Notes from the Oesper Collections

Hofmann Demonstration Apparatus

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The 19th-century German chemist, August Wilhelm Hofmann (figure 1), is well-known to historians of chemistry for his work in elucidating the chemistry of the amines, his early contributions to the synthesis of aniline dyes, and his discovery of the Hofmann degradation and elimination reactions. He also played a key role in the professional development of chemistry in both Great Britain and Germany – the former through his nearly 20-year directorship (1845-1865) of the Royal College of Chemistry in London (1) and the latter through his role, after his return to Germany, in the founding of the Deutsche chemische Gesellschaft and his service as that society's first president (2). After his death, the society's new headquarters were named the "Hofmannhaus" in his honor and the society commissioned a detailed book-length biography coauthored by no less a luminary than Emil Fischer (3).

Less often commented on by his more recent biographers is Hofmann's interest in chemical education and his development of a large number of standard 19th-century chemical demonstrations. The present author has drawn attention to some of these in previous publications and lectures (4, 5). Indeed, these demonstrations were so popular that laboratory supply houses soon began offering specially designed "Hofmann Demonstration Apparatus" for sale and several surviving examples of this equipment are to be found in the Jensen-Thomas Apparatus Collection.

Hofmann's interest in lecture demonstrations began in 1860 with the publication of a brief paper on a new method for illustrating the volumetric composition of ammonia (6) and was followed in 1865 by a lecture to the London Chemical Society "On Lecture Illustrations" (7). The many woodcuts used to illustrate the printed version of this lecture were obviously taken from the plates for his forthcoming book, *Introduction to Modern Chemistry Experimental and Theoretic,* which reproduced his introductory lectures at the Royal College of Chemistry and which was published the next year (8). He continued to refine and expand his repertoire of lecture demonstrations after his return to Germany and, in 1869, during his tenure as President of the German Chemical Society, he gave a detailed lecture on these newer developments to the society as part of a special meeting convened to celebrate the opening of his new chemical laboratory at the University of Berlin (9). His interest in this subject persisted unabated almost to the day of his retirement and, between 1870 and 1882, he continued to publish occasional updates (10).

Figure 1. August Wilhelm Hofmann (1818-1892).

The Sodium Spoon

As revealed in his published lectures of 1866, Hofmann's approach to introductory chemistry was to gradually introduce his students to basic chemical concepts in the course of experimentally demonstrating to them the composition of three simple inorganic compounds: hydrogen chloride, water, and ammonia (8).

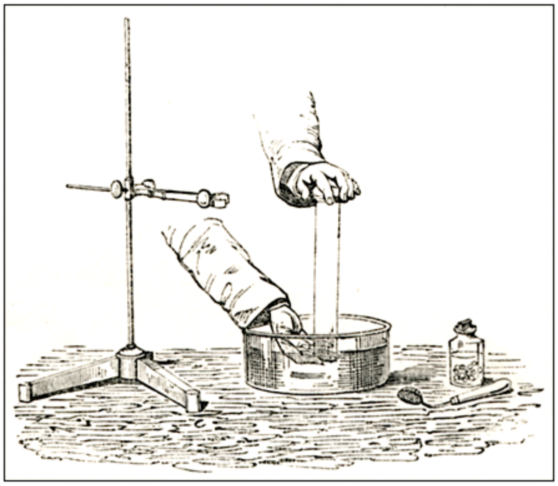

Figure 2. Hofmann's sodium spoon (right) as depicted in his published lectures of 1866.

He began in his first lecture by demonstrating their qualitative compositions, starting with the decomposition of water using sodium metal:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \quad [1]$$

Rather than letting a piece of sodium zip around randomly on the surface of a dish of water, as is so often done today, Hofmann needed to collect the gas being formed in order to properly demonstrate that it was indeed dihydrogen gas. To do this, he developed a wire mesh spoon, known as a Hofmann sodium spoon (figures 2-3), which allowed him to confine the reacting sodium beneath the mouth of an inverted cylinder of water in which he could collect the evolving gas by displacement and subsequently test it using a burning splint.

Electrolysis Apparatus

Having demonstrated the qualitative composition of his three compounds in Lecture I, Hofmann then proceeded in Lecture II to further demonstrate their quantitative compositions. Doing this gravimetrically would have been too time consuming and would not have lent itself to any easy visualization on the part of his audience. Consequently, Hofmann chose instead to demonstrate their quantitative compositions volumetrically via electrolysis of their aqueous solutions:

Figure 3. A later version of the Hofmann sodium spoon (Jensen-Thomas Apparatus Collection).

$$\text{Electricity} + 2HCl(aq) \rightarrow H_2(g) + Cl_2(g) \quad [2]$$

$$\text{Electricity} + 2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \quad [3]$$

$$\text{Electricity} + 2NH_3(aq) \rightarrow 3H_2(g) + N_2(g) \quad [4]$$

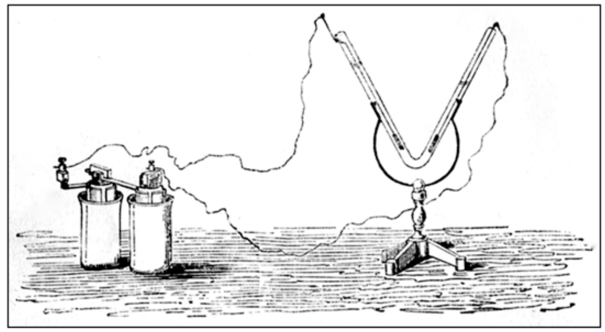

Figure 4. Hofmann's V-cell for electrolysis as depicted in his lectures of 1866. It is powered by two Bunsen carbon cells.

Figure 5. A later version of the Hofmann V-cell for electrolysis. It is being powered by a Grenet dichromate cell (Jensen-Thomas Apparatus Collection).

This approach also allowed him to introduce a discussion of both the ideal gas law and what we would today recognize as Avogadro's hypothesis. The resulting 1:1, 2:1, and 3:1 volume ratios further allowed him to gradually introduce the newly emerging concept of

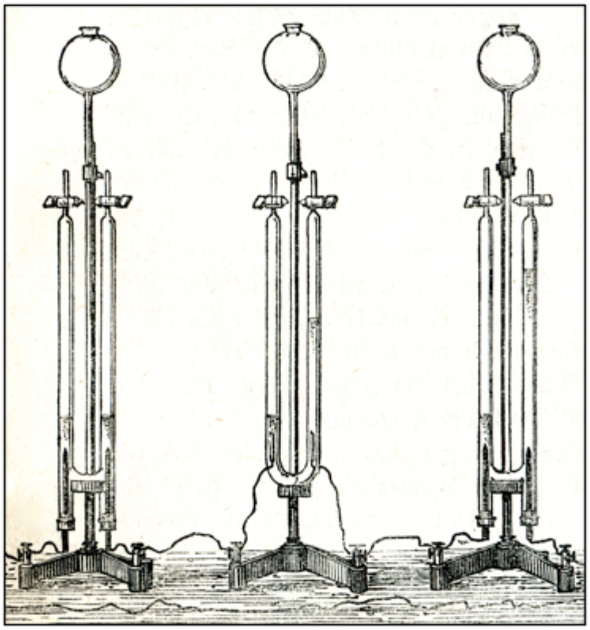

Figure 6. Hofmann's alternative U- (center) and H-cells (left and right) for electrolysis as depicted in his lecture of 1869 to the Deutsche chemische Gesellschaft.

Figure 7. A later version of the Hofmann U-cell for electrolysis based on his final design of 1869 (Jensen-Thomas Apparatus Collection).

atomic "quantivalence" or valence.

For most of his electrolysis demonstrations Hofmann made use of a V-shaped electrolysis cell (figures 4-5) powered by two Bunsen carbon batteries. However, in a later lecture he also introduced a U-shaped cell with a central fill tube. By 1869 this came with an attached addition funnel (figures 6-7) and he had also introduced yet a third variation in the form of an H-shaped electrolysis cell (figures 6, 8). This latter form is the version which has survived today and which is most commonly associated with his name.

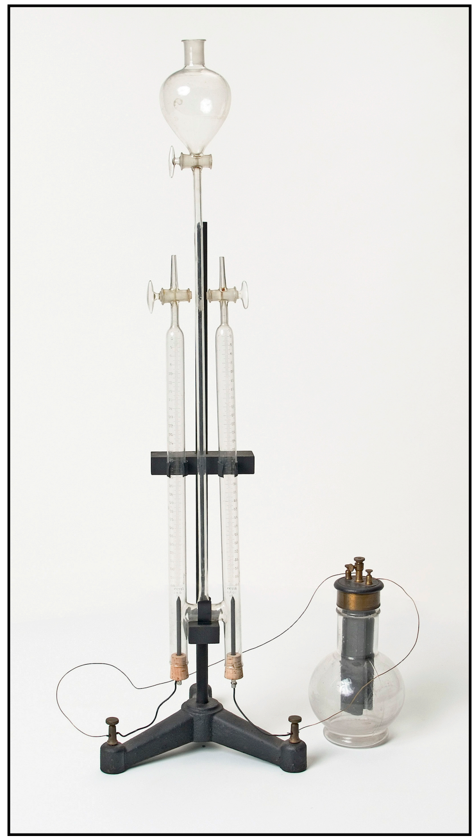

Figure 8. A later version of the Hofmann H-cell for electrolysis with carbon rather than platinum electrodes. It is being powered by a Grenet dichromate cell (Jensen-Thomas Apparatus Collection).

Eudiometric Apparatus

Having demonstrated the composition of his three compounds via analysis, Hofmann then proceeded in Lecture III to confirm his results via their volumetric synthesis using the gas-gas reactions:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad [5]$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad [6]$$

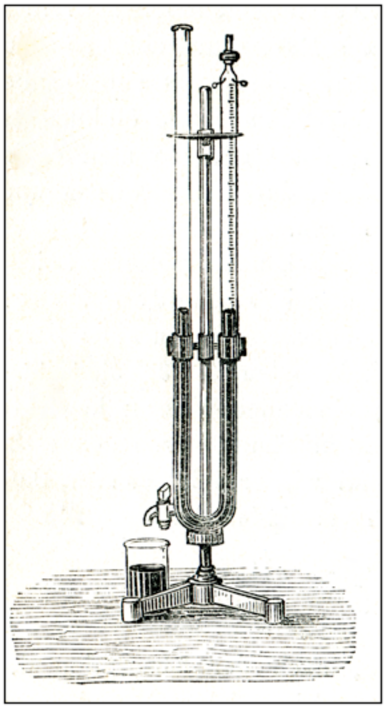

Figure 9. Hofmann's apparatus for demonstrating the volume changes in gas-gas reactions as depicted in his 1869 lecture to the Deutsche chemische Gesellschaft. The necessary activation energy was provided via a spark gap and an induction coil powered by two Bunsen carbon cells.

Figure 10. A later version of a Hofmann eudiometer used for demonstrating the volume changes in gas-gas reactions (Jensen-Thomas Apparatus Collection).

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g) \quad [7]$$

For this purpose he developed a piece of apparatus that was a cross between an eudiometer and a manometer (figures 9-10). A mixture of the reacting gases was added to the right arm of the U-tube through the glass stopcock and the changes in the mercury levels duly noted. The mixture was then sparked to initiate the reaction using the embedded platinum wires and an induction coil. Changes in the mercury levels then revealed whether there was a net decrease, increase, or no change in the total volume of the gases as a result of the reaction.

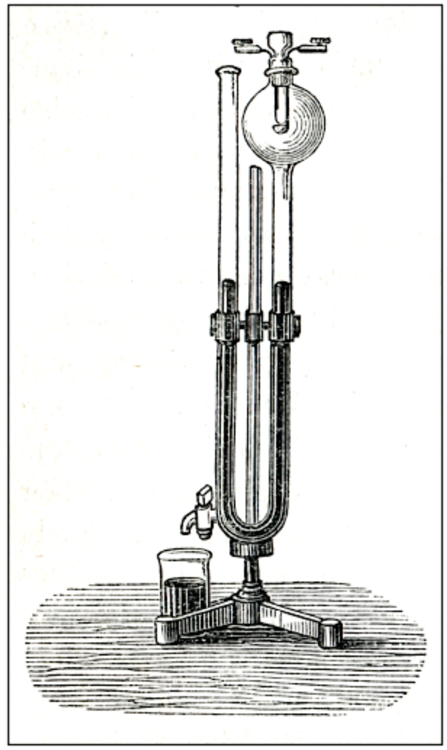

Figure 11. Hofmann's apparatus for demonstrating the volume changes in solid-gas reactions as shown in his lecture of 1869 to the Deutsche chemische Gesellschaft.

In 1869 Hofmann introduced a variation of this apparatus (figures 11-12) designed to demonstrate the volume changes accompanying gas-solid reactions, such as those between dioxygen gas and either solid carbon or sulfur:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad [8]$$

$$S(s) + O_2(g) \rightarrow SO_2(g) \quad [9]$$

The solid in question was placed in a small metal spoon located in the bulb at the top of the right arm of

Figure 12. A later example of a Hofmann eudiometer used for demonstrating volume changes in solid-gas reactions. The glass stopper at the top of the bulb is missing (Jensen-Thomas Apparatus Collection).

the apparatus. The handle of this spoon was actually a stiff metal wire that exited the top of the bulb and was connected to one terminal of a battery. A second wire was placed slightly above the spoon and connected to the latter via a fine platinum wire which rested on the spoon beneath the solid in question. Upon connecting this second wire to the battery in order to complete the circuit, the platinum wire was heated to incandescence and thus served to ignite the carbon or sulfur in the spoon. Whereas in the various electrolysis cells, the electrical energy was used to drive a series of otherwise thermodynamically unfavorable reactions uphill, in the various eudiometers it served instead as a source of activation energy to initiate a series of kinetically inert, but otherwise thermodynamically favorable reactions.

These variations hardly exhaust the list of Hofmann's demonstration innovations and by 1912 the laboratory supply catalog for the American firm of Eimer and Amend was listing over 34 items under the heading of "Hofmann Lecture Apparatus," some of which were mentioned in chemistry texts as late as 1939 (11, 12). However, with the exception of the H-shaped electrolysis cell, all of these have long since disappeared from the modern chemistry lecture hall.

Reference and Notes

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