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HISTORICAL NOTE

A belated tribute to the electrochemist Ernst Salomon

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Abstract The life of the German–Jewish electrochemist Ernst Salomon is reconstructed and his contributions to electrochemistry are described. Salomon published current–potential curves that presaged modern voltammograms, and he also invented the use of amperometry to indicate the endpoint of precipitation titrations.

Keywords Electrochemistry · History · Voltammetry · Amperometric titration

Ernst Salomon has not yet received the attention that he deserves in the history of electrochemistry, and the author of this paper attributes this to the fact that only from a modern perspective can one fully appreciate the importance of his work. This short historical note is written with the intention of publicizing his work, and hopefully fostering further studies of his life and activities.

Ernst Salomon (see Fig. 1) was born in Berlin, Germany, on April 23rd, 1874, the son of the merchant Herrmann Salomon. In 1880, he joined the Royal Pre-School and in 1883, the *Königliches Friedrich-Wilhelms-Gymnasium* (Royal Friedrich Wilhelms Gymnasium) which was situated in Bellvuestraße 15, Berlin-Tiergarten. In October 1892, he left the Gymnasium with the *Reifezeugnis* (the school-leaving certificate). It is interesting to note that two other famous German chemists also attended the same Gymnasium around the same time: the brothers Heinrich Biltz (1865–1943) and Wilhelm Biltz (1877–1943). Remarkably, the German–Jewish industrialist and politician Walther Rathenau (1867–1922) and the German–Jewish journalist and writer Kurt Tucholsky (1890–1935) were also students of that famous Gymnasium. In 1924, the Gymnasium was closed down by government decree, and in 1935 the building housed the infamous *Volksgerichtshof* (People's Court) responsible for so many death sentences against members of the resistance against the Nazi regime. According to the CV that Ernst Salomon provided at the end of his PhD thesis, he was of the Jewish faith, a fact that will later explain his fate.

After leaving the Gymnasium, Salomon became a student of the *Königliche Friedrich-Wilhelms-Universität* (Royal Friedrich Wilhelms University, which is now the Humboldt University) in Berlin, and with the exception of the winter semester 1893/94, when he studied at the Technical High School in Munich, he remained in Berlin until 1895. According to his own account he took courses in mathematics and natural science, and electrical engineering. For the latter course, he attended lectures and performed laboratory work at *Königliche Technische Hochschule Charlottenburg* (later the Technical University of Berlin). From 1895 to 1897 he was at the *Georg-August-Universität* in Göttingen, where he worked for his PhD with Walther Nernst. Salomon lists, among others, the following scientists as his teachers: in Berlin, Emil Heinrich du Bois-Reymond (1818–1896; physiologist) [1], August Kundt (1839–1894; physicist), Hans Heinrich Landolt (1831–1910; physical chemist), Adolf Karl Heinrich Slaby (1849–1913; electrical engineer), and in Göttingen, Walther Hermann Nernst (1864–1941; physicist), Otto Wallach (1847–1931; organic chemist), David Hilbert (1862–1943; mathematician), Felix Klein (1849–1925; mathematician), Theodor des Coudres (1862–1926; physicist), Friedrich Wilhelm Küster (1861–1917; physical chemist) [2], and Richard Abegg (1869–1910; physical chemist).

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Fig. 1 Ernst Salomon (reproduced from Ref. [7])

After finishing his PhD in Göttingen in 1897, Ernst Salomon spent a year as a scientific assistant at Nernst's Institute in Göttingen (where he was succeeded by Friedrich Dolezalek (1873–1920) [3]) and, in 1898, he joined the AEG Company in Berlin as an engineer in the incandescent lamp factory. In Göttingen, his position was again taken by Dolezalek [3]. At AEG, Salomon took care of the industrial implementation of Nernst's patents for his famous lamp, which contained a high-temperature ionic conductor [4, 5]. Although his PhD work was not directly related to Nernst's lamp, it may be assumed that he was familiar with Nernst's work on high-temperature electrolytic conduction. His progress through the AEG Company appears to have been rapid: he supervised the construction of a Nernst lamp factory in Paris, France, between 1901 and 1903. In June 1903, he participated in the 5th International Congress of Applied Chemistry in Berlin where his address is given as 'Courbevoie-Paris, 1 avenue Blanche' [6]. Little is known of his personal life over the next two decades. However, when the Osram Company was formed in 1919, Salomon became one of the members of its board of directors. On account of his Jewish background, he resigned this position in spring 1933, and in 1936 fled Germany. From a biographic entry in a book on eminent Germans from 1930 [7], it is known that his wife was Margarete Salomon, née Kottlarczik, and that they had three children. The same source gives for 1930 his home address in Berlin as 'Im Dol 15, Berlin Dahlem', a most prestigious and expensive living area. By some lucky circumstances, I was able to find some descendants of the family who actually built that house in 1913. According to them, the builder had to sell the house after World War I for financial reasons. Ernst Salomon purchased it; however, in 1933, the son of the house-builder bought it back through the right of pre-emption. The house was eventually destroyed in World War II. According to the same source, Ernst Salomon left Germany 1933 for England; however, I am not sure this is right, because in a letter of Salomon to Einstein [8, document 56-87.00] he mentioned that he left Germany in 1936, unfortunately not saying where he went first. From these letters and Einstein's reply, which are now in The Albert Einstein Archives at the Hebrew University of Jerusalem, it can be seen that Salomon was living in Santa Monica, California, in 1941/42, at #1042–2nd Street. He also mentioned that he had stayed briefly in New York, but moved to California for health reasons [8: document 56-87.00]. Unfortunately, all attempts to find children or grandchildren of Ernst Salomon have so far failed, and nothing is known about his death and burial place.

As mentioned above, Nernst had sent Salomon to the AEG factory in Berlin to help expedite production of his lamp. After his return to Göttingen, he was then supposed to habilitate (prepare a second thesis for a professorship), but instead he remained at AEG for 35 years. Later political developments in Germany, especially the brutal anti-Semitism, prompted Salomon to resign from his position at AEG in 1933 (see also Ref. [8], document 56-87.00). The reason he wrote to Einstein in November 1941 was that Salomon wanted to publish his memories of Nernst, who had just died, and Salomon wanted to know if Einstein could recommend a suitable journal "in this country", i.e., in the USA. He concluded the letter by saying that although Einstein might not remember him, he had actually met him in the house of Dr. Fritz Blau, where, many years previously, Einstein and Planck had discussed the most complex problems of modern physics; and in the house of Prof. Dr. Walter Levy, where he had listened to Einstein playing music; and also in the house of Richard Einstein, a cousin of Albert Einstein. In a later letter to Einstein [8, document 56-88.00], Salomon mentions that Professor Epstein of Pasadena had suggested a suitable journal, and also mentions that he (Salomon) had contacted Irving Langmuir, who did his PhD with Nernst in Göttingen, and whom he personally knew from that time, in order to get some additional information. However, Langmuir made some acerbic remarks about Nernst. Whilst admitting his scientific brilliance, Langmuir expressed less respect for Nernst's scientific honesty, and very little for his personal character. Langmuir's answer prompted Salomon to give up his plan to publish a memoir about Nernst, in part because he did not want to provoke controversy during World War II. Langmuir's remarks, mentioned obliquely in this letter to Einstein, have since been noted elsewhere [9]. By contrast, Salomon seems to have had only positive personal experiences with Nernst, and in the letters to Einstein, expressed high admiration for his old teacher (although he indicated that Nernst could be sharp, even offensive in discussions). Salomon wrote to Einstein that he would in any case write down his memories, and he would send them to Einstein. Since no such documents are

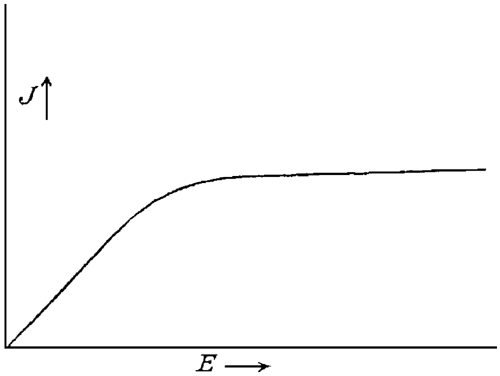

Fig. 2 Expected dependence of current on polarizing voltage, as given by Salomon in his PhD thesis (reproduced from [9] and slightly reworked electronically)

now in the archive, one wonders if they were ever completed. In a further letter [8, document 56-88.00] he also expressed his wish to write a book entitled "Migration of Culture" (part of the synopsis is attached to this letter [8, document 56-89.00]). Salomon intended to describe how Nazi politics and ideology had attempted to destroy the old culture of Europe, including Christianity and what they called 'cultural bolshevism', and how the old European culture had survived and migrated to the free countries of the world. Both Einstein and Thomas Mann [8, document 56-89.10], whom he also corresponded with, supported Salomon's book project with kind words. Unfortunately, the book was never published.

Following this brief sketch of Salomon's life, his contribution to electrochemical science needs attention. His PhD thesis of 1897 [10–14] was performed under the guidance of Nernst, and it was Nernst who gave him the ideas to be tested, as Salomon freely acknowledges in his introduction. In particular, Nernst had drawn his attention to the problem of the dependence of currents on voltages, and especially on testing some theoretical assumptions to calculate the current flowing through small polarizable electrodes. Here, the term 'current' needs some clarification: Salomon actually used the word "*Reststrom*" which is the German term for *residual current*, and so he means the almost constant current that flows under unstirred conditions some minutes after the application of a fixed potential. Today, we know that this is not really a steady state current, because the diffusion layer on both electrodes is constantly growing, but given Salomon's experimental apparatus, the current must have seemed almost constant. A truly steady state current would be realized only if a linear concentration gradient had built up between the two electrodes, after a long electrolysis time, and provided there were no edge effects. Such conditions did not exist in Salomon's experiments, where the electrodes, at least in case of silver and copper, were simply facing each other in a parallel manner. Solomon used the term residual current both for the ascending currents and for the limiting currents of the wave-shaped dependence of currents on potential.

Salomon starts his PhD thesis with the question raised by Helmholtz: "What is the reason for the seemingly unlimited flow of current between polarisable electrodes below the decomposition voltage?" Helmholtz had in mind, as an example, the electrolysis of water by two small platinum electrodes. Salomon soon realized that the case of water electrolysis was much more complicated than that of metal dissolution, especially when reversible electrodes such as silver-metal/silver-ion or mercury electrodes were used. Further, he realized that ion migration needed to be excluded, which he achieved by adding an excess of inert supporting electrolyte to the solutions. The theoretical bases of his studies were—in contemporary terms—(a) *Ohm's law* (the current is the ratio of [polarizing potential–equilibrium potential] divided by cell resistance), (b) *the Nernst equation* for a concentration cell (relating the equilibrium potential difference to the ratio of concentrations of metal ions on the two electrodes), and (c) *Fick's laws* of diffusion relating the amount of ions transferred from one electrode (the anode) to the other electrode (the cathode) due to the concentration gradient caused by the polarization. For calculating the rate of ionic flow from one side to the other, i.e., the current, one needs to know the concentrations of ions at the two electrodes, their diffusion coefficients, the areas of electrodes and their separation (the system was treated as if a linear concentration gradient existed between the electrodes as a result of steady state conditions. As said before, this was certainly only approximately true in Salomon's experiments). Combining the three relations, Salomon derived the following equation for the relation

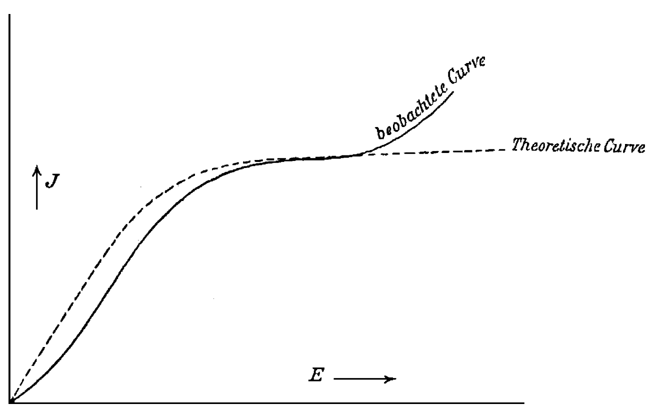

Fig. 3 Comparison of experimental data ('*beobachtete Curve*' = observed curve) and calculated data ('*theoretische Curve*' = theoretical curve) for mercury electrodes in a mercury solution, as given by Salomon (reproduced from [9] and slightly reworked electronically)

between the observed current I and the polarizing voltage E:

$$I = 2ac\left[\frac{10^{\frac{E-IW}{0.058}} - 1}{10^{\frac{E-IW}{0.058}} + 1}\right] \qquad (1)$$

Here c is the concentration of metal ions in the bulk solution; W is the cell resistance; and a is a constant. Figure 2 shows the expected dependence.

The derived Eq. 1, of course, did not consider the role of heterogeneous electrode kinetics, a problem not satisfactorily solved until the work of Erdey-Gruz and Volmer [15–17], and Gurney [18, 19], in the 1930s. But it did predict the occurrence of limiting currents. Salomon tested the validity of the outlined calculations by experiments. Figure 3 shows the comparison of experimental and calculated data for the case of mercury electrodes.

Salomon discussed the deviations between theory and experiment as follows: he has no explanation for the deviations at small potentials, and can only remark that these deviations vanish in slightly acidified and alkalized solutions. He assumes chemical interferences in the neutral solutions as the cause for the deviations. Today, one may speculate about a possible slow kinetics of the system in neutral solutions as the reason for the delayed current rise. The deviations observed in the limiting current range, he rightly interpreted as due to a second depolarization process, and he assumes the water electrolysis (hydrogen evolution) as the reason. He already observed that the current rise in the limiting region occurs about 200 mV earlier at silver electrodes than at mercury electrodes. This was surprising for him as he assumed that silver and mercury should behave similarly. The hydrogen overvoltage phenomena were also deeply mysterious at this time. Another reason for the deviations was later identified by Grassi [20] as free convection.

Although plots of current versus voltage had been reported earlier, it is not unreasonable to see Salomon's plots as forerunners of modern voltammograms. The conditions were chosen in such a way that migration was excluded, the electrodes were reversible, and the currents at each potential were nearly constant in unstirred solution. Indeed, if he had realized that the current depended exponentially on voltage, he would have pre-empted Tafel's great discovery of 1905, and if his working electrode had been much smaller than his counter electrode, he would have invented static voltammetry.

Another remarkable result of Salomon's PhD thesis was that he showed that the limiting currents could be used to indicate the equivalence point of precipitation titrations by titrating a chloride solution with silver nitrate [10, 14]. This is the first example of an amperometric titration. Whereas Salomon called this a titration with the "*Reststrommethode*" (residual current titration) or also galvanometric titration, Erich Lange [21] called it a 'limiting current titration' [22]. It is interesting to note that Salomon refers in his PhD thesis [10, page 27, footnote] to the work of Wilhelm Carl Böttger [23] who introduced potentiometry to indicate the end point of precipitation titrations. Salomon rated his amperometric method as much superior to the potentiometric method because the instrumentation for the current measurements was so much simpler. Of course, the development of modern potentiometric measuring devices [24] has changed the situation completely. It may be remembered that Salomon performed his studies at a time where the applications of electrochemical techniques to determine the endpoint of several titrations were discovered. Besides Böttger's potentiometric precipitation titration, Crotogino [25] must be mentioned who performed in 1900 the first potentiometric redox titration, and Küster [2], who was among the pioneers of conductometric titrations.

Ernst Salomon's contributions to electrochemistry and his striving to bring the Nernst lamp into large-scale production give him a worthy place in the history of electrochemistry. It is surprising that he is not mentioned in detail in any of the books published about Walther Nernst [9, 26, 27] , although he must have been very important to Nernst, as he was entrusted by him with one of his most important commercial ventures. Salomon's PhD work was not recognized by his contemporaries because it was viewed as little more than a test of some simple theoretical relations [28]. In his time, and even in the first half of the twentieth century, nobody could have foreseen the important role that voltammetry would eventually come to play in electrochemical research, nor did anyone recognize the importance of amperometric titrations. Of course, it is certainly not possible to compare Salomon's contributions with such seminal findings as those of Cottrell and Sand, or indeed of Tafel, but they are important enough to be remembered.

The author hopes that this historical note may trigger further research on the life and fate of this remarkable scientist.

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