

An American Pioneer in Platinum Metal Research

THE LIFE AND WORK OF WOLCOTT GIBBS

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This year marks the 150th anniversary of the birth of the man whom Ferenc Szabadváry has called "the first great personality in American chemistry" (1). According to Donald McDonald, Gibbs' work on the platinum metals "led to a considerable increase in the knowledge of the chemical properties of the salts of these metals but not to a satisfactory method for their separation on either an analytical or a commercial scale. His work was important and useful, and no record of the history of platinum should omit to mention it" (2). Strangely enough, Raleigh Gilchrist, in a review (3) that has been described as "the most effective condensation of acceptable wet methods of

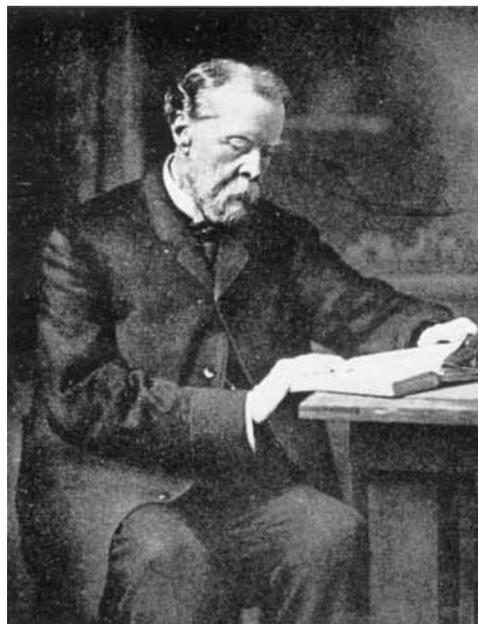
[platinum metal] separations on a macro scale published before 1943" (4), does not mention Gibbs among his 813 references. Nevertheless, Gibbs' method of separating rhodium by use of sodium sulphide (5) has more recently received attention (6). This brief review of Gibbs' research on the platinum metals is given with the hope that perhaps some of his now neglected procedures may yet be employed in newer methods of separation and determination.

Gibbs' Life

Wolcott Gibbs—he dropped his first name Oliver early in his career—was born in New York City on February 21st, 1822, of a

Wolcott Gibbs 1822–1908

Born one hundred and fifty years ago, Gibbs received a training in medicine but turned to chemistry and undertook a very varied programme of work, including some of the earliest research in the United States on the platinum metals. He has been called "the first great personality in American chemistry"



distinguished family (7). He graduated from Columbia College at the age of 19. After graduation he served in Philadelphia as assistant to Robert Hare, inventor of the oxyhydrogen blowpipe. In 1845, at the age of 23, he received the degree of Doctor of Medicine with a dissertation on a natural system of classification of the chemical elements. He never practiced medicine but in later life studied the physiological effects of chemical compounds upon animals.

Since at that time advanced scientific education was not readily available in the United States, Gibbs next spent several years studying in Europe. In 1849 he was appointed Professor of Chemistry at the newly established Free Academy, which later became the City College of New York and is now the City University of New York. He remained there for fourteen years during which time he produced in collaboration with Frederick Augustus Genth his first really notable research, a memoir entitled "Researches on the Ammonia-Cobalt Bases" (1856), that has become famous in the annals of co-ordination chemistry. In 1863, largely as a result of his recent research on the platinum metals, he was called to Harvard University as Rumford Professor in the "Application of Science to the Useful Arts", a position which he retained until his retirement in 1887. He continued to work in his private laboratory in his home at Newport, Rhode Island for several years. He died on December 9th, 1908, at the age of almost eighty-seven.

More than any other one man, Gibbs introduced into the United States the German system of research as a means of chemical instruction, a practice which is now taken for granted. Known primarily as an experimentalist rather than a theorist, Gibbs' work was extremely varied. In analytical chemistry, he is best known as the discoverer of electrogravimetry. He also invented several pieces of chemical apparatus. His later years were devoted to a vast, extremely complicated and almost unexplored field,

the chemistry of heteropoly compounds, which he called the complex inorganic acids. He was editor of the American Journal of Science and one of the founders of the U.S. National Academy of Sciences. His face is sculptured in relief on the wall of the Capitol in Washington, D.C.

Gibbs' Researches

Gibbs' work on the platinum metals can be divided into two parts—(1) osmium complexes (1858–1881), and (2) separation procedures (1860–1864).

Dioxotetraammineosmium(VI) Salts

Gibbs and Genth peripherally dealt with the platinum metals in their classic memoir of 1856 (8). On the theoretical side, they proposed "a new theory of the platinum bases" (platinum-ammines), while experimentally they prepared the hexachloroplatinates(IV) of their four cobalt-ammines. Yet their first publication devoted specifically to the platinum metals was a one-page "Preliminary notice of a new base containing Osmium and the elements of Ammonia", published in March of 1858 (9). In this, their last joint publication, they pointed out that their "investigation of the ammonia-cobalt bases . . . led us to direct our attention to the production of similar compounds with other metals".

Gibbs and Genth reinvestigated the yellow crystalline salt first discovered in 1844 by Edmond Fremy and called by him "osmiamide" (10). This compound, formulated by Fremy in pre-Karlsruhe terms as $\text{NH}_4\text{Cl} \cdot \text{OsO}_2 \cdot \text{NH}_2$ (actually $2\text{NH}_4\text{Cl} \cdot \text{OsO}_2 \cdot (\text{NH}_2)_2$) was prepared by adding ammonium chloride to a solution of potassium osmate: $\text{K}_2[\text{OsO}_4] + 4\text{NH}_4\text{Cl} \rightarrow [\text{OsO}_2(\text{NH}_3)_4]\text{Cl}_2 + 2\text{KCl} + 2\text{H}_2\text{O}$. Gibbs and Genth found that the compound, "of much interest from a theoretical point of view", was the salt of a cation (in their older terminology, base) which Gibbs later called "osmyl-ditetramin" to distinguish it from the as yet undiscovered "osmio-ditetramin" ($\text{Os} \cdot 4\text{NH}_3$, i.e., $[\text{Os}(\text{NH}_3)_4]^{2+}$,

which, incidentally, has still not been discovered). They prepared the hexachloro-platinate(IV) of this cation as well as a well-defined crystalline sulphate, nitrate, and oxalate. The full report including analysis was not published until more than twenty-three years later in 1881 (11) by Gibbs alone, who stated that:

"My researches on the metals of the platinum group were interrupted many years since by the want of a laboratory in which the separation and collection of osmic hyperoxide, OsO_4 , could be effected without serious danger to the air-passages and to the eyes. . . . The experimental part of the work here published was finished long since. I have delayed its publication in the hope of rendering it more complete, and especially of generalising the results in various ways. . . ."

Gibbs found that the chloride decomposed on heating according to the equation: $[\text{OsO}_2(\text{NH}_3)_4]\text{Cl}_2 \rightarrow \text{Os} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O} + \text{N}_2$, thus furnishing "perhaps the most simple and convenient method of obtaining pure metallic osmium". He also observed that a solution of the chloride produced a violet colour with potassium ferrocyanide. He described this reaction as "very delicate" and claimed that it "affords the best method yet discovered for the detection of minute quantities of osmic hyperoxide $[\text{OsO}_4]$ in the wet way". Gibbs gave specific directions for this test, which he claimed made it "possible to recognise quantities of osmium too small to be detected by the characteristic odour of the hyperoxide". He concluded his report by mentioning the possibility that, inasmuch as ruthenium forms RuO_4 analogous to OsO_4 , ruthenium might form a similar series of compounds $[\text{RuO}_2(\text{NH}_3)_4]\text{X}_2$. Such compounds have still not been discovered.

Analytical Separations

Inasmuch as Gibbs was primarily an analytical chemist, it is not surprising that his research on the platinum metals was directed largely toward analytical applications. In a published letter of March 30th, 1860, to one of the editors of the American Journal of Science (12), Gibbs, in addition to giving a preliminary report of his work on

osmium discussed above, declared: "I am confident that I shall be able to effect a perfect separation of all the metals of the platinum group".

In 1850, the existence of alluvial native platinum in California was reported. It was found in the gold placers at the western foot of the Sierra Nevada (13) and was normally much richer in osmiridium than are the better known larger deposits. In 1861, Gibbs published the first of his series of three articles entitled "Researches on the Platinum Metals", which firmly established his reputation as one of the foremost chemists in America. In his first article (14), he differentiated and contrasted the Siberian variety of osmiridium from the Californian variety. Although the amount of osmiridium obtained at the time did not exceed a few ounces for every million dollars' worth of gold, Gibbs predicted "large quantities of the ore will be obtained whenever important practical applications of the metals contained in it shall create a demand".

Gibbs then addressed himself to what had "always been considered as among the most difficult problems with which the chemist [had] to deal", viz., the separation of the different platinum metals from each other. Gibbs felt that "much remained to be done, especially as the Californian ore differs from the Siberian in the greater relative proportion of Ruthenium which it contains". In the course of his investigations, "at great expense of time and labour", Gibbs was "able to test upon considerable quantities of material, nearly all the methods of working the ores of osmium, etc., which have hitherto been employed". He gave critical evaluations, with modifications and improvements for the Californian ore, for the methods of Fremy (15), Persoz (16), Weiss and Döbereiner (17), Wöhler (18), Fritzsche and Struve (19), and especially Claus (20).

Claus' method of treating Siberian osmiridium consisted of fusing it with a mixture of potassium hydroxide and potassium nitrate, powdering the cooled melt, and

dissolving the resulting soluble potassium osmate (K_2OsO_4) and potassium ruthenate (K_2RuO_4) in cold water. Gibbs found that with the Californian ore even after three or four successive fusions a large quantity of black matter insoluble in aqua regia still remained. He therefore suggested: (1) fusion of the ore with sodium carbonate prior to the fusion with the potassium hydroxide-potassium nitrate mixture, which greatly facilitated the subsequent action of the oxidising mixture; and (2) boiling the oxidised fused mass with water containing alcohol, which reduced the potassium osmate to potassium osmite (probably $K_2O \cdot 3OsO_2$), thus avoiding escape of toxic osmium(VIII) oxide, and decomposed the potassium ruthenate to a mixture of insoluble ruthenium oxides, which remained with the oxides of the other platinum metals.

In his second paper (21), Gibbs declared "the problem of the complete separation of the metals of the platinum group worthy of a new investigation", and he proposed a method based on the results of his research on the reactions of potassium nitrite and sodium nitrite with all six platinum metals, which seems to be the first systematic study of the platinum metal nitro complexes.

In his third article (22), Gibbs presented a second general method of separating the four platinum metals (Pt, Ir, Rh, and Ru), which involved hexaamminecobalt(III) chloride, the "luteocobalt chloride" first discovered by Genth in 1847 (23), reported by him in an obscure German-language journal published in Philadelphia (24), and described in great detail in Gibbs and Genth's monograph of 1856 (8). The process was based upon the fact that the hexachlororhodate(III) and hexachloroiridate(III) of the hexaamminecobalt(III) ion are almost completely insoluble in boiling water and in boiling dilute hydrochloric acid, whereas the corresponding hexachloroplatinate(IV) and hexachlororuthenate(IV) are easily soluble.

Some of the substances formed in Gibbs' separation schemes are still not too well

investigated, and a new study employing modern methods would be a fitting tribute to Gibbs and might simultaneously yield some interesting data.

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