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A NEW DETERMINATION OF THE ELECTROCHEMICAL EQUIVALENT OF SILVER.

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THE discrepancy of the values for the mechanical equivalent of heat obtained by the electrical method and those found by the direct method¹ has suggested the possibility of the difference being due to an error in the standards used. The value of the ampere was suspected to be wrong and this led us to attempt a redetermination of its value by a new method. The electrochemical equivalent of silver has been repeatedly determined and was found to be 0.0011156 grm. by Mascart,² 0.00111794 grm. by Lord Rayleigh and Mrs. Sidgwick³ and 0.0011183 grm. by Fr. and W. Kohlrausch.⁴ In the first two cases an electrodynamic balance was used; in the last an accurate tangent galvanometer. Heydweiller⁵ compared Lord Rayleigh's and Kohlrausch's methods directly and came to the conclusion that the error in the two methods could not be larger than 0.1 %. Köpsel⁶ found 0.0011174 grm. with a balance built according to von Helmholtz's directions. The experi-

¹ A table with the results obtained by various methods since 1867 is given in *Phil. Mag.*, 39, 160, 1895; see also *Day, Phys. Rev.*, VI., 193, 1898, and *Johns Hopkins Univ. Circ.*, XVII., 54, 1898.

² *Journ. de Phys.* (2) 1, 109, 1882, and 3, 83, 1884.

³ *Proc. Roy. Soc.* 37, 144, 1884, or *Phil. Trans.* 2, 411, 1884.

⁴ *Sitzungsber. d. phys.-med. Ges., Würzburg*, 1884, *Wied. Ann.*, 27, 1, 1886.

⁵ *Inaug. diss., Würzburg*, 1886.

⁶ *Wied. Ann.*, 31, 268, 1887.

ments by Pellat and Potier,¹ using Pellat's absolute electrodymanometer, gave 0.0011192 grm. For a number of years Kahle has been at work at the Imperial Institute in Berlin using Helmholtz's current-balance,² but the definite report of this valuable investigation has not yet been published. In the preliminary report 0.0011182 grm. and 0.0011193 grm. are given according as the silver was deposited from a fresh or old solution.³

In all the experiments mentioned the value of the electrochemical equivalent of silver depends upon the accurate knowledge either of the acceleration due to gravity or of the horizontal intensity of the earth's magnetic field. We proposed to measure its value entirely independent of g or H by balancing the moment due to the electrodynamic action of the two coils of an absolute electrodymanometer, designed by us and made under our direction, against the torsional moment of a wire with very small elastic fatigue. The measurements are finally reduced to measurements of mass and length only and we believe our result to be accurate to at least one in five thousand.

Description of the Method. In our determination we made use of Poggendorff's potentiometer method for comparing electromotive forces. First, we found the ratio between the E.M.F. of two Carhart-Clark cells immersed in a large water-bath and the potential difference at the terminals of a coil of magnanin wire, when a current flowed through it, which just balanced the torsional moment of the suspending wire of the electrodymanometer due to one complete twist of the torsion head. The absolute value of this current was calculated from the dimensions of the instrument.

Let I be the calculated current,

E the E. M. F. of the cells,

R_1 the resistance necessary to balance E ,

R_2 the resistance necessary to balance the P. D. due to I ,

R the resistance of the magnanin coil ;

$$\text{then} \quad I = \frac{R_2}{R_1} \frac{E}{R}. \quad (1)$$

¹ Journ. de Phys., (2) 9, 381, 1890.

² Wied. Ann., 59, 532, 1896.

³ Zeitschr. f. Instrum. Kunde, 17, 144, 1897, and 18, 141, 1898.

Secondly, we balanced the E. M. F. of the cells against the Pot. Diff. due to the silver depositing current.

Let I' be this current,

R_1' and R_2' the resistances necessary for the balances,
 E and R the same as before,

$$\text{then} \quad I' = \frac{R_2'}{R_1'} \frac{E}{R}. \quad (2)$$

The silver deposited by the current I' is

$$q = zI't \text{ grms.} \quad (3)$$

where z is the electrochemical equivalent of silver ;

$$\text{but} \quad I' = I \frac{R_1}{R_2} \frac{R_2'}{R'}, \quad (4)$$

$$\text{therefore} \quad z = \frac{q}{It} \frac{R_1}{R_2} \frac{R_2'}{R'}. \quad (5)$$

We are thus independent of the absolute value of the E. M. F. of the standard cells and the resistance of the manganin coil.

We chose Carhart-Clark cells, in which the zinc sulphate solution is free from crystals at ordinary temperatures, rather than normal Clark cells, in which the zinc sulphate solution is always in presence of crystals, to avoid all time lag of electromotive force due to changing density after change of temperature. The Carhart-Clark cells have the further advantage of having only about one-half as great a temperature coefficient as the normal Clark cells.

The manganin coil had a negligible change in resistance within the limits of the temperatures at which we used it. The current through the silver voltameters was not measured directly by the electro-dynamometer. The reason for not doing so was that the electro-dynamometer was extremely sensitive, and it would have been almost, if not quite, impossible to control the current through the circuit from the beginning to the end of a set of observations at such a value as to balance the turning moment of the suspension due to exactly one turn of the torsion head of the instrument. This difficulty was due to several causes : first, the current diminished

gradually, due to polarization of the battery and heating of the coils; second, slight changes of temperature produced changes in the wire suspending the movable coil, from which resulted changes in the torsional constant and in the zero point; third, there were gradual though very small changes in the zero point due to elastic fatigue of the suspension. Besides these reasons it should be mentioned that an absolute electrodymanometer should be used with all four possible permutations of direct and reversed current through both coils.

Poggendorff's method gave an almost ideal means of holding all these diverse disturbing factors in control. Fig. 1 shows the arrangement of our apparatus.

In our experiments we used either two or three storage cells *BBB* to produce the current through two carefully adjusted resistance boxes *P*, *P'* by Nalder Brothers. The total resistance

Fig. 1.

was kept at 11,110 ohms, and the fall of potential through a portion *P* of this resistance, was balanced against the electromotive force of the standard cells *cc* or against the fall of potential through the manganin coil *R_m*. *K* is a Pohl's commutator, *G* a sensitive Kelvin galvanometer and *S* a successive contact key. In one arrangement the manganin coil was in circuit with the storage battery *bbb* and the electrodymanometer *ED*, in the other two silver voltameters were included in the circuit also.

The silver nitrate solution was made by weight 15% c. p. silver nitrate and 85% distilled water with a trace of silver oxide added to insure a neutral solution. The same solution was used on successive days. Kahle, in a recent paper,¹ has called attention to a difference he finds in the electrochemical equivalent of silver when determined from "fresh" and "used" solutions. We did not prepare a solution afresh for each determination. The close agreement

¹ Zeitschr. f. Instr., 17, 144, 1897.

between our different results would indicate that our solution remained constant for at least the last four days on which the experiments, which were used for the final calculations, were made. We used for silver voltameters two platinum bowls of 7.5 cm. diameter and 2.5 cm. height as kathodes and pure silver plates about 2.5 cm. diameter wrapped in filter paper and suspended by platinum wires near the centers of the bowls as anodes. We used currents slightly less than one ampère and kept the circuit closed for about one hour. Before using the bowls they were carefully cleaned, dried and weighed with accurate weights to the nearest tenth of a milligram by means of the method of double weighing. After opening the circuit the anode was removed, the solution poured back into its bottle and the bowls carefully washed twice with distilled water and left to soak for a day, during which time the water was renewed once. The bowls were emptied, dried in an air bath at about 130° and left to cool in desiccators. They were then weighed as before.

THE ELECTRODYNAMOMETER.¹

Our electrodynometer consisted of a fixed coil of 576 turns in a single layer of 41.633 cm. mean length and 48.118 cm. mean diameter and a movable coil of 45 turns of 8.805 cm. mean length and 10.0187 cm. mean diameter suspended at the center of the fixed coil by a single phosphor-bronze wire 0.0355 cm. in diameter and 100.5 cm. long. The current was led into the movable coil through two mercury cups below and in line with the suspension. The torque due to the current in the fixed coil and the conductors between the movable coil and the mercury cups was avoided by using a symmetrically divided circuit leading around the upper mercury cup to the mercury in the lower cup. There was, however, a slight torque due to the action of the current in the conductor leading from the upper cup to the point beyond which the lead wires were twisted together. The lead wires from the terminals of the fixed coil were carried along the surface, parallel to the axis, to binding posts at diagonally opposite corners of a square and the lead wires from the suspended coil were brought out to the other corners of

¹The instrument was constructed and many of the minor details suggested by Mr. R. H. Miller, the instrument maker to the university.

this square. The action of these lead wires is shown in the difference between the values of the current needed to balance a right-handed or left-handed twist of the suspension. The error due to this asymmetry was eliminated by reversing the current in the fixed coil.

In order to insure greatest accuracy in determining the angle of torsion we used one complete turn of the torsion head, which was determined by means of a mirror on the torsion head and a telescope and scale at a distance of about 150 cm. The torsion head could be read by means of a vernier to one ten-thousandth of a circumference, but we did not in general make readings on it directly, as the telescope, mirror and scale made a much more accurate determination of a complete turn possible. In our preliminary experiments we made use of half and quarter turns also and obtained concordant results.

The cylinder holding the fixed coil was built up of dry, clear pine wood about 2.5 cm. thick. Each layer consisted of five pieces, and successive layers broke joints. The grain of the wood ran around the cylinder. By this arrangement we succeeded in keeping the cylinder of uniform diameter, although the wood shrunk a little (one in five thousand) after it was put together. The layers were fastened together by both glue and brass screws. After the cylinder was built up, it was turned in a large lathe to the required diameter. It was then given many coats of shellac, outside and in, to keep it as nearly as possible moisture proof. It was then wound with 576 turns of number 23 (B. & S. gauge) single cotton covered wire, which afterwards was given eight coats of shellac to ensure good insulation. The insulation was tested and found perfect. The winding was helical except near the small opening through which the suspension passed, where short portions of six turns were displaced. To make the effect of this displacement as small as possible, three wires on each side of the hole were half sunk into the wood of the cylinder and three others were wound on top of them. By this means the mean radius of the coil was unchanged and the effect on the mean field within the suspended coil was not changed materially. The suspended coil was wound on a hollow vulcanite cylinder. The conductor was a copper ribbon made by rolling a

number 25 (B. & S. gauge) wire down to a thickness of .024 cm. The cylinder was connected to the suspension by means of a small brass rod about 0.2 cm. in diameter which was soldered above into a hollow brass cylinder, and below into a brass plate which extended the length of the cylinder and was fastened by screws to its ends. Where the brass rod passed from above into the vulcanite it was cut away on two sides so as to allow the coil to keep in a nearly helical form. The suspending wire was soldered into a brass cylinder which was fitted and pinned into the hollow brass cylinder mentioned above. The terminals of the suspended coil were at points along the bottom element of the vulcanite cylinder and were connected along the inner surface, one to the upper mercury cup by a straight wire soldered to a small brass pin with a platinum wire tip in line with the suspension, the other by a Y-shaped connection to two symmetrical rods which passed out on opposite sides of the upper mercury cup and were soldered into a cross bar which held a brass rod in line with the suspension. This rod supported a mirror and an adjusting weight, and held at its end a platinum wire which projected into the lower mercury cup. The adjusting weight was designed to make the mass of the system exactly equal to the mass whose moment of inertia and period of torsional vibration determined the torsional constant of the suspending wire. (See Fig. 3.)

The dimensions of both the suspended and fixed coils were intended to fulfill the requirement laid down by Gray¹ that the length and radius should be in the proportion of $\sqrt{3} : 1$. When both coils fulfill this requirement and when their centers coincide, all the terms of the series expressing the torque between the coils disappear except the first, seventh and following odd terms. If the dimensions of the fixed coil are large in comparison with those of the movable coil, all terms after the first may be neglected. Owing to shrinkage of the wood of the fixed cylinder, the fixed coil became somewhat too short to fulfill Gray's requirements; the suspended coil was much closer. Nevertheless, the correction necessary does not amount to even one in one hundred thousand.

We carefully leveled the fixed coil by means of a long level.

¹ Absolute Measurements in Electricity and Magnetism, Vol. II., p. 277, or Phil. Mag., 33, p. 62.

Then we adjusted the zero position of the movable coil by means of a set of concentric squares and circles on a circular board which was fitted into one end of the cylinder of the fixed coil. The suspended coil was turned parallel to the fixed coil and the height of the torsion head was adjusted until the center of the movable coil was opposite the center of the squares and circles. The torsion head was then given a half turn to test the level of the movable coil. This was found perfect. Next a scale was placed across the other end of the fixed coil and the leveling screws under one side of the instrument were adjusted to bring the axis of the fixed coil and the suspension into the same plane. The adjusting screws at the torsion head were then used to bring the line of the suspension into the middle circle of the large cylinder which corresponded very closely with the middle of the fixed coil. The positions of the mercury cups were then adjusted to bring the platinum tips to their centers. All the tests were then repeated and the position of the movable coil appeared exactly central and horizontal. We then turned the torsion head one-quarter revolution and verified the position by means of the concentric squares and the flat ends of the movable cylinder. Any error in the level of either coil would introduce an error proportional to the difference between unity and the square root of the cosine of the angle. No error of the magnitude of one part in ten thousand could have been present.

The electro-dynamometer was set up with the axis of the fixed coil approximately in the magnetic meridian and the axis of the movable coil exactly at right angles to that of the fixed coil. We chose this position to avoid having the movable coil act like a dip needle when the current was on. The effect of the earth's field was considerable, but was eliminated by reversing the current in both coils and adjusting its value until the same torque was produced. Let the current through the coils be represented by i_1 and $-i_2$ in the two cases and let a and b be coefficients to take account of the dimensions of the instrument and the value of the earth's field, then the torque f required to hold the movable coil in its zero position may be represented in the two cases as follows:

$$f = ai_1^2 + bi_1, \quad (6)$$

and $f = ai_2^2 - bi_2;$ (7)

eliminate b and we find $f = ai_1i_2,$ (8)

which shows that excluding the earth's field a current whose value was a mean proportional between the numerical values of the two actual currents, would had produced the same torque as each did with the earth's field acting.

To eliminate the action of the lead wires we must consider that a is replaced in one case by $c + d$ and with the connections of the coils changed by $c - d$, which gives two equations for the same torque f . i_3 and $-i_4$ are the new currents corresponding to i_1 and i_2 .

$$f = (c + d)i_1i_2. \quad (9)$$

$$f = (c - d)i_3i_4. \quad (10)$$

$$f = 2c \left(\frac{i_1i_2i_3i_4}{i_1i_2 + i_3i_4} \right) = c \sqrt{i_1i_2i_3i_4} \text{ nearly.} \quad (11)$$

This approximation, which is more convenient than the exact expression, introduces no error larger than one part in a million in any of our computations.

THE SUSPENDING WIRE.

The suspension of the movable coil was a phosphor-bronze wire soldered into brass cylinders at both ends. The larger cylinder served to hold the upper end of the wire in the torsion head; the smaller could be coupled to the movable coil in the manner described above. These brass cylinders with the position of the wire reversed served, one to support a hollow brass cylinder of known moment of inertia used in determining the torsional coefficient of the wire, the other to support the wire itself.

The wire obeyed Hook's law almost exactly, as will appear from observations made while the wire was undergoing torsional vibrations. The period of vibration in vacuo was affected by a change in amplitude from a small arc to a complete rotation by about one part in twelve thousand, and the logarithmic decrement was extremely small and practically the same at all amplitudes. A rise of temperature increased the period by about one part in five thousand per degree centigrade.

Elastic fatigue produced a small effect on the wire. If the wire, when supporting the movable coil, was given one complete twist and held in this position for several minutes and then allowed to untwist, it was noticed that the position of equilibrium was displaced in the direction of the twist by about one one-thousandth of a complete turn. Nearly the full effect was reached after ten minutes' twisting. On untwisting, it took a much longer time for the residual twist to disappear. In the use of the electrodymanometer we eliminated the effect of the elastic fatigue by twisting the wire once round and leaving it twisted for several minutes before beginning our observations. The current was adjusted until the movable coil hung in its zero position at right angles to the fixed coil. The circuit was then opened and the torsion head turned back to its zero position. The position of equilibrium of the movable coil was then quickly determined by using an auxiliary battery, and the torsion head was again given a full turn and enough more to allow for the deviation of the position of equilibrium from the zero position. The circuit was then closed and the current adjusted until the movable coil was in its zero position again. The circuit was then broken and the torsion head turned back one complete revolution and the position of equilibrium redetermined. This was repeated until the position of equilibrium was the zero position, or until successive positions lay on both sides of zero. The strength of current was indicated by the number of ohms in the box *P* of Fig 1.

The question naturally arises: Did our method of allowing for the slight elastic fatigue introduce any error? We think not. We made a number of observations to test this. We allowed the suspension of the electrodymanometer to rest over night. We then completed the circuit but did not twist the suspension. We adjusted the current to the right value to correspond to a complete turn and allowed the current to become quite steady without twisting the wire. After about twenty minutes we opened the circuit, noted the position of equilibrium which in general changed slightly owing to a change in temperature and closed the circuit again. After adjusting the zero for the change of temperature we then turned the torsion head a complete revolution and determined the number of ohms in *P* (Fig. 1) required to balance the current and noted the temperatures. We

kept adjusting the current so as to keep the movable coil in its zero position and noted the corresponding number of ohms in P . We continued this over a period of half an hour, or until conditions had become constant. From these observations we estimated by extrapolation what number of ohms in P would have corresponded to a balance at the instant of twisting the suspension. We then opened the circuit, adjusted the zero and determined the ohms corresponding to one complete turn of the suspension from this last zero. This value remained constant except for change of temperature, showing that the change due to elastic fatigue had ceased. Making allowance for slight changes in temperature we found that, *as nearly as we could determine, the current required to balance corresponded exactly to the current which we estimated would have produced a balance at the instant of turning the torsion head.* The difference was certainly not as great as one part in ten thousand. After several tests of this kind we got rid of the elastic fatigue before beginning observations. If we had neglected the effect of elastic fatigue, we would have got a value for the square of the current too large by one part in one thousand. This corresponds to an error of one part in two thousand for the current itself.

The temperature of the suspending wire was estimated at the time of each balance by means of two thermometers, one inside the case and one against the brass tube surrounding the wire. (The second thermometer was that used when the torsional constant of the wire was determined.) To facilitate rapidity of work the motion of the movable coil was limited to a small arc by the prongs of a wooden fork (see Fig. 3). Before the fork was used, we found that the suspended coil would, on occasion, swing through the position of stable equilibrium, on through a position of unstable equilibrium and finally come to rest in another position of stable equilibrium. The torque in the various positions may be represented by the combination of a simple cosine curve with an inclined straight line. The former represents the torque of the electric forces, the latter that of the suspending wire. In combining the two torques, account must be taken of the angle through which the torsion head has been turned. For equilibrium positions must be found in which the two ordinates are numerically equal but opposite in sign. The com-

bined curve has positions of equilibrium wherever the ordinate becomes zero. The positive values of this curve tend to increase the angle, the negative to decrease it. The odd positions correspond to stable and the even to unstable equilibrium. We used the second

Fig. 4.

position of stable equilibrium, as shown at 3, and adjusted the current until it corresponded to one complete turn of the torsion head with the movable coil in its zero position. With this arrangement we found that a position of unstable equilibrium was quite near by, and until we had used the wooden fork to stop the coil, it was quite difficult to avoid having the coil turn around while adjusting the current to its right value. The wooden fork completely eliminated this trouble.

TORSIONAL COEFFICIENT OF THE SUSPENDING WIRE.

The torsional coefficient of the phosphor-bronze suspension was investigated very carefully. We avoided changes in the length of the wire used by soldering its ends into the cylinders mentioned before. This was done at as low a temperature as possible. The larger cylinder fitted as exactly as possible into a hollow cylinder.

Two of these hollow cylinders were used by us and were made from rolled brass bars which we thought more uniform than cast brass. The moment of inertia of the combination was determined very carefully. We weighed them with brass weights which we compared with a set of standard weights, tested by the United States Bureau of Weights and Measures and we measured their dimensions by means of a Brown and Sharpe vernier caliper. We tested the graduation of the vernier caliper by means of a dividing engine and found it accurate. As the dimensions of the movable coil were measured by the same instrument any error due to a faulty unit would disappear. The length and outer radius of the hollow cylinders were in the ratio of $\sqrt{3} : 1$ ¹ and consequently any slight error in the axis of rotation would produce a minimum disturbing effect on the moment of inertia. To the bottom of the central cylinder a small mirror was fastened with glue. The moment of inertia of both mirror and glue was computed and added to that of the brass. The moment of inertia of the wire was negligibly small. The second hollow brass cylinder—as nearly as convenient the duplicate of the first—was provided as a check to the first. It was thought that if air holes were present in either cylinder or in both, it would be hardly probable that the same results would be obtained from both. Identical values from the torsional constant of the wire were obtained from both, and it is probable therefore that the real and calculated moments of inertia were the same. Cylinder *I* was taken as our standard and cylinder *II* was used as a check only.

The inner smaller cylinder had at its one end a short projection, on which the larger hollow cylinders rested. Its moment of inertia is, therefore, considering it as two cylinders of diameters *d* and *D*, and length *L* and *l*, respectively,

$$I = \frac{M}{8} \left(\frac{La^4 + lD^4}{La^2 + lD^2} \right). \quad (12)$$

¹ Limb, Compt. rend., 114, 1057, 1892.

DATA FOR THE BRASS CYLINDERS.

<i>A.</i> Inner Cylinder.	<i>B.</i> Hollow Cylinder <i>I</i> .
$M = 47.547$ grms.	$M = 675.950$ grms.
$d = 1.268$ cms.	$D = 4.9915$ cms.
$D = 1.378$ cms.	$d = 1.272$ cms.
$L = 4.331$ cms.	$L = 4.3345$ cms.
$l = 0.085$ cms.	$I = 2241.87$ cm. ² gm.
$I = 9.5599$ cm. ² gm.	

D. Moment of Inertia of Mirror. *C.* Hollow Cylinder *II*.

$I = 0.465$	$M = 674.3474$ grms.
	$D = 4.9915$ cms.
	$d = 1.272$ cms.
	$L = 4.324$ cms.
	$I = 2236.56$ cm. ² gm.

Total Moment of Inertia for Cylinder *I* = 2251.89 cm.² gm.
 for Cylinder *II* = 2246.58 cm.² gm.

We made a long series of observations on the periods of torsional vibration of the system. To avoid the disturbing influence of the air, we enclosed the system in a long glass vacuum cylinder set in bearings at both ends. The system was set in torsional vibrations by turning the glass cylinder. Within the cylinder was a good thermometer reading directly to 0°.2 C. and a small barometer. During tests the pressure of the air was kept down to about 2.5 cm. of mercury, although a pressure of several times that amount did not affect the period of vibration by more than a negligible amount (for our purposes). We noticed that when the tension of the wire was relieved for some time, a considerable time was necessary before renewed tension brought the wire to the same condition as before. This effect was very slight and produced a variation in the period of vibration of the order of less than one part in ten thousand.

We carefully investigated the temperature coefficient of the wire, and found in general that the period increased with the temperature at the rate of one part in five thousand per degree centigrade. From observations with rapidly falling and rising temperatures near zero, we obtained some evidence of a hysteresis effect in the period

of vibration. Cold weather did not continue long enough for us to settle the matter definitely. With slowly rising or falling temperatures no such effect was detected.

We also carefully investigated the effect of amplitude of vibration on the period. We here noticed a small effect. The variation of the period between very small amplitudes of vibration and one whole turn from the position of equilibrium was of the order of one part in twelve thousand. We decided that this was due to friction with the small amount of air in the glass cylinder and molecular friction in the wire itself, and that, as these elements would be lacking when in use in the electro-dynamometer, the right period for our purposes was the period for small amplitudes. The logarithmic decrement was very small and produced no appreciable effect on the period for small amplitudes.

From these investigations we concluded that the phosphor-bronze wire was well suited to use as a suspension in an absolute electro-dynamometer. We were well satisfied with its action when in the instrument.

DETERMINATION OF THE PERIOD.

Our method was a slight modification of Kohlrausch's method. On the bottom of the rotating cylinder was a mirror. Around the glass cylinder containing the rotating system was a circular scale subdivided into centimeters and millimeters at a distance of 15 cm. from the mirror.

The scale was observed through a telescope at a distance of about 150 cm. The instrument was set up in a room in which there was a Standard Riefler clock, the ticks of which could be heard distinctly. We determined the exact time, when a tick coincided with the passage of the mirror through the middle point of the swing and repeated these observations. The number of vibrations made during the interval between the first and the following coincidence was found by dividing the interval by an approximate period (obtained by inspection) and taking the whole number nearest the quotient. Dividing the interval by this whole number we obtain a more nearly accurate value for the period. Repeating this we can easily obtain an accuracy of 0.001 second within 200

swings. The method of procedure will become clear from the examples given in the following tables.

The absolute rate of the clock will not come into account in the final determination of the electrochemical equivalent, if the time during which the silver is deposited is also measured with the same clock. We did not, therefore, determine the absolute rate, but referred all measurements of time made during the investigation to this Riefler clock as a standard.

Our first object was to determine in how far the elastic fatigue came into account in our measurements. Tables I. to III. give three series undertaken at different temperatures. In every case the logarithmic decrement is very small and nearly constant, from which we can conclude, that if there is any elastic fatigue, it is very slight. The correction for damping was too small to have any influence on our result. The amplitude of the vibrations varied considerably in the different tests and decreased to about one-half of its initial value during each series.

TABLE I.

Time of Transit.	No. of Swings.	Interval.	Period.	Right.	Left.	Amplit.	Log. dec. ¹	Temp.
37' 39"	0			70.9	29.1	41.8		22°.6
47 01	47	562	11.957	70.2	29.7	40.5	.000292	22 .4
56 59	97	1160	11.958	69.5	30.3	39.2	.000288	22 .2
81 18	219	2619	11.9589	68.0	31.8	36.2	.000285	21 .9
130 20	465	5561	11.95912	65.25	34.44	30.81	.000285	22 .0
203 17	831	9938	11.95909	61.9	37.65	24.25	.000283	22 .0
232 59	980	11720	11.95918	60.94	39.0	21.94	.000286	22 .1

TABLE II.

Time of Transit.	No. of Swings.	Interval.	Period.	Right.	Left.	Amplit.	Log. dec. ¹	Temp.
38' 15"	0			62.9	37.4	25.5		16°.0
61 10	115	1375	11.9570					15 .8
76 31	192	2296	11.9580	61.3	38.7	22.6	.000273	16 .0
94 51	284	3396	11.9570	60.75	39.3	21.45	.000264	16 .0
107 48	349	4173	11.9570	60.3	39.7	20.6	.000266	15 .5
202 48	825	9864	11.9564	57.8	42.2	15.6	.000259	15 .5
211 37	870	10402	11.8563	57.5	42.5	15.0	.000265	15 .7
229 21	959	11466	11.9561	57.12	42.88	14.24	.000264	15 .7
247 41	1051	12566	11.9562	56.75	43.22	13.53	.000262	15 .4

¹ In common logarithms per swing.

TABLE III.

Time of Transit.	No. of Swings.	Interval.	Period.	Right.	Left.	Amplit.	Log. dec. ¹	Temp.
42' 07"	0	0		75.7	24.3	51.4		
47 41	28			75.35	24.55	50.8		7°.00
55 26	67			74.9	25.0	49.9	.000291	6 .65
58 01	80	954	11.925	74.8	25.15	49.65	.000188	6 .65
60 24	92	1097	11.9239	74.52	25.38	49.14	.000212	6 .70
62 59	105	1252	11.9238					6 .70
65 34	118	1407	11.9237	74.2	25.8	48.4	.000221	6 .70
70 32	143	1705	11.9237	73.9	26.0	47.9	.000214	6 .65

The second set was taken with the brass cylinder *I*, the first and third with the brass cylinder *II*.

It has been mentioned above that the amplitude of the vibrations had a small influence upon the period. The following series of observations shows this very well.

TABLE IV.

Time of Transit.	No. of Swings.	Interval.	Period.	Temperature.
7'55"	0	0		18°.30
23 27	78	932	11.94872	18 .25
31 37	119	1422	11.94958	18 .25
37 11	157	1876	11.94905	18 .20
62 41	275	3282	11.94907	18 .10
70 27	314	3752	11.94905	18 .12

The amplitude varied from 55 to 46.5 scale parts.

TABLE V.

Time of Transit.	No. of Swings.	Interval.	Period.	Temperature.
20'00"	0	0		18°.40
35 20	77	920	11.9480	18 .42
43 18	117	1398	11.9487	18 .20
50 52	155	1852	11.9484	18 .20
58 50	195	2330	11.9487	18 .15
66 36	234	2796	11.9487	18 .05
73 58	271	3238	11.9483	18 .05
81 56	311	3716	11.9485	18 .05

¹ In common logarithms per swing.

Amplitude varied from 9.5 to 8.8 scale divisions.

The difference between the period for the two amplitudes is even a little smaller than appears from this on account of the lower average temperature in the second case, which tends to decrease the period.

INFLUENCE OF TEMPERATURE UPON THE PERIOD.

While in the preceding experiments we had simply decided that the phosphor-bronze wire was well fitted for use in the electro-dynamometer and no account had been taken of the thermometer correction, the following experiments were undertaken to determine the temperature coefficient of the wire and a new thermometer, subdivided into $.2^{\circ}$ C. was put into the vacuum cylinder.

The following table shows the effect of a change of temperature on the time of vibration of the system. The period was determined in the manner described above. We note here only the final period. These observations are selected out of a large number made with the same wire. The values in the second column denote the average temperature.

TABLE VI.

Date.	Temperature.	Period.
April 4th	14°.84	11.94083
5th	5 .91	11.92275
5th	9 .15	11.9283
9th	18 .20	11.94905
13th	19 .32	11.9527

We cannot be perfectly sure about the low temperatures, because it was rather difficult to keep the room at a constant temperature, while we were working in it. Nevertheless it seems apparent that the temperature-coefficient of the wire increases with rising temperature.

The observations in Table VI. were taken with the big hollow cylinder *II*, and before the wire was fixed for the final determinations. That the temperature coefficient was not changed when the wire was soldered into the brass cylinder, which was to hold the movable coil of the electro-dynamometer, is apparent from the fol-

lowing table. These observations were taken with the wire, when ready for use in the electrodymanometer and with hollow cylinder *I*.

TABLE VII.

Date.	Temperature.	Period.
April 20th	20°.19	11.96791
June 30th	23 .06	11.97492
June 30th	24 .72	11.9798
June 31st	26 .89	11.9851

The first observation was taken before, the last three after, the determinations with the electrodymanometer.

The temperature coefficient between 15° and 30° is .00022.

The results are plotted in Fig. 5, *I* being the curve for Table VI., and *II* the curve for Table VII.

Fig. 5.

EXPERIMENTS WITH THE ELECTRODYNAMOMETER.

In our final experiments we balanced the moment of torsion due to a complete twist of the wire, against the electrodynamic action between the two coils of the electrodymanometer. The moment of torsion of the wire for a twist of unit angle is

$$w = \frac{4\pi^2 K}{T^2}, \quad (13)$$

where K denotes the moment of inertia of the rotating system and T the period of vibration corrected for damping.

The strength of the field at the center of the stationary coil is

$$H = \frac{4\pi N}{\sqrt{D^2 + L^2}} I = hI, \quad (14)$$

where N is the number of turns in the stationary coil,
 D and L its mean diameter and mean length,
 I the current expressed in C. G. S. units.

The area of movable coil, multiplied by the number of turns of

the same is
$$A = \frac{\pi d^2 n}{4}; \quad (15)$$

so that the moment of torsion due to the action of the two coils upon each other is, if they are at right angles to each other,

$$w' = hAI^2 = \frac{\pi^2 Nnd^2}{\sqrt{D^2 + L^2}} I^2. \quad (16)$$

The equation of equilibrium is then, the twist being 2π

$$\frac{\pi^2 Nnd^2}{\sqrt{D^2 + L^2}} I^2 = 2\pi w = \frac{8\pi^3 K}{T^2}, \quad (17)$$

or
$$I = \frac{1}{Tr} \sqrt{\frac{2\pi K \sqrt{D^2 + L^2}}{Nn}}, \quad (18)$$

where r is the radius of the movable coil.

Substituting the numerical values given on pages 261 and 270, and taking for the time of vibration of our system 11.9853 at 27° , we obtain as the theoretical value of the *current necessary to balance the torsional moment due to a twist of 2π , of the wire at the temperature 27° ,*

$$I = 0.98158 \text{ AMPÈRE.}$$

To compare this value with the silver depositing current, we made use of Poggendorff's method in the manner described above. (See Fig. 1.)

1. *Balance between the E. M. F. of the Standard cells and the difference of potential over the manganin resistance, due to the current necessary to counteract the twisting moment of the wire.*

As the source of the current through the instrument we used a storage battery with a voltage of about 72 volts. In the following tables we have given the experiments in the order in which they were taken. In the first column is given the arrangement of the coils. In arrangement 2 the current was flowing through the movable coil in the direction opposite to that which it had in the arrangement 1, while the direction of the current through the stationary coil remained the same in both arrangements. This was done to eliminate the error due to the lead wires between the two coils. The difference in our results for the balancing current in the two cases is small, but quite apparent. In the second column the number of ohms necessary for a balance with the current through the whole instrument in one direction is given, in the third the same with the current reversed; these two currents correspond to i_1 , and $-i_2$ or i_3 and $-i_4$ of equation (11).

The fourth column shows the number of ohms necessary to balance the E. M. F. of the two Carhart-Clark cells, the following, the E. M. F. of the cells, supposing the value at 24° to be 1.435 volts. The following two columns contain the temperatures of the electro-dynamometer (t_d) and the cells (t_c) respectively. The value

TABLE VIII.

Arrangement.	R_a	R_b	R_1	E. M. F.	t_d	t_c	I''
1	7901.5	7773	4944.1	2.86878	26°.35	24°.95	.98284
2	7897	7765.7	4944.1	2.86878	27 .8	24 .95	.98246
2	7896	7764.6	4942.9	2.86795	28 .09	25 .6	.98236
1	7902	7773	4942.8	2.86744	26 .68	26 .0	.98274
2	7898.6	7770.7	4943	2.86744	26 .95	26 .0	.98242
2	7902.6	7773.4	4944.9	2.86808	26 .03	25 .5	.98242
1	7904	7774.1	4944.85	2.86795	27 .39	25 .6	.98284

of the manganin resistance was taken as 4.626 ohms. The current I'' corresponding to zero earth's field and reduced to 27° of the electro-dynamometer is given in the last column and shows, for the same arrangement, no larger discrepancy than one in ten thousand.

The average value 0.98261 amp. for the two arrangements is greater than the calculated value 0.98158 in the ratio 1.00105. This ratio can be used later to correct the value found for the electrochemical equivalent.

Since we were not sure of the temperature coefficient of the Carhart-Clark cells at the high temperatures at which they were used, a separate experiment was made to find the variation of their E. M. F. with temperature. A Clark cell (United States Standard) was always kept at a constant temperature and the temperature of the experimental cells changed. No observations were taken immediately after a change, in fact in general, the temperature had been practically constant for several hours. Supposing the E. M. F. of a Carhart-Clark cell to be 1.435 V. at 24° C. we found the following values.

TABLE IX.

Temp.	E. M. F.
22°	1.43628 volts.
23	1.43564
24	1.43500
25	1.43436
26	1.43372

These values have been used in Table VIII.

Instead of calculating I'' we may correct the resistances R_a and R_b to the values they would have had, if the electrodymanometer had been at 27°, using the temperature coefficient, found for the wire, and correct R_1 to 24° of the cells.

TABLE X.

Arrangement.	R_a	R_b	R_1
1	7900.4	7771.9	4946.3
2	7898.4	7767.1	4946.3
2	7897.8	7766.4	4946.4
1	7901.5	7772.5	4947.2
2	7898.5	7770.6	4947.4
2	7901.0	7771.8	4948.2
1	7904.5	7774.6	4948.3

Calling R_a' and R_b' the resistance found with the arrangement 1, R_a'' and R_b'' those with arrangement 2, we find as the resistance

necessary for a balance, if there were no influence of the earth's magnetism or asymmetry in the instrument,

$$R_2 = \sqrt{R_a' R_b' R_a'' R_b''}$$

The values of R_1 and R_2 calculated from the numerical results are

$$R_1 = 4947.2 \text{ and } R_2 = 7835.5$$

therefore
$$I = 1.58383 \frac{E}{R} \text{ amp.} \quad (1a)$$

2. *Balance between the E. M. F. of the Standard cells and the difference of potential due to the silver depositing current.*

The method of procedure during these experiments was the following: As in the preceding we used the storage battery, having about 70 ohms in series with the two voltmeters. Before sending the current through the voltmeters it was allowed to flow through the resistance, in order to heat it up, and a preliminary balance was taken. Then by means of a switch the silver voltmeters were thrown in series with the rest of the circuit. By means of this precaution we obtained a very constant current and the small changes taking place were so regular that there was no difficulty in taking an average of the resistances necessary for a balance during the hour the current was running. In taking the average we were careful to allow for the time-interval between consecutive balances. Out of a number of observations we have selected four in which the changes in the resistances were small, on the average about 20 ohms in 7500 ohms during the hour, and in which the temperature of the Standard cells was nearly 24° . The change of the E. M. F. of the Standard cells never exceeded 2 in 50000 during the whole hour.

The rate of the clock was repeatedly compared with the rate of the Riefler clock and it was found that one hour of the Riefler clock was equal to 3601.3 seconds of the other.

In the first two of these determinations two Standard Carhart-Clark cells were used, whose E. M. F. was a little smaller than that of the cells used in the rest of the experiments. The ratio was found to be 1.00243. In the following table R_2' is the average resistance necessary to balance the current and R_1' the resistance to balance the E. M. F. of the cells. In the fourth column are given the cor-

rected values of R_1' , *i. e.*, the resistances that would balance the cells if they were at 24° C.; in the following the temperature of the cells and in the last the electro-chemical equivalent worked out under the supposition that the values of E (2.870 volts) and R (4.626 ohms) are correct.

In the first case the duration of the experiment was only 40 minutes, in the rest, 60 minutes.

TABLE XI.

Date.	R_2'	R_1'	R_1' corr.	t	Silver deposit.	z
June 4th.	7622.15	4830.71	4842.6	24°.14	2.6211 grms.	1.11795 10^{-3}
" 19th.	7529.25	4911.05	4919.2	22 .3	3.82301	1.11789
" 27th.	7530.69	4938.79	4938.4	23 .82	3.8094	1.11807
" 30th.	7664.86	4943.75	4944.9	24 .5	3.8718	1.11796
					Mean value =	1.11797 $\times 10^{-3}$

Multiplying the mean value for z , 0.00111797 grm., by 1.00105 (the ratio found above) we obtain $z = 0.0011192$ grm. per ampère per second.

Taking the mean of R_1' , R_2' and q , the silver deposited in one hour, we obtain

$$R_1' = 4911.3 \text{ ohms.}$$

$$R_2' = 7586.7 \text{ ohms.}$$

$$q = 3.8589 \text{ grms.}$$

Substituting these values and those obtained above for I_1 , R_1 and R_2 in our formula (5)

$$z = \frac{q R_1' R_2}{It R_1 R_2'}$$

we find as the electrochemical equivalent of silver

$$z = \frac{3.8589 \times 4911.3 \times 7835.5}{.98158 \times 3601.3 \times 4947.2 \times 7586.7} \text{ grms.}$$

$$z = 0.0011192 + \text{grm. per ampère per second.}$$

This is about 1/9% larger than the accepted value. It agrees with the average value of Pellat and Potier and with the value Kahle found when using an old solution of silver nitrate. Kahle gives for

this, in his preliminary report (*Zeitschr. f. Instr.*, XVII., 144, 1897), a value almost identical with ours, 1.1193 mgrm. Our experiments with the silver voltameters were taken with a solution that had been used three or four times before. Moreover it is of interest to note that the discrepancy between Rowland's and Griffith's value of the mechanical equivalent of heat disappears, when we use as the unit of current one about .11% larger than the ampère.

Glazebrook found as the E. M. F. of the Clark cell 1.4342 volts at 15°, using as the electrochemical equivalent of silver the accepted value 0.001118 gm. A recalculation of the E. M. F. on the basis of the value found by us gives

$$E = 1.4327 \text{ volts at } 15^{\circ}\text{C.}$$

Kahle's value is 1.4328 volts.

Kahle has found that the E. M. F. of a Standard cell is more constant and gives better results than a silver voltometer, though the latter will always be the ultimate standard.

With our apparatus we can easily determine the E. M. F. of a Standard cell by direct comparison, knowing accurately the resistance of the manganin coil. It is intended to continue the experiments with special reference to the E. M. F. of the Clark cell.

In conclusion we wish to express our sincere appreciation for the substantial recognition accorded to our work by the American Association for the Advancement of Science and to thank Professor Carhart for the cells he allowed us to use and the great interest he has shown in the progress of our investigation at all stages.

Since the above was printed Kahle has published his investigations on the use of the silver-voltmeter,¹ and we are now able to compare more accurately his results with ours. There are three important points to be considered.

1. The solution used. What Kahle terms an "old" solution is one originally neutral, which became more and more acid, as it was employed in the voltameters. Larger deposits were obtained with this than with the "fresh" solution, the difference often exceeding one part in one thousand. On addition of Ag₂O this discrepancy

¹ *Zeitschr. f. Instrum.-Kunde*, Aug. and Sept., 1898.

diminished considerably. Since we used from the beginning the silver-oxide to insure neutrality, we did not observe the irregularities in crystallization and color of the deposited silver, that are so characteristic in his experiments. Nevertheless the addition of the oxide seems to produce a deposit about five parts in ten thousand larger than what Kahle found with his standard solution.

2. Method of washing the solution. Kahle observes in general that with warm water and correcting for the solution of silver in the warm water the deposit is about one to two parts in ten thousand smaller than what he obtained by a treatment with cold water. Our method of letting the crystals soak in cold water for a whole day seems to be more thorough than Kahle's, who rinsed the deposit three or four times until he was unable to show the presence of silver in the water by means of HCl.

3. Platinum or silver cathode. Kahle found that the silver deposit was larger, if previously some silver had been deposited on the cathode. It stands to reason that this difference is relatively the more apparent the shorter the time of electrolytic action and the smaller the mass of silver deposited during the experiment, and we can not expect as large a relative discrepancy, since we deposited about four times as much silver as Kahle. In fact, in this particular point we cannot corroborate Kahle's results. In the first two observations of Table XI. the silver was deposited on silver, in the last two on the clear platinum cathodes. We believe that the influence of moisture during the weighing may be sufficient to explain the discrepancies in our results, though we were careful to weigh in closed balance cases, the air of which was dried by calcium-chloride.

For a final comparison, taking into account the first two points mentioned, we have therefore to add to Kahle's value for the electrochemical equivalent of silver (0.0011183 grm.), about six or seven parts in ten thousand. This would make Kahle's value 0.001119 grm. as compared with our 0.0011192 grm.

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FIG. 3.
General View.

FIG. 4.
Suspended Coil.

Patterson and Guthe: Electrochemical Equivalent of Silver.
[Views of the Electrodynamometer.]

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General View.

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