Physics. — *"A determination of the electrochemical equivalent of silver."* By G. VAN DIJK and J. KUNST. (Communicated by Prof. H. HAGA.)

The principal determinations of the electrochemical equivalent of silver have yielded the following values:[1])

MASCART	0,011156	1884
F. and W. KOHLRAUSCH	0,011183	1884
Lord RAYLEIGH and Mrs. SIDGWICK	0,011179	1884
PELLAT and POTIER	0,011192	1890
KAHLE	0,011183	1898
PATTERSON and GUTHE	0,011192	1898
PELLAT and LEDUC	0,011195	1903

The difference in these numbers is due, partly to the method of the determination of the strength of the current, partly to the way of constructing and using the voltameter.

In most of the investigations the strength of the current was measured by means of an electrodynamometer in some form or other, either directly or indirectly with the aid of a standard cell (cell of CLARK). F. and W. KOHLRAUSCH used a tangent galvanometer.

For the voltameter the circumstances differed as to the composition and the concentration of the electrolyte, the shape, the dimensions and the composition of the cathode, the way of washing and drying the silver deposit.

The "Bedingungen unter denen bei der Darstellung des AMPÈRE die Abscheidung des Silbers stattzufinden hat" are inserted in the "Reichsgesetzblatt" of May 6, 1901, p. 127 [2]) among the regulations of the law concerning the electric units sub § 5*a*.

In connection with the rather considerable difference between the values found for the electrochemical equivalent of silver, a new investigation as to the value of this quantity in which the above mentioned conditions are followed, did not seem to be superfluous to us. The tangent galvanometer has been chosen for the measurement of the strength of the current. Owing to the high degree of accuracy with which the constant of this instrument, and the hori-

[1]) MASCART. Journ. de Phys. (2) 3, p. 283, 1884 F. and W. KOHLRAUSCH. Wied. Ann. 27, p. 1, 1886. Lord RAYLEIGH and Mrs. SIDGWICK. Phil. Trans. 2, p. 411, 1884. PELLAT and POTIER. Journ. de Phys. (2) 9, p. 381, 1890. KAHLE. Wied. Ann. 67. p. 1, 1899. PATTERSON and GUTHE. The Phys. Review 7, p. 251, 1898. PELLAT and LEDUC. Compt. Rend. 136, p. 1649, 1903.

[2]) Also Zeitschr. f. Instrumentenk. 6 Heft. 1901, p. 180.

zontal intensity of the terrestrial magnetism and its space- and time-variations may be determined, this method is very well adapted for a laboratory, which has been built without iron and in a place, where no vibrations or stray currents in the earth are to be feared.

Determination of the horizontal intensity of the terrestrial magnetism: H.

To this purpose we have followed the bifilarmagnetic method of F. KOHLRAUSCH (Wied. Ann. 17, p 737, 1882). The absolute bifilar magnetometer was fastened at the top of a high wooden tripod. 90 c.m. to the north and to the south of it the tangent galvanometers were erected on pillars of freestone cemented on the bottom with plaster. The dimensions of the magnetometers of these galvanometers are about the same as those of the "Elfenbeinmagnetometer" of KOHLRAUSCH, but they differ from it in an important detail. The needle with the mirror of the "Elfenbeinmagnetometer" oscillates within a small cylindric space, whose sides are only a few millimeters apart and parallel to the plane of the mirror. In this way the damping has been obtained. The local influence of the instrument is nearly exclusively determined by the magnetic or diamagnetic properties of the material of which the front and back sides consist, which is usually glass. In consequence of the small distance between the needle and the glass walls this influence is variable with their relative position. This renders the magnetometer in this form unsuitable for observations which require a somewhat longer time, as we are not sure of a constant position of the needle. It is therefore that we have modified the instrument in such a way that the distance of the needle from the fixed parts of the apparatus is large enough, the damping being obtained in another manner. The space in which needle and mirror oscillate is a vertical, thinwalled turned cylinder of wood with an internal diameter of 4 c.m. The frontwall has been pierced and round the hole a rim has been cemented in which the glass front fits. A vane of mica is suspended on the cross, which supports the mirror and to which the needle is riveted. This wing can move in a narrow space which is found in the base of the instrument and whose width amounts to a few m.m. In this way a strong air-damping has been obtained.

In order to determine the local influence the magnetometer was turned round the needle, sometimes in positive and sometimes in negative direction; each time over an angle of 5°. Before the mirror a telescope with a scale was placed, and the distance had been regulated such, that turning an angle of 5° corresponded to 50 cm. of the scale. From different series of observations, in which the variations of the declination were read from another magnetometer, it appeared that turning an angle of + 5° or — 5° from the position of equilibrium caused a deviation of the mirror from + 0,003 c.m. to — 0,002 c.m. for one of the magnetometers and from + 0,003 c.m. to — 0,007 c.m. for the other. (The sign + indicates that the turning of the mirror and of the magnetometer are in the same direction.) These numbers are the mean values of a series of usually 10 observations. The needle had a different position in different observations, either more foreward or more backward; no fixed relation between the deviation and the place of the needle could be observed. We have equated the local influence to zero; the error ensuing from this will not amount to more than to some hundredthousandths.

A rectangular turned copper ring 8,4 m.m. large and 3,6 m.m. thick, supported by a wooden frame formed the circuit of the tangent galvanometer, which was placed south of the bifilar magnetometer. It resembles the apparatus described by KOHLRAUSCH Wied. Ann. 15, p. 552, 1882.

The circuit of the tangent galvanometer placed to the north was formed by a copper wire of 0,059 cm. diameter, tightly strained round a marble disc, the magnetometer can be placed in a triangular opening, which is cut out of the disc.

In order to determine the local influence, the magnetometer was supported free from the other part of the tangent galvanometer and this was turned over an angle of 30° round it to either side. We found that turning the marble galvanometer from + 30° to — 30° caused a deviation of the mirror in one series of — 0,002 cm., another time of 0,000 cm. For the other galvanometer this deviation amounted to + 0.004 cm. This difference may be ascribed to experimental errors, and therefore no influence of the instrument exists here either.

The ratio of the values of H at the place where the bifilar magnet, and at those where the needles of the magnetometers were suspended, was determined with the local-variometer of KOHLRAUSCH; a bifilar variometer indicated the time-variations of H.

From the observations with the local-variometer — the corrections for the time-variations being applied — the ratio of the values of the intensity of the magnetic field was derived as the average value of a series of numbers, whose extreme values differed less than $\frac{1}{10000}$.

The ratio of H at the places of the bifilar magnet and of the needles inside the magnetometers may be deduced from these data.

The distance between the suspension-wires above and below, the length of the wires and the weight which they support, are of primary importance for an accurate determination of the value of $H \times M$ for the bifilar magnetometer (M = magnetic moment of the magnet). The wires run above and below closely along two small scales divided in $^1/_2$ m.m. The distance between the wire and the two adjacent divisions of the scale is determined by a microscope with ocular scale. (1 m.m. corresponds to about 23 divisions of the ocular scale) and the distance between the divisions of the two scales is determined with a comparator. The distance is about 12.4 cm. These measurements have been performed before and after the observations (August 1903); the difference of the distance of the wires found in the two determinations amounted to:

above 0,004 m.m. below 0,002 m.m.

The mean value of the two determinations has been taken as the distance during the observations. It does not differ more from those values than $\frac{1}{60000}$.

The length of the wires has been determined before, after, and a few times between the observations with the aid of a glass scale. The extreme values of the lengths reduced to the same temperature differed 0,13 m.m.; the length of the wires being about 232 cm. An error of 0,1 m.m. causes an error in the result of $\frac{1}{46000}$.

The pieces, suspended on the wires are: the horizontal cross-bar with its vertical rod and the bearer of the magnet which are made of aluminium, the magnet, and a vane of mica in diluted glycerin for the damping. These different pieces (with the exception of the mica-vane) have been weighed separately and together; the difference was 1 mgr., the total weight about 160 gr. The weight of the mica-vane with its suspension-wire, immerged in the liquid so far as during the observations, was determined at: before the observations, 1,444 gr., afterwards 1,457 gr., average value 1,450 gr. The error which may ensue from this difference is not great · a difference of 7 mgr. gives an error of $\frac{1}{46000}$ in the result.

In order to determine the value of $\frac{M}{H}$, we must measure the polar distance of the magnet and the distance of the centers of the needles.

The polar distance of the magnet, 16,06 cm. long, was derived from the deviations of the magnetometer-needles caused by the magnet when placed normal to the magnetic meridian in two different positions symmetrical with respect to these needles. Two determinations in which the distances were chosen: 80 and 100 cm., and 75 and 105 cm. yielded the values 13,40 and 13,23 cm. The difference may be due to experimental errors. A variation of $\frac{1}{40}$ m.m. of one of the distances, causes — ceteris paribus — a variation in the value of the polar distance larger than the difference between the two values found. We have taken for the polar distance the mean value 13,31 cm. This agrees fairly well with $^5/_6$ of the length. ($^5/_6 \times$ length $= 13{,}38$).

In order to ascertain the distance between the centers of the needles, we first determined the difference of their distance from the cocoon silk suspension-fibres. This difference was derived from the deviations of the needles caused by the magnet, as well in one of the positions of the magnetometers as when they had changed place, care being taken that the silk fibres had the same positions both times. In two observations this difference amounted to 0,007 c.m. and 0,009 c.m.; average value 0,008 cm. A difference of distance of 0,001 cm. has an influence on the result of $\frac{1}{120000}$.

The distance of the silk fibres was measured by projecting the fibres from two telescopes, 180 cm. apart and at a distance of about 5 m. from the magnetometers, on a horizontal scale placed behind them.

It appeared that the walls of the tube of the magnetometer had no influence on the course of the rays.

We determined the value of H before and after the time of the passage of the current, in order to arrive at the mean value of H during that time. During all this time the indications of the local-variometer of KOHLRAUSCH, erected in a room with nearly constant temperature, were read, during the determinations of H every 2 minutes, in the time between those determinations every 5 minutes.

The value of H during the passage of the current was derived from the constants of the variometer, the mean reading during the first determination of H and during the passing of the current and the value of H found in the first determination of H. The same calculation was performed with the second determination of H. The two values found in this way for H during the passage of the current differed in most cases only $\frac{1}{9000}$ or not even so much. Only a few times the difference amounted to $\frac{1}{6000}$ or $\frac{1}{4500}$. The mean of the two values of H found in this way, was taken as value of H.

The tangent galvanometers.

Five diameters of the tangent galvanometer "north" were measured by comparing them with a standard meter by means of a katheto-meter; they differed less than 0,1 m.m. Before the observations we found for the mean value of the external diameter: 41.3833 c.m. $t = 14°\,5$, after the observations we found 41.3842 c.m., $t = 17°.5$. Reduction of the former value to the temperature $t = 17°.5$ yields 41.3843 c.m. So the agreement is perfect.

The ring of the tangent galvanometer "south" was not so perfectly circular; moreover its shape was not quite constant. Yet the different determinations yielded mean values for the diameter which agreed very well. Ten diameters have been measured, five on each side, the distances of which were as nearly equal as could be obtained. The values found are:

after the observations $2\,R = 40{,}445$ cm. $t = 17°.3$

before the observations 40,443 cm. $t = 14°.5$

a still earlier determination yielded 40,446 c.m., at $t = 19°.8$. When reduced to equal temperature these values differ much less than $\frac{1}{40.000}$.

For the *determination of the intensity of the current* sometimes one, sometimes the other tangent galvanometer was used. The current was supplied by a battery of 3 or 5 accumulators; resistances of about 20 ohms, two voltameters, a commutator and one of the galvanometers were inserted in the circuit. The intensity of the current varied between 0.30 and 0.45 ampères, the quantity of silver deposited was about 1 gram; the current passed therefore during 48 or 32 minutes. Half a minute after the current was closed the deflection of the tangent galvanometer was observed for the first time, and further every minute. While the current passed through one of the galvanometers, the variations of the declination were observed on the other. At $^1/_4$ and at $^3/_4$ of the interval during the passage of the current, the current was reversed; during the short time required for the reversal, a short circuit was formed, so that the current did not pass through the galvanometer; the error arising from this circumstance is however so small, that it cannot have any influence on the result. The influence of the reversal of the current in one of the galvanometers on the reading on the other may be calculated with a sufficient degree of accuracy from the dimensions of the galvanometer, their mutual distance, and the approximated knowledge of the intensity of the current. Before, after and between the different determinations the two galvanometers were read at the same time in order to ascertain their course. The time was determined with a chronometer, which ticked 120 times a minute, every day it was compared with an astronomical clock of great accuracy.

The voltameters.

The cathodes consisted of platinum, two of them were cup-shaped, the third was a cylinder ending in a hemisphere; a silver rod served as anode. In order to intercept particles, which might fall from the anode a SOXHLET filtering-paper finger was placed round it, manufactured by SCHLEICHER and SCHÜLL. A 20°/₀ neutral solution of $Ag\,NO_3$ formed the electrolyte. This was partly obtained from E. MERCK, Darmstadt, partly from the firm J. W. GILTAY, formerly P. J. KIPP and SONS, at Delft.

Two voltameters were placed in the circuit in order to ascertain that no irregularities occurred in the deposition of the silver. In most cases the weight of the deposit at the cathode agreed to within 0,1 m.gr., once it amounted to more than 0,2 m.gr. The mean value of the two weights was assumed for the weight of the deposited silver.

The weights used for the weighing had been corrected by testing them to a standard kilogram.

In the same way all scales used for the measurements have been compared with a standard meter, whose divisions are again compared with a standard length of 2 d.m. whose corrections were accurately known.

The distance from the scales to the bifilar magnetometer and the galvanometers was measured with a wooden scale of 3 meters. Marks were made at distances of 1 meter and brass scales divided into m.m. could slide along the ends; these scales ended in points of ivory. For the galvanometers the distance from the scale to the glass front was measured, for the bifilar magnetometer the distance to the mirror. For each observation these distances were measured and also the distance of the silk fibres of the magnetometers. The different corrections for the inclination of the mirror, the thickness of the glass front, the distance from the front to the mirror, etc. were applied to the distance.

The length of the scale of 3 meters proved not to be perfectly

Numero	H	i	t	p	a North galvano-meter	a South galvano-meter
1	0.18186	0.039083	2160.05	0.94417	0.011184	
2	0.18187	0.043462	2160.05	1.05014		0.011186
3	0.18156	0.041659	2160.05	1.00647	0.011185	
4	0.18150	0.041711	2160.05	1.00759		0.011183
5	0.18157	0.045081	1920.05	0.96799		0.011184
6	0.18160	0.045481	1920.05	0.97657	0.011183	
7	0.18159	0.039307	2400.06	1.05477		0.011181
8	0.18202	0.038134	2400.06	1.02354		0.011184
9	0.18191	0.038588	2400.06	1.03565	0.011183	
10	0.18160	0.038770	2400.06	1.04007	0.011178	
11	0.18161	0.031629	2880.07	1.01895		0.011183
12	0.18157	0.036271	2640.06	1.07048	0.011179	
13	0.18162	0.036644	2400.06	0.98335		0.011181
14	0.18189	0.030924	2880.07	0.995[illegible]1	0.011182	
15	0.18170	0.030813	2880.07	0.99248	0.011184	
16	0.18198	0.030284	2880.07	0.97501		0.011179
17	0.18164	0.040637	2160.05	0.98136	0.011180	
18	0.18123	0.043140	2160.05	1.04181		0.011180
19	0.18155	0.033[illegible]82	2640.06	0.98849		0.011183
20	0.18192	0.037478	2400.06	1.00565		0.011180
21	0.18163	0.039023	2400.06	1.04695	0.011179	
22	0.18140	0.035231	2640.06	1.03997	0.011181	
23	0.18163	0.037327	2400.06	1.00162	0.011181	
24	0.18191	0.037678	2400.06	1.01106		0.011181
				Mean value	0.0111816	0.0111821
					±0.00000066	±0.00000060
					(mean error).	

H denotes the horizontal intensity, i the intensity of the current, t the time, p the weight of the silver-deposit, a the electrochemical equivalent. All these quantities are measured in c. g. c. units.

constant; it had increased about 0,2 m.m. during the time from before till after the observations. A determination of a part of the length, which was performed between the observations, convinced us that the change had taken place gradually. The mean value of the length before and after the observations is used as the length of the scale for all observations.

This will have but a very small influence on the result; it will cause the first of the values found for the equivalent to be somewhat too large, the last to be somewhat too small. The difference however does not amount to more than $\frac{1}{16000}$. The distance from the scales to the galvanometers was about 314,2 cm., that to the bifilar magnetometer about 317,5 cm.

We have made 24 determinations of the electrochemical equivalent of silver. The annexed table (p. 448) shows the results.

The values for the electrochemical equivalent a deduced from the observations with the different galvanometers differ less than $\frac{1}{20000}$.

As the mean value of all determinations we find:

$$a = \underline{\underline{0.0111818}} \pm 0.0000004. \text{ (\textit{mean error})}.$$

In connection with the agreement between the different observations, we are of opinion that this number is accurate to $\frac{1}{10000}$.

The observations will be published later in extenso.

Physical Laboratory, University Groningen.

(January 21, 1904).