ART. IX. — *A One-Volt Standard Cell;* by HENRY S. CARHART.

[Read before the National Academy of Sciences, Washington, April 21, 1893.]

THE calomel cell, consisting of mercury in contact with mercurous chloride and zinc in a solution of zinc chloride, was first described by von Helmholtz in 1882.* Without any knowledge of its previous invention I made the same cell six years ago and have still the first sample made at that time. Ostwald† refers to a calomel cell giving one volt E. M. F. at 15° C., the density of the zinc chloride being 1·409 at 15°, and the temperature coefficient +·00007 volt per degree.

Within the last few months I have taken up the calomel cell again with a view of adjusting it to precisely one volt, making a careful determination of its temperature coefficient, and investigating its reliability.

* Sitzber. der Akad. der Wiss., p. 26, Berlin, 1882.
† Zeitschrift für Physikalische Chemie, vol. i, p. 403.

It is now well known that the E. M. F. of a voltaic cell with zinc immersed in a solution of one of its salts decreases with increase of density of the solution.* Within limits therefore the E. M. F. of a cell can be varied by changing the density of the solution of the zinc salt. Thus the E. M. F. of a Clark cell was found to vary from 1·434 volts with a solution saturated at 20° C. to 1·481 volts with a 5 per cent solution, a variation of nearly three and one-third per cent.

The variation of the E. M. F. with density is even greater in the case of zinc chloride. With zinc chloride 16 per cent increase of density produces 3 5 per cent decrease in E. M. F. An equal increase of density of zinc sulphate is accompanied by only half the percentage decrease of E. M. F. Hence greater care is necessary in standardizing a solution of zinc chloride than of zinc sulphate.

Taking the Clark cell with excess of crystals of zinc sulphate as the standard, having an E. M. F. of 1·434 volts,† at 15° C., I have found that the density of the zinc chloride solution required to give one volt is 1·391 at 15° C. Ostwald's density gives too low a value. It was probably adjusted to correspond with the legal ohm.

The cell is made in the same form as my Clark standard. In the bottom of the tube is pure mercury in contact with a platinum wire; on this a paste of mercurous chloride and the zinc chloride solution; a cork diaphragm follows, holding the mercury and paste firmly in position, especially with some asbestos packing under the cork; zinc chloride is then added to the proper depth, and an amalgamated zinc rod, supported by a cork, completes the electrical combination of parts. The cell must be hermetically sealed as usual. Such a cell is perfectly portable and gives promise of long life. Its internal resistance is about 1500 ohms, and it does not appear to suffer permanent change by heating to 50° C. or even to 60°. The cell six years old already mentioned is still in good condition and has apparently maintained its E. M. F.

An interesting feature of this cell is its small positive temperature coefficient. It is well known that the coefficient of the Clark and the Daniell standard is negative. The calomel cell has a coefficient of about +·00009 within working limits of temperature. In the following table will be found the data of one series of observations on the temperature coefficient:

* Carhart, this Journal, Nov. 1884, p. 374.

† Report of the B. A. Committee, Edinburgh Meeting, 1892.

TABLE I.

No. 30. Clark. Resistance to balance.	Temp. C.	Resistance to balance.	No. 8. $ZnCl_2$ Temp. C.	Electromotive force in volts.
9401	18°·25	6572	13°·7	1·0000
		6608	48·9	1·0055
		6604	48·0	1·0049
		6598	45·4	1·0040
		6592	40·7	1·0031
		6589	36·4	1·0025
9402+	18°·25	6586	30·2	1·0020
		6583	26·7	1·0016
		6581	23·7	1·0013
		6579	20·4	1·0010
		6577	17·2	1·0007
		6576	15·0	1·0005
9403	18°·1	6573·5	10·0	1·0001

The E. M. F. of the Clark is taken as 1·434 at 15°; temperature coefficient −·00077. It will be observed that the cell does not recover its normal E. M. F. immediately on descending temperatures. This hysteresis phenomenon however is small, amounting only to an error equivalent to about three degrees of temperature. The entire change of temperature of about 40° took place within three hours. The observations of the table are plotted in the curve of fig. 1. The curve is approximately a straight line between ten and forty degrees. Beyond

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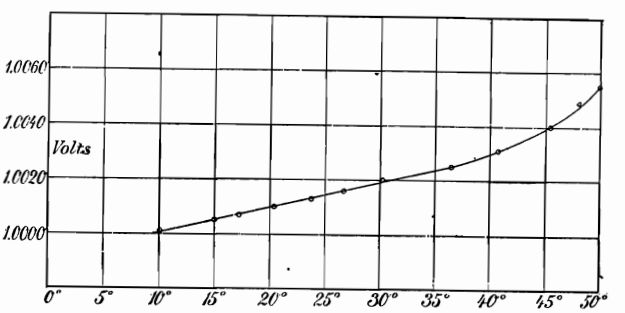

this point the coefficient increases rapidly. The equation of the curve contains not only a quadratic term but one which is a function of a still higher power of the temperature. The following equation fits the observations fairly well:

$$E_t = 1 + \cdot 000085(t-15) + \cdot 0000006(t-15)^2 + \cdot 00000001(t-15)^3.$$

Between ten and thirty degrees the relation between E. M. F. and temperature may be expressed as follows:

$$E_t = 1 + \cdot 000094(t-15).$$

The coefficient is therefore a little less than $\frac{1}{1000}$ per cent per degree. A neglected variation of temperature of 10° C. can cause an error of only $\frac{1}{100}$ per cent.

In another paper* I have given an analysis of the temperature coefficient of both the Clark and the Daniell cell when the former contains no excess of zinc sulphate crystals, and have shown that this coefficient is a purely thermo-electric phenomenon at the contact of a metal and a liquid. Further investigations confirm this conclusion that the temperature coefficient of a voltaic cell is the result of the superposition of the two thermo-electromotive forces of the metal and the salt in contact with it on the two sides of the cell, whenever this coefficient is not complicated with oxidation effects and the solution and recrystallization of salts. In the old Clark cell almost exactly half the temperature coefficient is due to changes in density of the solution by reason of the presence of an excess of zinc sulphate crystals.

These dissolve when the temperature rises and again slowly crystallize out on a falling temperature. Time is required for diffusion, and the cell is therefore slow in reaching its electrical equilibrium after a temperature change. This time lag may extend over several days. It is very appreciable when the temperature change does not exceed one degree an hour.

Whether a resultant temperature coefficient shall be positive or negative depends upon the relative values and the signs of the two thermo-electromotive forces at the two sides of the couple. To measure these electromotive forces of thermal origin I have made use of an experimental cell consisting of two glass tubes 12^{cm} long and 1^{cm} to 2^{cm} in diameter, joined near the top by a small tube 17^{cm} long, having near the middle a narrow bore made by thickening the walls of the tube. When it is desirable to use two liquids a plug of asbestos is placed at the narrow part of the connecting tube to aid in filling without admixture of the liquids and to diminish diffusion. When the thermo-E. M. F. between a metal and a liquid is to be determined the experimental cell is filled with the liquid and wires of the same metal, cut from one piece, are inserted in the two limbs. One limb is then kept in melting ice and the other is raised to different temperatures, and the resulting E. M. F. measured. For this latter purpose the most exact method, giving practically an electrostatic measurement, is to balance the E. M. F. of a standard cell against the fall of potential over the requisite resistance in a circuit of constant high resistance (10,000 ohms), as in the Rayleigh or compensation method of comparing electromotive forces.† The experimental cell is then

* London Electrician, June 12, 1891; Carhart's Primary Batteries, pp. 136–150.
† Phil. Trans., Part II, 1884, p. 441.

put in series with the standard cell, and the resistance in the shunt of the main circuit required to maintain a balance shows both the value and the direction of the E. M. F. of the experimental cell as compared with the standard.*

By this method the mean thermo-E. M. F. of $Cu-CuSO_4-Cu$ per degree between 0° C. and 50° C. I have found to be +·00073 volt. The positive sign indicates that the metal in the warm solution is positive externally to the one in the cold, or the metal in the cold plays the part of the zinc of a voltaic couple. Bouty† gives the E. M. F. of $Fe-FeSO_4-Fe$ as zero. It follows that a couple consisting of $Fe-FeSO_4-CuSO_4-Cu$ should have a positive temperature coefficient, and this coefficient should be the same whether the whole cell is heated or only the copper—copper sulphate side. Experiment confirms the first conclusion at least. The E. M. F. of the cell at 15° C. was found to be 0·625 volt, and at 29°·4 C., 0·637 volt. The change is therefore +0·000833 volt per degree and the coefficient is $0{\cdot}000833 \div 0{\cdot}625 = 0{\cdot}0013$, or over $\frac{1}{10}$ per cent.

Theoretically it should be

$$0{\cdot}00073 \div 0{\cdot}625 = 0{\cdot}0012.$$

The above combination is now used as an iron gravity battery, and the change in its E. M. F. with a sudden change of the temperature of the room had attracted my attention before I had investigated the temperature coefficient. After the above iron-copper cell had been left standing for twenty-four hours, with a piece of iron wire in the connecting tube of the experimental cell to intercept the $CuSO_4$ which might diffuse over, the E. M. F. was found to be 0·651 volt at 14°·4 C.; and for a range of 7·7 degrees the temperature coefficient was 0·0012. This is exactly the value obtained from theoretical considerations.

Another case in point is that of the voltaic series

$$Ni-NiSO_4-CuSO_4-Cu.$$

The E. M. F. was quite variable and only an approximate measurement could be made. The temperature coefficient was positive and equal to 0·0084, or over $\frac{8}{10}$ per cent per degree C. The actual change in E. M. F. was greater than this, for the E. M. F. continued to fall on standing and the change by heating was thus in part masked.

The thermal-E. M. F. of copper—copper sulphate is positive, while that of nickel—nickel sulphate is negative. Hence the temperature coefficient of the above series should be positive and equal to the sum of the two thermal E. M. F.'s. The result is positive but not equal to the sum of the two thermal

* Carhart's Primary Batteries, p. 137. † Journal de Physique, vol. ix, p. 229.

E. M. F. values. Perhaps no closer numerical agreement could be expected in the case of a variable E. M. F.

In the light of the above conclusions and with thermo-electric data furnished by Bouty and by Chroustchoff and Sitnikoff* it is easy to draw the conclusion that the temperature coefficient of the calomel cell should be negative and of small value. The thermo–E. M. F. or value of $\frac{dE}{dT}$ for $Zn - ZnCl_2 - Zn$ is given by Bouty as 0·000696; Chroustchoff and Sitnikoff found that of $Hg - Hg_2Cl_2 - ZnCl_2 - Hg_2Cl_2 - Hg$ to be 0·00066 between 0° and 50° C.

Hence the coefficient should be,

$$0{\cdot}00066 - 0{\cdot}000696 = -0{\cdot}000036.$$

The value of $\frac{dE}{dT}$ for zinc in zinc salts given by Chroustchoff and Sitnikoff would give a larger negative coefficient than the above.

I have therefore investigated this subject to ascertain if this case furnishes an exception to the law of temperature coeffi-

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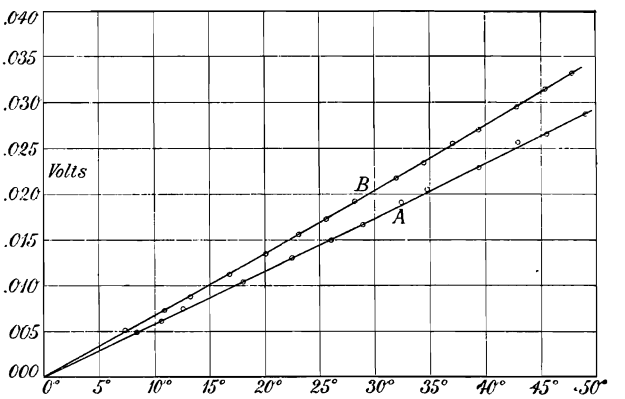

cients already announced. The result confirms the law and shows Bouty's result to be in error The determinations were made by means of the experimental cell in the manner already indicated. Tables II and III contain the observations which are expressed graphically in the two curves of fig. 2, in which

A. relates to $Zn - ZnCl_2 - Zn$, Table II, and
B. to $Hg - Hg_2Cl_2 - ZnCl_2 - Hg_2Cl_2 - Hg$, Table III.

* Comptes Rendus, vol. cviii, 1889, p. 937.

TABLE II.

Difference of Temperature.	Total E. M. F. in volts.	E. M. F. per degree C.
49°·0	·02876	·000587
45·5	·02662	·000585
42·9	·02570	·000579
39·4	·02295	·000582
34·8	·02050	·000589
32·4	·01913	·000590
28·9	·01668	·000577
26·1	·01499	·000574
22·5	·01301	·000578
18·0	·01040	·000580
12·6	·00750	·000595
10·6	·00612	·000577
8·4	·00490	·000583
	Mean,	+·000584

TABLE III.

Difference of Temperature.	Total E. M. F. in volts.	E. M. F. per degree C.
47°·8	·03314	·000693
45·4	·03146	·000693
42·8	·02949	·000689
39·4	·02706	·000686
37·1	·02554	·000688
34·4	·02340	·000680
32·1	·02174	·000677
28·2	·01928	·000687
25·6	·01729	·000675
23·1	·01561	·000675
20·1	·01353	·000673
16·8	·01125	·000669
13·2	·00882	·000668
10·9	·00730	·000669
7·4	·00517	·000698
	Mean,	+·000681

Both of these thermal E. M. F.'s are positive. The temperature coefficient should therefore be

$$0{\cdot}000681 - 0{\cdot}000584 = 0{\cdot}000097 \text{ as a mean.}$$

This corresponds very closely indeed with the value found by observation on a one-volt cell. It will be observed that it is only necessary to take the difference of the above electromotive forces to obtain the temperature coefficient, since the E. M. F. of the cell is one volt. The coefficient is positive because the value of $\frac{dE}{dT}$ for the positive side of the cell is in excess of that for the negative side.