GABRIEL LIPPMANN AND THE CAPILLARY ELECTROMETER

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Early Potentiometry

Early workers in the field of potentiometry faced a serious problem. The type of cell commonly used in potentiometric studies could supply only a tiny current and often had a high internal electrical resistance. If the electromotive force (emf) of such a cell is to be measured accurately, the apparatus must draw essentially no current from the cell. One obvious approach is to oppose this emf with another that is exactly equal, and is generated externally. This is the basis of the "compensation method," devised by Johann Christian Poggendorf in 1841 and later improved by others (1).

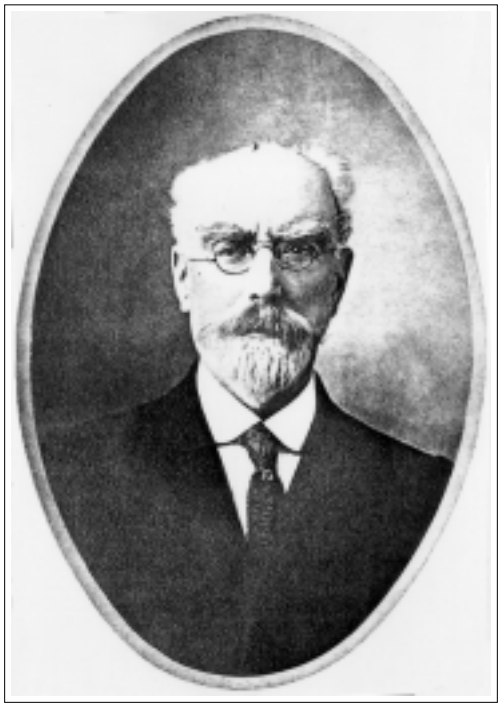

Figure 1. Gabriel Lippman, *Proc. R. Soc. London* **1922**, *101A*, i-iii.

The problem here lies in the detection of balance, that is, of the so-called "null point." The electromagnetic galvanometer is essentially a current-measuring device, but a galvanometer of the mirror type may serve when the cell resistance is not too high. However, this high-sensitivity galvanometer is not very convenient and is easily damaged by overload. The development of the nearly currentless capillary electrometer solved the problem. This device had the added advantage of simplicity and, with some later forms, of comparative robustness.

Lippmann

The studies that led to the invention of this electrometer and to the formulation of the associated theory were not the work of a lifetime, but of that of a beginner, Gabriel Lippmann (Fig. 1). He was born near Luxemburg on August 16, 1845. His parents moved to Paris and eventually he was admitted to the École Normale. Pursuing only the topics that aroused his interest, Lippmann was not an ideal student. He failed in the examination that would have qualified him as a teacher (2). Nevertheless, his latent abilities were recognized and he was given the opportunity to study in Heidelberg, where the celebrated physicist, Gustav Robert Kirchhoff (1824-1887) was professor.

Lippmann saw a then well-known demonstration that involves a drop of mercury covered by dilute H_2SO_4. When touched by an iron wire, the drop contracts but

regains its original shape on removal of the wire. The agitation of a mercury drop in contact with a voltaic cell was first observed by William Henry in 1800. Between Henry's observation and the work of Lippmann, Partington cites seven additional reports of the same phenomenon, the most important being John Draper's 1845 observation of the depression of an electrified thread of mercury confined in a capillary tube (3).

Lippmann, recognizing that the effect must be due to a connection between electric polarization and surface tension, developed the concept that led to the design of the capillary electrometer in Kirchhoff's laboratory. Having been granted a Heidelberg Ph.D. in 1873, Lippmann returned to Paris, where he obtained a second doctorate in 1875. After various appointments he became professor of mathematics at the Sorbonne in 1883, and then of physics in 1886. He held the latter position for the remainder of his life.

The Capillary Electrometer

Lippmann's publications on electrocapillarity began with a brief note in French (4). He explained that the contraction of the mercury drop was due to the electrical polarization of its surface, thereby changing its "capillary constant." Among other comments was that, if a mercury-dilute H_2SO_4 interface was formed in the capillary tip of a tube containing mercury, the observation by microscope of the displacement of the interface provided a sensitive measure of the emf applied to the system. Fortunately, while in Kirchhoff's laboratory, he had been able to use an electrostatic electrometer of the type invented by William Thomson (later, Lord Kelvin) (1824-1907) and described by him in 1867 (5). When this instrument was connected in place of the polarizing source, it could be shown that a mechanical displacement of the interface resulted in a deflection of the electrometer. The effect was found to be independent of the shape of the surface, but proportional to the change in its area. The note concluded with intriguing remarks about an electrocapillary motor that had been constructed. Almost simultaneously, Lippmann published in German a description of this motor and of the principles outlined above (6). Two years later an even more extended French paper appeared (7).

A detailed description of the motor, shown in Fig. 2, is beyond the scope of the present article. Battery power is applied alternately to the pistons of bunched capillaries that work in cylinders containing mercury. These stand in a trough containing dilute H_2SO_4. Vertical movement of the pistons leads to left-right oscillation of overhead piece *v* and hence to the rotation of wheel *R*, through the agency of crank *x*. The motor demonstrated that (i) electrical energy could be converted into mechanical energy by use of the principles that Lippmann had developed and (ii) that electrocapillary forces were by no means insignificant.

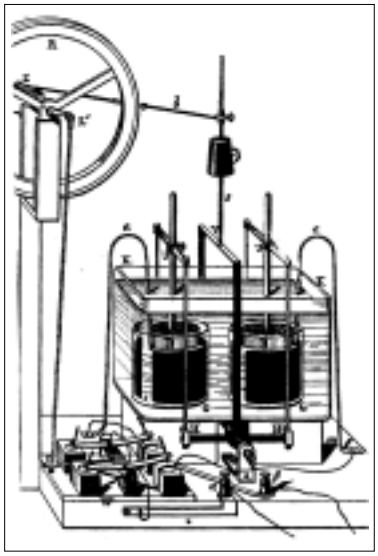

Figure 2. Electrocapillary motor; Ref. 5, p 522.

Lippmann pointed out that, hitherto, determinations of capillary constant or "tension superficielle" had not been satisfactory. He mentioned a paper by Georg Hermann Quincke (1834-1924), then professor of physics at Würzburg (8). Quincke had attempted to refute the results given by Lippmann in 1873. Quincke attributed the changes in superficial tension to the presence of impurities and concluded that capillary phenomena could not provide a measure of electrical effects. Lippmann's comment on this paper was that it showed the state of affairs when he began his work.

Both experiment and theory were used by Lippmann to establish his two "laws:"
I. The capillary constant extended at the surface of separation of mercury and sulfuric acid is a function of the electrical difference that is at this surface. II. When, by mechanical means, a liquid surface is deformed, the electrical difference at this surface varies in a sense such that the "tension superficielle" developed by virtue of the first law opposes continuation of the movement.

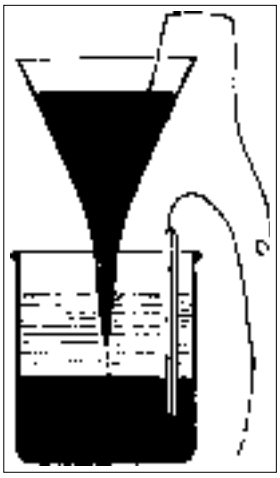

Figure 3.
Electrocapillary source of current; Ref. 5, p 512

The assembly shown in Fig. 3 provided "une experience curieuse," based on the above principles. Drops of mercury fall from the very narrow tip of the funnel through dilute H_2SO_4 and into a pool of mercury. Wires a and b connect the masses of mercury to a galvanometer, which at once indicates that electricity is flowing. This flow continues indefinitely, provided that mercury from the growing pool is restored to the funnel. When a drop of mercury forms and grows, the electrical difference at its surface increases and the mercury in the funnel becomes negative with respect to the mercury in the pool. The electrical effect is enhanced when the drop of mercury reaches the pool.

Fig. 4 shows Lippmann's high-sensitivity capillary electrometer. The tip of the vertical tube A is drawn out to a very fine capillary and bent as shown. The tip dips into dilute H_2SO_4 contained in vessel B, at the bottom of which is a pool of mercury. The height of the column of mercury in A is such that the liquid interface in the capillary can be satisfactorily viewed through a microscope with an eyepiece scale. Wires a and b connect the two masses of mercury to the source of the emf to be measured, or rather to be compared with that of another source. For example, it was common practice to use the zinc-copper Daniell cell as a standard and to assign unit value to its emf. Lippmann provided several examples of such comparisons, such as of the emfs of the Daniell and of the Leclanché cell.

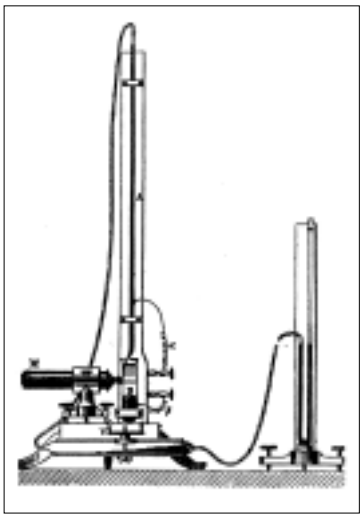

Figure 4. Lippmann capillary electrometer; Ref 5, p 532

Users of the electrometer soon became aware of the importance of providing a fresh mercury surface before the next observation; otherwise the response might have been irregular. With electrometers of the Lippmann type, pressure may be temporarily increased, so that a drop of mercury is expelled from the capillary.

In a paper of 1880, Lippmann mentioned claims concerning the sensitivity of the capillary electrometer that he had found in the literature (9). One claim indicated measurement to 1/10000th that of a Daniell cell, i.e., to about 0.1 mV, another to 1/30000th.

Almost immediately after the appearance of Lippmann's preliminary note (4), a "capillary galvanoscope" made by Werner Siemens (1816-1892) was reported (10). This device, intended for testing rather than for measuring, was obviously less sensitive than the Lippmann instrument. A 0.5-mm diameter horizontal capillary that curves slightly upwards joins two vertical mercury-containing tubes. A small drop of dilute H_2SO_4 is situated at the middle—the highest point—of the capillary. The application of an emf moves the drop to an extent indicated by an attached scale. However, the convex form of the capillary hinders extensive displacement. On breaking the circuit and short-circuiting, the drop returns to the mid position.

Applications

It is doubtful whether anyone appreciated the utility and simplicity of the capillary electrometer more than Wilhelm Ostwald (1853-1932). He developed the form shown in Fig. 5 while still at the Riga Polytechnicum (11). No new principles were involved, but the device was easy to construct and to use. An externally threaded brass tube is cemented to glass tube A, which contains a column of mercury. A collar M, which is screwed onto the brass tube, rests upon a small stand ring. Rotation of M then raises or lowers tube A. The capillary, which is drawn out from thermometer tubing, is cemented into the lower end of A. A second small stand ring restricts the lateral movement of this end, and a rubber stopper supports tube P. This contains dilute H_2SO_4, into which the capillary dips, and also a pool of mercury. The microscope is aligned by adjustment of screws on the platform, and electrical connections are made through sealed-in platinum wires.

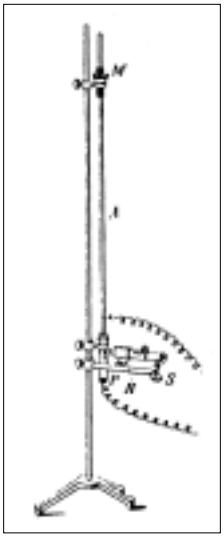

Figure 5. Ostwald's version of the Lippmann electrometer; Ref. 5, p 404

Following Ostwald's move to the University of Leipzig in 1887, his students and associates made much use of the capillary electrometer, either of the original

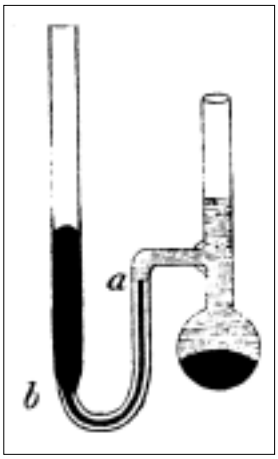

Figure 6. Compact capillary electrometer; Ref. 11, p 555.

form or of later ones. Ostwald may have suggested the more compact form shown in Fig. 6. This form was used in a potentiometric study of mercury (12) and also by other workers in Ostwald's laboratory. The application of the electrometer to acid-base titrimetry was the subject of an extensive investigation (13). Fig. 7, based on a sketch given by Max Le Blanc (1865-1943) in his paper on amalgams (14), shows a sloping-capillary high sensitivity form of electrometer. Le Blanc and also Anton Robert Behrend (1856-1926), who used this type of instrument in a study of potentiometric titration (15), attribute the device to Ostwald..

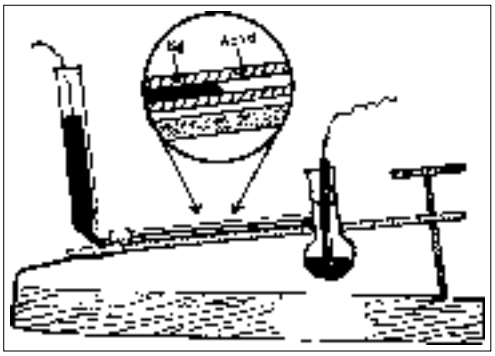

Figure 7. High-sensitivity sloping-capillary electrometer; Redrawn from Ref. 13

Robert Luther, one of Ostwald's assistants who became sub-director of physical chemistry in 1901, devised the totally sealed form of electrometer shown in Fig. 8 (16). Obviously this is easily portable and can be stored in any position. Transfer of liquid through cross tube b permits the adjustment of the position of the liquid interface in capillary c.

Historical Perspective

Practical electronics began with the invention of the vacuum triode in 1917. By then, any reference to the capillary electrometer might be expected to be one of mere mention. A brief scan of the first four decennial indices of *Chemical Abstracts* shows that this was not so. For example, the value of the capillary electrometer in numerous titrimetric analyses was pointed out in 1919 (17). Then a new form of this device was described in 1942 (18). This was mid-year of a war, so that easily-damaged galvanometers could not be repaired quickly. The device shown in Fig. 9 was intended to be a user-safe substitute for a galvanometer. A common cause of trouble with capillary electrometers in general had been the precipitation of Hg_2SO_4 within the capillary. In experiments with a Luther-type electrometer, it was found that this kind of trouble did not occur if the usual dilute H_2SO_4 was replaced by 20% $HClO_4$. This improvement was incorporated in the new device shown. An enlargement K is joined at A to capillary C. If an excessive emf is applied, electrolysis takes place in K, rather than in C. Thus the mercury-acid interface in C is so little disturbed that, after brief short-circuiting, it returns almost exactly to the initial position. Yoke I_1 is merely a support, while I_2 is a wide capillary that ensures the equalization of pressures in the vertical limbs.

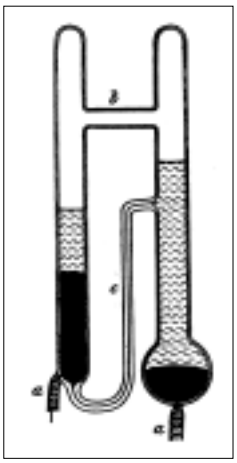

Figure 8. Luther capillary electrometer; Ref. 15, p 426

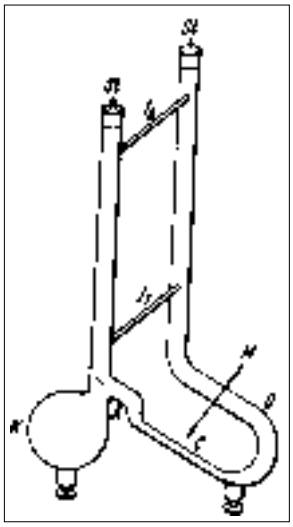

Figure 9. Uhl electrometer; Ref. 17, p 326

Lippmann did not abandon his interest in electrocapillarity after he had published the work that led to the development of the electrometer. However, his research spread to other topics, such as to the determination of electrical units and to the exact measurement of time. He had been thinking about the possibility of photography in color for some years before he published a note on this topic in 1889 (19). Thereafter, the bulk of Lippmann's publications was concerned with this form of photography. In 1891 he demonstrated a method for producing permanent color photographs. He was awarded the 1908 Nobel Prize for Physics "for his method of reproducing colors photographically based

on the principle of interference." In his Nobel Lecture, he demonstrated that colors were indeed produced by interference in a nonpigmented emulsion. He admitted that the exposure, one minute in sunlight, was too slow for portraiture. With modern dyestuffs-based color photography, the necessary exposure is of course only a fraction of a second.

Lippmann died aboard ship on July 12, 1921, while returning from a visit to Canada; but by no means did interest in the development and use of the capillary electrometer die with him.

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