

## MORRIS LOEB, WALTHER NERNST, AND THE TRANSFERENCE NUMBER

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The activities of Morris Loeb (1863-1912) (Fig. 1) had been of concern for some time, in terms of surveys of the students of Wilhelm Ostwald (1853-1932) at the University of Leipzig (1,2). Fortunately, the recent appearance of an account of Loeb's remarkable career (3) has allowed the present paper to be largely restricted to Loeb's major work at Leipzig.

Loeb was a student at Harvard from 1879 to 1883, where he was greatly influenced by Wolcott Gibbs (1822-1908), a major figure in the development of electrogravimetry (4). Loeb was almost certainly initiated into the field of electrochemistry by Gibbs. He never forgot his mentor, who probably advised him to undertake further studies in Germany. In Berlin, under the supervision of August Wilhelm Hofmann (1818-1892), Loeb investigated the reactions of phosgene with various amidines (5,6). Loeb submitted his dissertation in March, 1887 and, his Ph.D. secured, moved to Leipzig, where Ostwald had been appointed Professor of Physical Chemistry.

Ostwald's growing reputation may have been the reason for Loeb's decision. However, a move away from organic chemistry was in line with Loeb's feelings after

his tenure in Berlin (3). A few years later, Max Le Blanc (1865-1943) also went from Hofmann's laboratory to that of Ostwald. Le Blanc, who later clarified our understanding of decomposition voltages of solutions of acids, bases, and salts, nearly gave up chemistry after obtaining his Berlin Ph.D. (7). Fortunately, he changed his mind!

At Ostwald's suggestion, Loeb studied the apparent molecular weight of iodine in various solvents (8,9). He then began to work with Walther Nernst (1864-1941) (Fig. 2) on ionic velocities in solutions. Nernst, who received the Nobel Prize for Chemistry in 1920, was then beginning his highly successful career as Ostwald's first academic assistant. In fact, Nernst and Loeb both obtained their doctorates in 1887. Nernst's advisor was

the Würzburg physicist Friedrich Kohlrausch (1840-1910). With such a mentor, Nernst was almost certainly the initiator of the joint project.



*Figure 1.* Morris Loeb

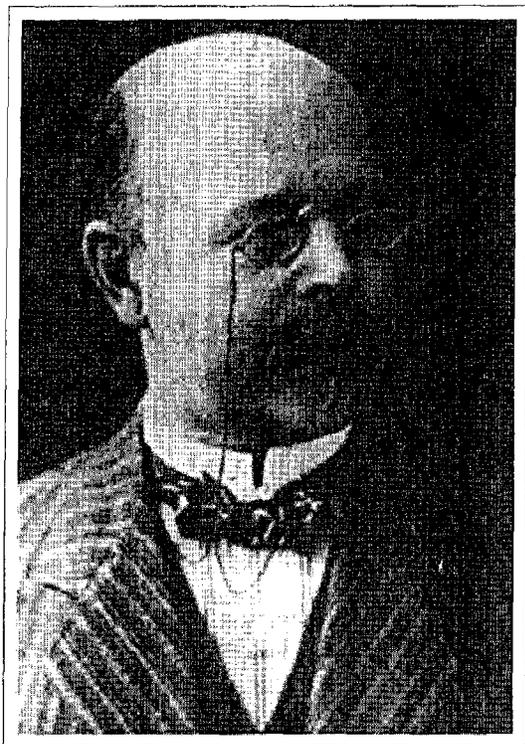


Figure 2. Walther Nernst

When a solution is electrolyzed, equivalent quantities of ions are discharged at the respective electrodes. This might seem to imply that the change in electrolyte concentration around the anode would be the same as around the cathode. In fact, the changes are usually dissimilar. In 1853, Johann Wilhelm Hittorf (1824-1914) (Fig. 3) had shown that, when a current is passed through a solution of an electrolyte, the anions and the cations migrate toward the respective electrodes with unequal velocities. In three papers, the last of which appeared in 1859, he described the measurement of the *transference numbers* (10). These are the fractions of the total amount of electricity carried by the anion and by the cation, respectively. In 1879 Kohlrausch, following up on Hittorf's work, introduced the concept that the equivalent conductivity  $l$ , of an electrolyte is the sum of the ionic conductivity of the cation,  $u$ , and that of the anion,  $v$  (11). Thus:

$$l = u + v \quad (1)$$

Because  $u$  and  $v$  are proportional to the mobilities of the respective ions, the transference number,  $n$ , of the anion and that of the cation,  $(1-n)$ , can be expressed as:

$$n = v/(u + v) \text{ and } (1-n) = u/(u + v) \quad (2)$$

With a minor exception, the symbols are those used by Loeb and Nernst (12, 13).

Transference numbers can be determined in various ways (10). In the Hittorf method, a chemical coulometer is connected in series with an electrolysis apparatus which, for example, contains  $\text{AgNO}_3$  solution of known weight composition  $y_1$ . Appropriate electrodes, silver in this case, are located such that changes in the composition of the solution are confined to the regions around each electrode; the intermediate portion of the solution should remain unchanged.

Consider a hypothetical extreme case where  $n = 1$ ; *i.e.*, all of the current is carried by the anion. Then the concentration of  $\text{Ag}^+$  in the anode region should rise to  $y_1 + y_2$ , where  $y_2$  is the amount of  $\text{Ag}^+$  formed by  $x$  coulombs of anodic dissolution. At the other extreme, when  $n = 0$ , the  $\text{Ag}^+$  concentration in A should remain at  $y_1$ . In a real case, the final concentration will lie between the extreme limits, so that  $1 > n > 0$ . The effect can be expressed in another way: *The ratio of the weight of the metal deposited to the amount of metal lost by the fluid around the cathode (or its equivalent, the amount gained around the anode) represents the share of the negative ion, the anion, in the total movement* (13).

Loeb and Nernst pointed out that Hittorf had needed fairly concentrated solutions to obtain sufficiently ac-

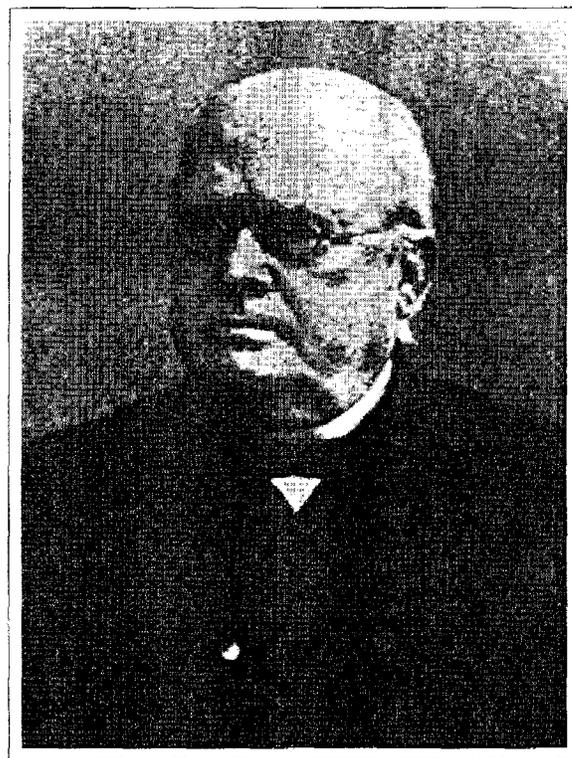


Figure 3. Johann Wilhelm Hittorf

curate analyses. These workers used the apparatus shown in Fig. 4 for their projected study of dilute solutions of various silver salts. The design allowed the apparatus to be mounted in a thermostatic bath. The anode, near the bottom of compartment A (where the solution will become more dense), is the coiled end of a silver wire that is sealed into a thin glass tube. The free end of the wire passes through a short tube in the stopper and then through a piece of rubber tubing that is normally closed by a spring clip. A silver foil roll forms the cathode in compartment B, which has a similar spring clip closure. The bulb-like bottom of B traps particles of silver that may fall from the cathode. With the clip on A closed, gentle aspiration at the tube on B allows the apparatus to be filled through tube C to the level shown. After Tube C is capped, the apparatus is mounted in the bath and brought to the desired temperature. After the electrolysis, C is uncapped

and, by gentle blowing at tube B, suitable portions of the solution are delivered into weighed vessels for subsequent titrimetric determination of silver. In some experiments the total electricity was small and would have deposited less than 20 mg of silver in the coulometer. In such cases, this total was obtained as the product of run time and the current, which was kept constant. This current was measured as the voltage drop across a standard resistor.

After making corrections for minor changes in the anolyte density and in the concentration of the intermediate portion of the solution, Loeb and Nernst found 0.524 as the transference number ( $n$ ) of  $\text{NO}_3^-$  in approximately 0.1M  $\text{AgNO}_3$ . They repeated the determination at various temperatures and dilutions. In agreement with Hittorf, they showed that considerable dilution did not change the value of the anion transference number. The

numbers for various other silver salts were then determined in a similar manner. The demonstration that transference numbers could be determined at low concentra-

tions was not the main aim of Loeb and Nernst's research. They were more interested in the validity of Kohlrausch's conductivity equation (Eq. 1), which was based on the *total* amount of electrolyte. The fact that some of Kohlrausch's results failed to support this relationship proved to be the impetus for the work undertaken.

The formulation of the ionic theory and Ostwald's studies on the conductivities of numerous electrolytes in dilute solutions (14) provided strong support for the view that only the ionized portion of a solute contributes to the conductivity. Thus Kohlrausch's concept is strictly true only when the electrolyte is completely dissociated, i.e., when the concentration approaches zero. The uni-univalent silver salts studied by Loeb

and Nernst are strong electrolytes; and at very low concentrations their molecular conductivities,  $l$ , are close to the maximum values,  $l_0$ , which apply to zero concentrations (15). Using the approach of Kohlrausch, Loeb and Nernst assumed that the  $l_0$  value for a given salt could be estimated from the measured value of  $l$  at a concentration of  $8 \times 10^{-4}$  M, the lowest in their studies. A further assumption was that the transference numbers, which had been shown to be constant over the concentration range 0.025 to 0.01 M, would have the same values at zero concentration. Then the product of the transference number,  $(1 - n)$ , of  $\text{Ag}^+$ , the common ion in the series of salts, and the  $l_0$  value of the corresponding salt, would be the ionic conductivity of this ion at 25° C. The validity of this approach was upheld by the results of experiments with eight different silver salts, where values of this product ranged from 585 to 597 (average 591). The conductivities, which were actually measured

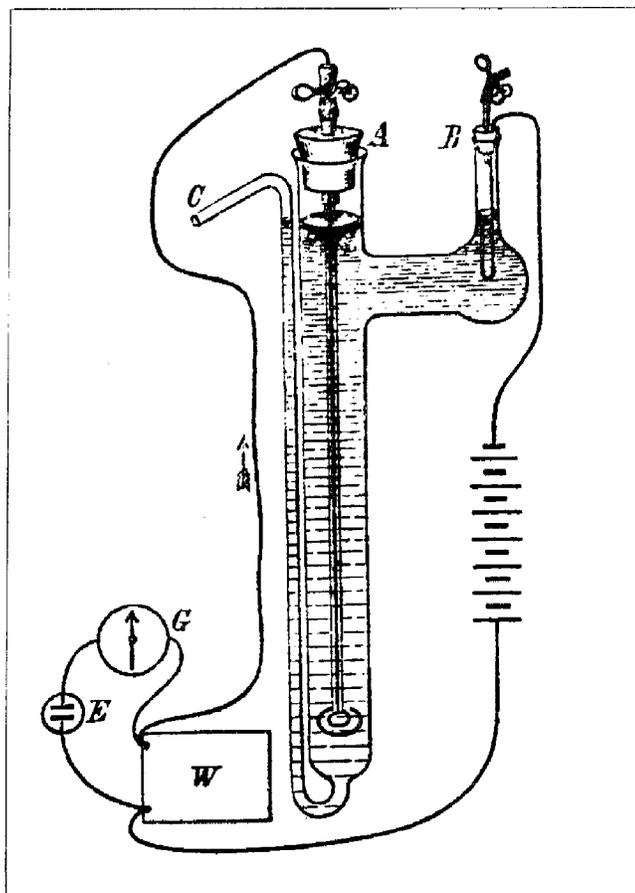


Figure 4. Apparatus designed by Loeb and Nernst.

by Nernst, were based on that of mercury, which was assigned unit value. Thus the given numbers do not agree with modern values. From data obtained at 25°C and 0°C, these workers calculated the temperature coefficients of the  $I_0$  values of their salts and of the ionic conductivities.

Although attainable with high accuracy, conductivity measurements indicate the molar or equivalent values,  $I$ , for the electrolyte, and not the individual contributions of the anions and cations. However, knowledge of the relevant transference number allows calculation of the respective ionic conductivities from conductivity data, as was shown by Loeb and Nernst. Their work was a notable step in the then rapidly developing field of electrochemical phenomena and their interrelationships.

Loeb's activities after his return from Leipzig have been well documented (3). As professor at New York University, his publications, although not extensive, ranged widely. Examples are the use of aniline to absorb cyanogen in gas analysis, molecular weight determination, the ionic theory, the adducts of sodium iodide and various alcohols, and an attempt to find any effect of magnetism on chemical reactivity. He was devoted to the profession of chemistry and strove for its betterment. When he became Chairman of the New York Section of the American Chemical Society in 1909, his inaugural address naturally referred to the satisfactory growth of the section (16). He then turned to the lack of public recognition of the value of the industrial chemist, and how this situation might be improved. Noting that American chemists were often handicapped by lack of chemicals, many of which had to be imported, he suggested the establishment of a "museum," from which less common chemicals could be issued or loaned. His far-reaching idea was that the "museum" might even prepare official standards if given suitable staffing.

Loeb remained active nearly to the end of his life, so that his death, on October 8, 1912, came as a shock to those who knew him.

### ACKNOWLEDGMENT

This work was partially carried out under the Research Fellowship Program of the Science Museum, London, and the research facilities of the Chemical Heritage Foundation, Philadelphia.

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