On the Electrochemical Equivalent of Water

Wilhelm Weber

Abstract

English translation of Wilhelm Weber's 1841 paper "Ueber das elektrochemische Aequivalent des Wassers", [Web41b] and [Web42].

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1 On the Electrochemical Equivalent of Water

By Wilhelm Weber[1,2,3,4]

After Faraday's numerous experiments,[5] there seems to be no doubt that in the event of chemical decomposition by the galvanic current, for each body the decomposed mass of the same to the related quantity of current, i.e. to the amount of electricity passed through the cross-section of the circuit during the decomposition, is in constant proportion no matter how the galvanic current is produced and in what state the decomposed body may be. The other equally important result found by Faraday must be added to this important law saying that chemically equivalent masses of different bodies need the same amount of electricity (equal quantities of current) to decompose them. For example, 9 grams of water and 36.5 grams of hydrochloric acid are chemically equivalent masses and, according to Faraday, need equal amounts of electricity to be decomposed to oxygen and hydrogen gas, and chlorine and hydrogen gas, respectively. If one then speaks of electricity as of a body that combines with other bodies (with the constituents of the decomposed body) according to their chemically determined equivalent relationships, and if one assumes a certain quantity (positive or negative) of electricity as a measure, and then determines the masses of other bodies which combine with it, so Faraday calls the latter electrochemical equivalents to distinguish them from the chemical equivalents to which they are proportional. The chemical and electrochemical equivalents differ only in the various measures on which they are based, namely on the unit of mass[6] of oxygen (or hydrogen) for those, and on the unit of mass of electricity for these. Faraday himself has not specified the mass of electricity, which he accepts as a unit. However, if one wanted to take the mass which combines with the mass unit oxygen (or hydrogen)

[1] [Web41b] and [Web42].

[2] Translated by H. Härtel, haertel@astrophysik.uni-kiel.de and http://www.astrophysik.uni-kiel.de/~hhaertel/index_e.htm. Edited by A. K. T. Assis, www.ifi.unicamp.br/~assis

[3] The notes by H. Weber, the editor of the third volume of Weber's *Werke*, are represented by [Note by HW:], while the Notes by A. K. T. Assis are represented by [Note by AKTA:].

[4] [Note by HW:] *Results from the Observations of the Magnetic Association in 1840*, edited by Karl Friedrich Gauss and Wilhelm Weber, Leipzig, 1841, p. 91-98 and *Annalen der Physik und Chemie*, edited by J. C. Poggendorff, Volume 55, Leipzig, 1842, pp. 181-189.

[5] [Note by AKTA:] Michael Faraday (1791-1867). See [Far33] and [Far34].

[6] [Note by AKTA:] *Masseneinheit* in the original German text.

in water to form oxygen gas (or hydrogen gas), the two types of equivalent masses would be completely identical. Therefore, if electrochemically equivalent masses are to mean something different than chemically equivalent masses, they must be measured according to another fundamental unit[7] of electricity, which is derived from another class of electrical effects. The class of the magnetic effects of electricity in galvanic currents is the most suitable for this, since these effects have been reduced to absolute measurements in the teaching of magnetism and precise measurement methods have been developed for them.

As absolute measure of electricity (positive or negative or both together) is taken hereafter the amount of electricity that has to go through the cross-section of a conductor in the time unit (second), which limits the unit area in one plane, to produce in the distance identical effects as the absolute basic unit of free magnetism.[8]

It will now be of particular interest, based on this absolute measure of electricity, to determine the electrochemical equivalent of any body, e.g. that of water, from which it is then easy to derive the electrochemical equivalents of other bodies according to the laws discovered by Faraday with the help of their chemically determined equivalents to which they are proportional. The determination of the electrochemical equivalent of water on the basis of the measure of electricity specified above is now to be the subject of this article.

For this purpose, it is necessary to observe any measurable magnetic effect of the galvanic current while a certain quantity of water is being decomposed. To do so, neither the effect of the current on the Pouillet's sine-galvanometer,[9] nor on the tangent-galvanometer from Nervander can be used,[10] because these instruments though they can give correct comparisons of the current intensities, they cannot give absolute measurements. The instrument described in the previous article[11,12] therefore seems to be the only suitable for this task. Indeed, this is the easiest and most convenient method if it is not about finer measurements, and even these could be carried out with this

[7] [note by AKTA:] *Grundmaasse* in the original German text. This expression can also be translated as "basic unit" or "basic dimension".

[8] [Note by AKTA:] That is, as a magnetic dipole with a magnetic moment = 1. The axis of this dipole must be considered orthogonal to the current loop.

[9] [Note by AKTA:] Claude Servais Mathias Pouillet (1790-1868). His sine-galvanometer (*Sinus-Boussole* in German) is described in [Pou37].

[10] [Note by AKTA:] Johan Jakob Nervander (1805-1848). His tangent-galvanometer (*Tangenten-Boussole* in German) is described in [Ner33].

[11] [Note by HW:] Wilhelm Weber's *Werke*, Vol. III, p. 8.

[12] [Note by AKTA:] [Web41a, p. 8 of Weber's *Werke*].

instrument if it itself would be used in the finer manor specified above,[13,14] namely with a very much larger copper circle and a very small needle, hung on a thread, like in a magnetometer, and provided with a mirror so that it can be observed with a telescope and a scale.

In the absence of the finer version of such an instrument, I have used an instrument based on other principles and intended for other purposes, of which I should briefly mention what is necessary for the present purpose. When applying this instrument, no magnetic needle is used, but only the conductor of the galvanic current itself.

A copper wire, isolated with silk and of known length is carefully wound on a cylindrical pulley[15] of a certain diameter, so that all turns come very close to a system of concentric circles. The area of these circles can be equated with the area covered by the wire, which is based on the length of the wire, the diameter of the pulley and the number of turns. This can be easily calculated, and will be denoted by S.

The two ends of the wire lead to two small mutually insulated metallic hooks on the pulley, to which two other not overspun fine wires are attached, on which the entire wired pulley is suspended in a *bifilar* manner.

The *bifilar* suspension of the pulley on the latter two wires has a dual purpose: *firstly*, the same as with the bifilar-magnetometer, in order to obtain a certain directional force[16] D and then to determine all the forces acting on the pulley and trying to turn it. Although this directional force could be calculated from the length of the suspension wires, their spacing and the weights they carry (insofar as their own elasticity does not have to be taken into account), the same can be found more precisely through the experiments specified in the *Intensitas*[17] for determining the moment of inertia, which can

[13] [Note by HW:] Ibid, p. 10

[14] [Note by AKTA:] [Web41a, p. 10 of Weber's *Werke*].

[15] [Note by AKTA:] *Rolle* in the original German text.

[16] [Note by AKTA:] *Direktionskraft* in the original German text. It can also be translated as "directing force".

[17] [Note by AKTA:] Gauss's work on the intensity of the Earth's magnetic force reduced to absolute measure (*Intensitas vis magneticae terrestris ad mensuram absolutam revocata*) was announced at the Königlichen Societät der Wissenschaften zu Göttingen in December 1832, [Gau32]. The original paper in Latin was published only in 1841, although a preprint appeared already in 1833 in small edition, [Gau41] and [Rei19]. Several translations have been published. There are two German versions, one by J. C. Poggendorff in 1833 and another one in 1894 translated by A. Kiel with notes by E. Dorn; a French version by Arago in 1834; two Russian versions, one by A. N. Drašusov of 1836 and another one by A. N. Krylov in 1952; an Italian version by P. Frisiani in 1837; an English extract was published in 1935, while a complete English translation by S. P. Johnson and edited by L. Hecht appeared in 1995; and a Portuguese version by A. K. T. Assis in 2003: [Gau33], [Gau34], [Gau36], [Gau37], [Gau94], [Gau35], [Gau52], [Gau75], [Gau95] and [Ass03].

be referred to here.

Secondly, these two suspension wires have the special purpose that they form the bridge through which the current is fed both from the outside to the wire and back again, without the slightest impairment of the mobility of the roll, as would be the case if you need metal tips attached to the pulley and dipped into mercury wells where the inevitable friction does not allow measurements.

The bifilar suspension ensures that even when the current passes through the pulley, its position and the vibrations can be observed with the same freedom as the position and the vibrations of the bifilar magnetometer. It is therefore permitted to use the same fine tools for their observation, namely to attach a mirror to the pulley and to observe the image of a distant scale with a telescope. In this way, the path to the finest galvanic measurements is paved without using magnetic needles.

It is easy to first set up the tripod on which the pulley is suspended so that the pulley maintains the same position when a current of any strength is passed through the pulley, sometimes forwards and backwards, and then to rotate the whole system around a vertical axis by 90°. Then the instrument for the execution of our measurement is prepared.

The measurement then consists in the fact that the same current, which decomposes the water in the water decomposition apparatus, is passed through our instrument, where the force of the horizontal part of the earth's magnetism causes a deflection. This deflection must be observed closely in short intervals during the duration of the water decomposition. It is then easily understood that the absolute intensity G of the galvanic current for any moment in time while the deflection φ is observed is given by the following equation:

$$STG = D \tan\varphi \ ,$$

where T denotes the absolute horizontal intensity of the earth's magnetism at the observation site. If T is known and S and D are exactly determined, as stated above, the intensity G can be calculated from the observed deflection φ. From all φ-values for the period t where the water decomposition occurred, the amount of electricity E that passed through the pulley and was used for the decomposition of the water can be determined with great accuracy according to

$$E = \int G dt$$

according to the absolute units specified above. If we hereby divide the amount of the decomposed water W expressed in milligrams, the quotient

W/E gives the amount of water which is decomposed by the absolute amount of electricity specified, i.e. the desired electrochemical equivalent of water.

After this description of the measurement method used, the results of the measurements can be briefly summarized.

The wire wound on the pulley formed 1130 turns; the periphery of the roll was 164 millimeters; the length of the wire 253 600 millimeters. This results in S:

$$S = 4\ 638\ 330 \text{ square millimeters.}$$

The moment of inertia of the rolle K was found according to known regulations:

$$K = 779\ 400\ 000\ .$$

The period of oscillation t,[18] which changed somewhat with temperature, was

for the first and second measurement $t = 8.0702$"	118 111 000 ,
for the third and second measurement $t = 8.0803$"	117 817 000 ,
for the forth and fifth measurement $t = 8.0904$"	117 523 000 ,

from which the values of the directional force $\pi^2 K/t^2$ follows,[19] given in the last column.

At the time of these experiments in Göttingen, the absolute horizontal intensity T of the earth's magnetism could be measured after an almost simultaneous measurement in the magnetic observatory with the result

$$T = 1.7833\ ;$$

however, these observations were not made in an iron-free establishment, but in a room of the astronomical observatory[20] where there was a great deal of iron at moderate distances. The horizontal intensity at this observation point

[18] [Note by AKTA:] Gauss and Weber utilized the French definition of the period of oscillation t which is half of the English definition of the period of oscillation T, that is, $t = T/2$. For instance, the period of oscillation for small oscillations of a simple pendulum of length ℓ is $T = 2\pi\sqrt{\ell/g}$, where g is the local free fall acceleration due to the gravity of the Earth, while $t = T/2 = \pi\sqrt{\ell/g}$.

[19] [Note by AKTA:] Weber is here utilizing the equation of motion of a rigid body as $\tau = -D\varphi = K\ddot{\varphi}$, where K is the moment of inertia of the body, $\tau = -D\varphi$ is the torque or rotational moment acting on it when it suffers a deflection φ, while D is the directional force acting on the body.

[20] [Note by AKTA:] *Sternwarte* in the original German text.

was therefore compared with that in the magnetic observatory by means of comparative measurements, and the absolute intensity of the earth's magnetism for the place where the experiments were carried out resulted in:

$$T = 1.7026\ .$$

Finally, the simultaneous observation of the water decomposition apparatus and the galvanometer in the five measurements gave the following results:

	Decomposed Water in milligrams	Time interval for the decomposition	Amount of electricity based on absolute measures
1.	14.2346	1168"	1522.44
2.	14.2026	1280"	1504.92
3.	14.0872	1137.5"	1506.46
4.	14.0812	1154"	1501.43
5.	13.9625	1263"	1484.90

From this it follows for the electrochemical equivalent of water the following five results:

0.009 350	−0, 000 026
0.009 437	+0,000 061
0.009 351	−0, 000 025
0.009 337	−0, 000 039
0.009 403	+0,000 027

therefore as a mean value 0.009 376.[21]

The differences between the individual measurements from this mean are noted in the last column.

It should be added that the amount of the decomposed water was determined as usual, from the volume of the evolved gases, and both gases were collected and measured. In order to avoid the absorption of the gases by the water, the former was collected over a mercury trough, which Professor Wöhler[22] was kind enough to lend. The water to be decomposed consisted of

[21] [Note by AKTA:] From this mean value we obtain $1/0.009376 = 106.655 \approx 106\frac{2}{3}$. In later works Weber will utilize this value $106\frac{2}{3}$ whenever referring to the electrolytic unit of current. See, for instance, [WK56, p. 600 of Weber's *Werke*] with English translation in [WK03, p. 290] and Portuguese translation in [WK08, p. 96]; [KW57, pp. 614, 649 and 650 of Weber's *Werke*] with English translation in [KW19, p. 8]; and [Web62, p. 88 of Weber's *Werke*].

[22] [Note by AKTA:] Friedrich Wöhler (1800-1882).

a few drops, which, mixed with sulfuric acid, occupied the sealed end of an S-shaped tube (and represented the function of a retort). The atmospheric air was completely excluded. Two platinum wires, which were melted into the tube and passed through the water without touching one another, were used to conduct the galvanic current through the water. The decomposition of water had started long before the start of the measurement. The gas was measured humid. The walls of the tube in which it was collected had been moistened with distilled water before being filled with mercury. The influence of temperature and barometer readings were also taken into account properly. The observations were all carried out jointly by Professor Ulrich[23] and the undersigned.

As for the result itself, the consistency between the five measurements can be seen as a new confirmation of the Faraday theorem that the same amount of electricity is always needed to decompose the same amount of water. If conditions permit in the future, to make that confirmation even more striking, these measurements will be repeated under even more modified conditions. Similar measurements will also be made for other bodies instead of water, e.g. will be carried out with hydrochloric acid.

If one finally compares the result of these measurements with those of the previous article[24,25] on the maximum of the current intensity of different columns, one obtains, as already mentioned there, knowledge about the rate of water decomposition which can be achieved with the galvanic current under particularly favourable conditions. From this it can be judged whether the galvanic current is a practical tool for the production of oxygen and hydrogen gas. It requires no further discussion that the collected result are useful in the experiments made with Faraday's Volta-electrometer for determining the absolute amounts of electricity more precisely, and for concluding the magnetic effects that could be produced.

[23] [Note by AKTA:] Georg Karl Justus Ulrich (1798-1879).
[24] [Note by HW:] Wilhelm Weber's *Werke*, Vol. III, p. 10.
[25] [Note by AKTA:] [Web41a, p. 10 of Weber's *Werke*].

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