AN ABSOLUTE DETERMINATION OF THE E.M.F. OF THE CLARK CELL.

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A NEW determination of the electrochemical equivalent of silver was made a year ago by Patterson and Guthe[1]. The electro-dynamometer employed for the purpose was fully described in their paper. Briefly a movable coil is suspended by a phosphorbronze wire approximately a meter long. The center of the movable coil is placed at the center of a fixed coil consisting of one layer of 576 turns of wire. The dimensions of both coils were intended to fulfill the requirements laid down by Andrew Gray[2] that the length should be as $\sqrt{3}$ to 1. The expression for the current is then

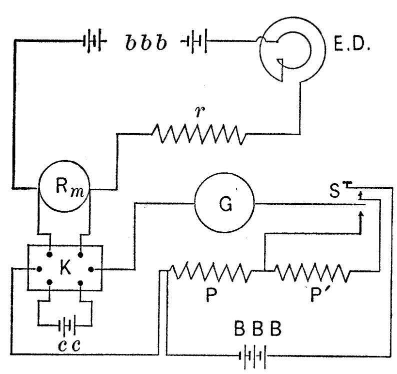

Fig. 1.

$$I = \frac{1}{Tr}\sqrt{\frac{2\pi K\sqrt{D^2 + L^2}}{Nn}}$$

for a twist of the wire through an angle 2π. In this formula

T is the period of vibration of a weight M suspended by the phosphor-bronze wire.

K, the moment of inertia of the mass M.

D, the diameter of the fixed coil.

L, the length of the fixed coil.

N, the number of turns of wire on the fixed coil.

[1] PHYS. REV., Vol. VII., No. 39, Dec., 1898.

[2] Abs. Meas. in Electricity and Magnetism, Vol. II., p. 277.

n, the number of turns of wire on the movable coil.

r, the radius of the movable coil.

The electrochemical equivalent of silver found by Patterson and Guthe was 0.0011192 gm. per ampère per sec.

With such an instrument to measure the current, and with an appropriate coil of known resistance, it is obviously easy to compare the fall of potential of a measured current over this coil with the E. M. F. of a Clark standard cell. This work we have taken up the past year.

The Clark Cells.

Two cells were made in accordance with the specifications legalized by act of Congress in 1894. They are of the Rayleigh H-form as modified by Kahle. One of them was made in the autumn of 1897 and the other in October, 1898. They do not differ more than one part in ten thousand. The negative consists of a zinc amalgam one part zinc to nine parts mercury. The mercurous sulphate was washed as directed in the legal specification, and the zinc sulphate was rendered neutral with zinc oxide. The amalgam and the mercurous sulphate are covered with crystals of zinc sulphate to a depth of about one cm.

Each cell is mounted in a case the top of which is fitted with a bayonet joint and is supplied with four legs. When the hard rubber top is removed it carries the cell with it. The legs serve for a support in a bath of petroleum. The temperature was taken by a thermometer graduated to fifths. It was made by Haak, of Jena, and has the certificate number 11021 of the Reichsanstalt. At 15° it reads 0.05° too low as certified by the Reichsanstalt.

Method of Measurement.

The two Clark cells were connected in series. Their electromotive force was not balanced directly against the fall of potential over the manganin coil, but by Poggendorff's method the E. M. F. of the cells was first balanced against the fall of potential over a resistance P in Fig. 1, and then the fall of potential over the manganin coil R was balanced in the same way, while the current was adjusted so as to balance the torque of the phosphor-bronze wire of the electrodynamometer with a twist of one complete turn. Between the resistance boxes P and P', each of 10,000 ohms, was placed a shunted Kohlrausch cylindrical bridge wire whose 1000 divisions had a resistance of 1.7 ohms. This arrangement enabled us to balance to fractions of an ohm. The resistance in this circuit was thus kept at 10,000 ohms plus the resistance of the shunted bridge wire, the contact on which was adjustable to secure a balance. The resistance R over which the fall of potential was measured was the same manganin-coil used in the determination of the silver equivalent. The value was determined by comparison with two standard one-ohm coils made by Wolff in Berlin and tested by the Reichsanstalt. The certificates are numbered 160 and 163.

If I is the current measured by the electrodynamometer, E the E. M. F. of the two cells, R_1 the resistance in P necessary to balance E, R_2 the resistance to balance the P. D. due to I, and R the resistance of the manganin coil, then

$$E = RI\frac{R_1}{R_2}.$$

If I be put equal to a/T, in which a is made up of the constants in the expression for I already given, then

$$E = R\frac{R_1}{R_2}\cdot\frac{a}{T}.$$

The axis of the movable coil was placed at right angles to the magnetic meridian to avoid dip. Moreover, it was necessary to reverse the current through the stationary coil without reversing through the suspended coil so as to eliminate a small disturbance due to the manner of leading in the current to the movable coil. Hence it was necessary to use all four permutations of direct and reversed currents through the two coils.

DATA AND RESULTS.

The following table gives the resistances necessary for a balance by the Poggendorff method of comparison. In arrangement 2 the current was reversed through the movable coil without reversal through the fixed coil as compared with 1. R_a is the resistance to balance with the current in one direction, R_b the resistance to balance with the current reversed through the entire instrument, and R_1 the resistance to balance the e. m. f. of the two standard cells. The column headed t is the temperature of the phosphor-bronze wire.

TABLE I.

Date.	Arrangement.	Ra	Rb	R_1	t	T
May 27.	1	7303.8	7299.0	4631.9	23.0°	11.9850
	2	7422.25	7418.9	4631.9	23.4	
" 30.	1	7324.5	7320.0	4644.3	22.9	11.9847
	2	7443.0	7440.7	4644.3	23.2	
" 31.	1	7329.5	7323.7	4647.5	24.25	11.9875
	2	7449.4	7445.0	4647.5	24.2	

The value of the resistance R to give a balance if there were no earth's field or asymmetry in the electrodynamometer would be very approximately $\sqrt{R_a{}'R_b{}'R_a{}''R_b{}''}$, where the primes refer to arrangement 1 and the seconds to arrangement 2.

The resistance of the manganin coil was found to be 4.6304 ohms at 23°. Its temperature coefficient is very nearly zero at this temperature. Three comparisons were made with the Wolff coils by the Carey Foster method. Two additional English one-ohm coils were first compared with the German coils, and then all four in series with the manganin coil.

Referring again to the formula for the electromotive force,

$$E = R\frac{R_1}{R_2}\cdot\frac{a}{T},$$

we have to find the constant

$$a = \frac{1}{r}\sqrt{\frac{2\pi K\sqrt{D^2 + L^2}}{Nn}}.$$

The constants of the electrodynamometer in this formula are as follows:

r, 4.9968 cm.; K, 2251.89 cm^2.-gm.; D, 48.108 cm.;
L, 41.621 cm.; N, 576; n, 45.

The period of vibration of the weighted phosphor-bronze wire was determined at several temperatures just before its use in the electrodynamometer and again immediately afterwards. The period was slightly longer than it was a year ago, but the temperature coefficient was unchanged for the new temperature curve, Fig. 2, is parallel to the old one. It is highly probable that this wire has suffered some oxidation during the year.

The dimensions of both coils were measured over again. The movable coil had to be rewound, as the flattened copper wire was loose. The new dimensions are appreciably smaller than those for a year ago. The rubber continues to shrink somewhat, and it is proposed to try new materials for the purpose hereafter. The periods T in the table are taken from the curve I, Fig. 2, at points

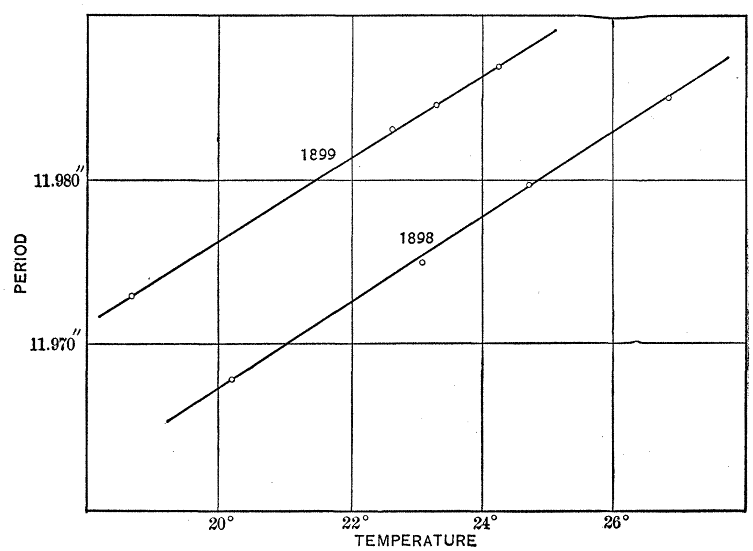

Fig. 2.

denoted by the mean temperatures. Substituting the numerical values we have the following results for the cells at the reading of 15° on the thermometer :

May 27, $E = 1.43355$ volts.
May 30, $E = 1.43333$ volts.
May 31, $E = 1.43305$ volts.

The dimensions of the movable coil were taken immediately after the last set of observations. Since it is known that its dimensions change by shrinking, and as a smaller value of r increases the value of the constant a, and hence the value of E, it is evident that any shrinkage between May 27 and May 31 tends to increase the value of E from the first set of observations. We have accordingly thought best to give the first determination half the weight of the other two. The result, after correcting for the thermometer error of 0°.05, is

$$1.4333 \text{ volts at } 15^\circ \text{ C.}$$

If we allow equal weights for the three determinations, the result differs by only one unit in the fourth decimal place. Since the two cells themselves differ by one part in ten thousand, and since we do not claim a degree of accuracy greater than one part in five thousand, the fourth decimal place is of course in doubt.

In 1892 Glazebrook and Skinner made a very careful determination of the E. M. F. of the Clark cell by the silver voltameter method, assuming 0.001118 as the silver equivalent. The result was 1.4342 at 15°.[1]

Kahle in 1898 found by means of a Helmholtz electrodynamometer the value for the modified H-form, 1.4328 at 15°.[2] But Kahle says that the silver equivalent for a solution neutralized with silver oxide is five parts in ten thousand higher than for a solution not so neutralized. He obtained for the silver equivalent 0.0011182. But neither he nor Glazebrook apparently neutralized with silver oxide. Hence if we employ 0.0011187 for a solution not neutralized by silver oxide and recalculate from Glazebrook's data, the result is 1.4332 at 15°. This is practically identical with ours.

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[1] Phil. Trans. (A), Vol. 183, p. 567, 1892.

[2] Zeitsch. f. Instrum. Kunde, June, 1898.

NOTE.—Since this paper was written the two Clark Cells used in the investigation have been taken by Professor Carhart to Berlin, and through the courtesy of the President of the Reichsanstalt, Professor Kohlrausch, of the Director of the technical department, Professor Hagen and of Professor Lindeck, the opportunity has been afforded of making several series of comparisons with the standards of the Reichsanstalt in Charlottenburg.

Unfortunately cell No. 2 was injured during the long journey, but No. 1 remained in good condition. No. 2 was often compared with No. 1 in Ann Arbor and was never more than one part in 10,000 lower than No. 1.

The result of three elaborate series of comparisons is that the E. M. F. of No. 1 is one part in 20,000 higher than the mean of all the normal Clark cells in both departments of the Reichsanstalt. This difference is well within the degree of accuracy attempted in this investigation.