entitled *Geschichte der Wissenschaften in Deutschland*. The initiator of this project was Leopold von Ranke (1795-1886), one of the founders of modern critical historiography, whose goal was to write history "wie es eigentlich gewesen ist", that is, without thematic, didactic, or rhetorical coloration. Kopp had been strongly influenced by this German objectivist historiographical movement as early as the 1840s (2).

The result of this contract emerged in the early 1870s as *Die Entwickelung der Chemie in der neueren Zeit*. (3). Kopp did not, however, succeed in making this a history of German chemistry, despite (as he wrote Liebig in January 1871) numerous attempts to follow Ranke's national program (4). In his preface, dated April 1873, he took the offensive; he averred that science, being international by nature, can only be written from an internationalist perspective (5). The work was indeed aggressively international. The first two-thirds of the long crucial final chapter, covering the development of theories of molecular constitution during the most recent period (1840-1860), scarcely mentioned a German name - until he introduced the development of structure theory by August Kekulé (6). In effect, Kopp found Ranke's critical historiography