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THE VARIOUS DETERMINATIONS OF THE E.M.F. OF THE CLARK CELL.

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LATIMER CLARK in a communication to the Royal Society, May 30, 1872, made some general statements that are now known to be eminently true. He concludes the abstract of his paper as follows:[1] "The standard of electric potential is second only in importance to that of the standard of electric resistance; and the use of such a standard * * * admits of a variety of applications which it is believed will be found of great value in electrical research." It was many years before these statements were generally believed by electricians, but it has now come to be recognized that a good standard cell is of greater importance than a silver voltameter. The electromotive force of the Clark cell is now known with greater precision than the electrochemical equivalent of silver. The recent literature bearing on this constant, and its relation to the value of the mechanical equivalent of heat, render a recapitulation and reduction of its various determinations of considerable interest.

The earliest determination is that of Latimer Clark himself. It has the merit of being an absolute potentiometer method. The two elements of the determination were the measurement of a current and a resistance. The former was made by means of the electrodynamometer constructed for the British Association, or by the use of a sine galvanometer. The potential difference between

[1] Proc. Royal Soc., Vol. 20, p. 444, 1872.

the terminals of his current-measuring instrument was balanced against the E.M.F. of his standard cell. The resistance entering into the result was that of the electrodynamometer or the sine galvanometer. No current was taken from the standard, and its E.M.F. was equal to the product of the current and the resistance of the instrument.

The mean of eighteen trials with the electrodynamometer was 1.45735 at 15.5° C. The mean of thirteen with the sine galvanometer was 1.45621 at the same temperature. The final mean value was then 1.45678 at 15.5° C., or as given by Clark, 1.457 British Association units. But one B. A. unit equals 0.9866 international ohm. Therefore Clark's value reduced to present units at 15° is 1.4378.

So far as ascertained the next determination of the E.M.F. of the Clark cell was made by the writer in January, 1882, in Berlin.[1] The measurement was incidental to another investigation and was confined to a single cell belonging to the Physical Laboratory of the university. The method was the now well-known one of the silver voltameter. It is substantially the same as that employed by Clark, with the silver voltameter substituted for the electrodynamometer. The fall of potential over a known resistance was balanced against the E.M.F. of the standard cell. The results were not published till after Lord Rayleigh had made his determination of the electrochemical equivalent of silver in 1884. The published value was 1.434, but no corrections were made to reduce the E.M.F. to 15°, and the ratio of the Siemens unit of resistance to the ohm was taken to be $\frac{100}{106}$. It is perhaps worth while to make these corrections now when the requisite coefficients are well known. The following are the data:

Trial.	Temp. of Cell.	Res. in S. U.	Temp. of Res.	Silver Dep. per min.
1	18°	20	19°	0.0051 gm.
2	17	20	19	0.0051 "

$$\text{The current } I = \frac{0.0051}{0.001118 \times 60} = 0.07603 \text{ ampère.}$$

[1] Amer. Jour. Sci., Vol. XXXVIII., Nov., 1884.

The resistance box was correct at 20°. With a temperature coefficient of 0.0004 for German silver, 20 Siemens units equal 19.992 at 19°, and $19.992 \times 100/106.3 = 18.807$ ohms. Then

$$E = IR = 0.07603 \times 18.807 = 1.4299 \text{ volts.}$$

But the cell was at a temperature of 18° in the first trial and 17° in the second. The formula now used for temperature corrections of the Clark cell at the Reichsanstalt is

$$E_t = E_{15} - 119 \times 10^{-5}(t - 15) - 7 \times 10^{-6}(t - 15)^2.$$

This formula gives for the correction in the first case 0.0036, and in the second case, 0.0024. We have therefore

Trial 1	1.4299 + 0.0036 = 1.4335
Trial 2	1.4299 + 0.0024 = 1.4323
Mean at 15°	1.4329

No great weight is to be attached to this determination because the resistance used was not standardized, nor is it certain that its temperature was exactly indicated by the thermometer. The Clark cell was a large one containing a thermometer with its bulb within the contents of the cell. The balance with the silver voltameter was carefully maintained, the weighings were made after careful drying, and the deposit was washed in such a way as to avoid loss.

The next determination is that of Lord Rayleigh in 1884.[1] The method employed was a modified potentiometer method, the current being measured by the current balance which Lord Rayleigh used in his research on the electrochemical equivalent of silver. The value which Lord Rayleigh derived from all his determinations was 1.454 B. A. units at 15°. To reduce to volts the correction factor expressing the B. A. unit in terms of the ohm was introduced. The factor used by Lord Rayleigh was one B.A. unit equals 0.9867 ohm, giving the E.M.F. of the Clark cell 1.435 volts at 15°. If we employ the factor 0.9866 adopted by the British Board of Trade to convert B. A. units into ohms or volts, then Lord Rayleigh's value for the Clark cell is 1.4345 volts at 15°.

[1] Phil. Trans. Royal Soc., Part II., 1884.

Another determination with the silver voltameter is that of A. v. Ettinghausen.[1] He assumed Kohlrausch's second value for the silver equivalent, 0.0011183, and found for the E.M.F. of the Clark cell at 15.5°, 1.433 volts. If we correct for the electrochemical equivalent, 0.001118 instead of 0.0011183, and reduce to 15°, we have 1.434 volts.

A very elaborate investigation of the Clark cell was made by Glazebrook and Skinner in 1891–92.[2] The current was measured by the silver voltameter. Great precautions were taken to keep the standard resistance at a constant temperature. The mean of nine determinations was 1.4342 volts at 15°. To reduce to 15° the authors of the paper used the coefficient—0.00077. This gives a slightly smaller correction than the Reichsanstalt formula. Since the cell was always above 15°, the corrections are positive; the mean difference is two units in the fourth decimal place. Reduced to a common temperature coefficient, the final result of Glazebrook and Skinner's investigation is 1.4344 volts.

This is almost identical with the value derived from Lord Rayleigh's paper. He used for temperature corrections the coefficient —0.00082, which is equivalent to that of the Reichsanstalt formula for small ranges of temperature.

A good deal of interest attaches to the work done at the Reichsanstalt on Clark and Cadmium cells, and great confidence is felt everywhere in the results attained. In 1896 Kahle made an absolute measurement of the E.M.F. of the H-form of Clark cell by means of the Helmholtz absolute electrodynamometer.[3] This very elaborate instrument is fully described in Kahle's paper which is published as a contribution from the Reichsanstalt. For the E.M.F. at 0° C. he found 1.4488 volts. A direct comparison for the Clark at 0° minus the Clark at 15° gave $E_0 - E_{15} = 0.0166$. Hence at 15° the E.M.F. of the Clark cell found by Kahle is 1.4322 volts. The volt here corresponds to the international ohm, but not to the volt a sdefined in the legal definition of the Clark cell. The above value for the Clark cell has not been used by the Reichsanstalt.

[1] Zeitschrift für Elektrotechnik, 1884, XVI. Heft.
[2] Phil. Trans. Royal Soc., Vol. 183 A, 1892.
[3] Wied. Annal., Vol. 59, 1896, p. 573.

For about four years the Reichsanstalt has employed the following values:

Clark cell: 1.4328 int. volts at 15° C.
Cadmium cell: 1.0186 int. volts at 20° C.

The cadmium cell is the same as the Weston except that the $CdSO_4$ solution contains an excess of crystals, while the Weston is made with a solution saturated at 4° C. The manner in which the value 1.4328 for the Clark cell was obtained may be gathered from a paper by Jaeger and Kahle on "Mercury-Zinc and Mercury-Cadmium Elements as Standards of Electromotive Force." [1]

Three series of measurements were made with a large number of cells to determine the two ratios,

$$\frac{\text{Clark } 15°}{\text{Cadmium } 20°} \text{ and } \frac{\text{Clark } 0°}{\text{Cadmium } 20°}.$$

The results for the three series are shown in the table:

Date.	$\frac{\text{Clark } 0°}{\text{Cadm. } 20°}$	$\frac{\text{Clark } 15°}{\text{Cadm. } 20°}$	Clark 0° — Clark 15°
March, 1896	1.4227	1.4066	0.0164
Jan., 1897	1.42277	1.40676	0.01631
Nov., 1897	1.42280	1.40660	0.01650
Means	1.42277	1.40663	0.01642

The last column is easily obtained from the preceding two. The next step in fixing the E.M.F. of the Clark cell is Kahle's long series of determinations with the silver voltameter.[2] Assuming 0.001118 as the silver equivalent, he obtained for the Clark at 0° 1.44945, and for the cadmium at 20°, 1.01849. The ratio of these two numbers is 1.42313, or 0.00036 greater than the result of the direct comparison. Since the ratio of the silver voltameter measurements is affected by a greater uncertainty than the one directly observed, the difference is divided between the two electromotive forces obtained by the silver voltameter in proportion to their mag-

[1] Wied. Annal., Vol. 65, 1898, p. 926.
[2] Wied. Annal., Vol. 67, 1898, p. 1.

nitudes. The value for the Clark at 0° is thus reduced to 1.44923. Subtracting the fall of E.M.F. between 0° and 15°, and we have Clark at 15° equals 1.4328 volts.

Similarly the Cadmium cell becomes 1.0186 at 20°. While this method is something of an improvement on the old one with the silver voltameter, it is yet fundamentally the same and leaves much to be desired.

A year ago Professor Lindeck and myself made several series of observations at the Reichsanstalt to redetermine the ratios between the Clark at 0° and at 15° and the cadmium at 20°. A large number of cells, new and old, were used. The precautions taken to maintain a constant temperature during a series of observations proved highly satisfactory. The comparisons were made rapidly by means of the well-known compensating apparatus devised at the Reichsanstalt and made by Wolff in Berlin. Three series of comparisons gave as a mean for the ratio Clark 15°/Cadmium 20°, 1.40679.[1]

Nine Clark cells were then placed in a petroleum bath and completely surrounded by pounded ice for five days. Eight series of comparisons gave, Clark 0°/Cadmium 20° = 1.42283.

These new ratios of the Clark at 0° and at 15° compared with the Cadmium at 20° give, Clark 0° — Clark 15° = 0.01634. Then by the method of reduction used by Dr. Kahle, 1.44929 — 0.01634 = 1.43295 at 15°.

The above new ratios are published in the last "Thätigkeitsbericht" of the Reichsanstalt, but the recommendation is made that the old value for the E.M.F. of the Clark cell at 15°, viz., 1.4328 should be retained. This recommendation does not appear to be quite reasonable, since the new ratios are derived from more concordant series of observations than the old ones, and their application to Kahle's results from the silver voltameter deposits gives a value very near 1.433 volts at 15°.

During the summer of 1899 an absolute determination of the E.M.F. of the Clark cell at 15° was made by myself and Dr. Guthe. The fall of potential over a known resistance was compared by a potentiometer method with the E.M.F. of two Clark

[1] Zeitschrift für Instrumentenkunde, June, 1900, p. 176.

cells of the modified H-form joined in series.[1] The current was measured by our absolute electrodynamometer of simple construction.[2] The resistance was determined in terms of two one-ohm coils with Richsanstalt certificates. The result of three determinations was E.M.F. of Clark at 15° is 1.4333 volts.

This value we do not consider final. The measurement may be made under improved conditions, and the suspended coil wound on a hard rubber cylinder was probably not exactly circular in section. A new porcelain cylinder with a guaranteed external diameter has been obtained from the Royal Porcelain Works in Berlin through the courtesy of Mr. Louis J. Magee, of that city. It has not yet been mounted in the electrodynamometer. A large porcelain cylinder will also be tried for the fixed coil.

Finally an interesting side light has been thrown on the value of the E.M.F. of the Clark cell by the fact that Griffiths' determination of the mechanical equivalent of heat by an electrical method gave a result larger than Rowland's by a constant small amount of one part in 400 or 500. Since the E.M.F. enters the result as the square, an error in the E.M.F. of the Clark cell of about one part in 1,000 would explain the discrepancy. This would mean a value of a little less than 1.433 instead of 1.434.

In a recent communication to the Royal Society on a new determination of the mechanical equivalent of heat by an electrical method differing from that of Griffiths, Barnes, of McGill University,[3] points out that his result is higher than those obtained by direct mechanical methods. He attributes the discrepancy to an incorrectness in the assumed value of the E.M.F. of the Clark cell. A value of 1.43325 instead of 1.4342 volts causes the discrepancy to disappear.

In the light of such facts it is interesting to place before us a tabular view of the several determinations which I have briefly described, and which I have reduced to common terms:

[1] PHYS. REV., Vol. IX., No. 5, 1899, p. 288.
[2] PHYS. REV., Vol. VII., No. 39, 1898.
[3] London Electrician, Oct. 19, 1900.

Observer.	Date.	Method.	Result.
Clark.	1872	Absolute.	1.4378
Carhart.	1882	Silver Voltam.	1.4329
Rayleigh.	1884	Absolute.	1.4345
Ettinghausen.	1884	Silver Voltam.	1.434
Glazebrook & Skinner.	1892	" "	1.4344
Kahle.	1896	Absolute.	1.4322
Jaeger & Kahle.	1898	Silver Voltam.	1.4328
	1899	" "	1.4329
Carhart & Guthe.	1899	Absolute.	1.4333

If we omit Clark's determination, because his cells set up with boiled zinc and mercurous sulphates are not comparable with the others, only three absolute determinations have been made. The mean of these is 1.4333 volts at 15°.

A study of the above table can hardly fail to produce the conviction that the E.M.F. of the Clark cell at 15° C. is nearer 1.433 than 1.434 volts.

UNIVERSITY OF MICHIGAN, Dec. 1, 1900.