ART. XLV.—*Relation between the Electromotive Force of a Daniell Cell and the Strength of the Zinc Sulphate Solution;*
by H. S. CARHART.

THE investigation here described was carried out in the physical laboratory of the University of Berlin in the spring of 1882, and was undertaken with a view to ascertain whether the variation in the strength of the zinc sulphate solution surrounding the zinc plate of a Daniell cell affected the electromotive force, and to what extent.

It is well known that different experimenters have found different values of the electromotive force of a Daniell element. Thus Sir William Thomson found a value of 1.122 volts; Latimer Clark, 1.11; Kohlrausch, 1.138.* These different results may be partly due to difference of method; but it is easy to ascertain that slight changes in the condition of the plates or in the concentration of the solutions modify the value of the electromotive force to an appreciable extent. The method employed in this investigation was essentially the compensation method of Poggendorff.† The two poles of the battery A, the electromotive force of which is required, are

connected with two points C E of a second circuit containing a battery B of higher electromotive force than A. The resistance between C and E is then varied by means of the rheostat R, till no current flows through the circuit of battery A. The difference of potential between the points C and E is then the electromotive force to be measured. By Ohm's law, the product

* Everett's Units and Physical Constants, p. 146.

† Wiedemann's Elektrizität, p. 633.

of the resistance inserted between C and E and the strength of the current in the main circuit equals the difference of potential between the two points, or the electromotive force of A.

The current was measured by a silver voltameter (S) with pure nitrate of silver. The resistance employed at R was in Siemens units. The deposition of silver was continued for ten minutes; the cup was then washed with great care, dried in a hot air chamber, and weighed after cooling, fractions of milligrams being obtained by observing the swing of the pointer.

The Daniell cell consisted of a U tube of the form employed by Kohlrausch in measuring the resistance of electrolytes,* the bend of the tube being much smaller than the two branches. The lower portion was first filled with a saturated solution of pure zinc sulphate; saturated copper sulphate was then added to one branch and a percentage solution of zinc sulphate to the other. The sulphates were so added that the surface of separation between two solutions in contact was quite clear and sharp. This was effected by first placing a small disc of cardboard on the surface of the liquid in the tube and then carefully pouring the other liquid on it from a pipette. No sensible diffusion took place during the time required to make the observations.

The galvanometer in the circuit of A was a sensitive one and was observed with a telescope and scale at a distance of about two meters. After a little experience a balance was readily obtained by the greater or less immersion of the silver plate in the nitrate of silver solution of the voltameter; and it was tested from time to time during the deposition of the silver and corrected if necessary. The galvanometer never showed a deflection of more than a few scale parts—perhaps five of the millimeter force divisions. The electromotive of A was thus measured with minimum liability to polarization and by a method entirely independent of the internal resistance of the cell. The only resistance required is that between C and E, and this can easily be measured by means of a rheostat.

The temperature of the rheostat and of the cell was observed at every trial. The extreme limits of variation in the temperature of the cell was $3^{\circ}2$ C.

The table exhibits the results; but the final reduction, as shown in the last column, was not made till after the recent report of the Paris commission on the legal ohm, and the publication of the results of Lord Rayleigh's experiments with the silver voltameter.† The values of the electromotive force, given in the column next to the last in arbitrary units, were reduced to volts as follows:—

* Wiedemann's *Elektricität*. p. 590.

† *Nature*, March 20, 1884, p. 495.

TABLE.

Per cent. of ZnSO ₄	Temp. of Rheostat	Resis. in Siemens Units.	Silver deposited in one minute.	Product of resistance and silver.	Corrected for temp. of rheostat.	Mean value of product.	E. M. F. in volts.
0	20°	11	6·727 mgs.	73·997	73·997	73·997	
1	18·8	11	7·277 "	80·037	80·000	80·000	1·125
3	18	11	7·339 "	80·729	80·664	80·584	1·133
	19·5	12	6·710 "	80·520	80·504		
5	17·8	11	7·423 "	81·653	81·581	81·216	1·142
	17·3	11	7·358 "	80·938	80·851		
7·5	17·3	11	7·239 "	79·632	79·546	79·620	1·120
	18·3	11	7·250 "	79·750	79·694		
10	17	11	7·224 "	79·464	79·369	79·490	1·118
	19·3	11	7·239 "	79·634	79·612		
15	20	11	7·219 "	79·409	79·409	79·305	1·115
	18·3	11	7·205 "	79·255	79·201		
20	17·3	11	7·170 "	78·870	78·785	79·008	1·111
	17·5	11	7·210 "	79·310	79·231		
25	16·3	11	7·199 "	79·189	79·072	78·997	1·111
	16·6	11	7·184 "	79·030	78·923		

Mean, 1·122

The ratio of the Siemens unit to the congress or legal ohm is 100 to 106, or, 50 to 53. According to Lord Rayleigh a current of one ampère deposits 4·025 gms. of silver in an hour, or 67·08 mgs. a minute. Therefore if C, R and E represent current strength, resistance, and electromotive force in ampères, ohms, and volts, and e the electromotive force in the arbitrary unit of the table, we have the following equation,

$$\left(R \cdot \frac{53}{50}\right) (C \times 67 \cdot 08) = e;$$

$$\text{whence } R C = \frac{e}{\frac{53}{50} \times 67 \cdot 08} = \frac{e}{71 \cdot 105} = E.$$

It is only necessary then to divide the quantities in column seven by 71·105 to reduce them to volts.

The method employed is amply sustained by the results obtained with a Latimer Clark standard cell. Two trials gave the same result. I give only one of them.

Time of deposition of silver,	10 min.
Resistance between C and D,	20 S. U.
Temperature of rheostat,	19°
“ Clark’s cell,	18°
Weight of silver cup after deposition,	26·1963 gms.
“ “ before “	26·1453 “
Silver deposited in 10 min.,	0·051 “
“ “ 1 min.,	5·1 mgs.
$5 \cdot 1 \times 20 = 102 = e.$	
$102 \div 71 \cdot 105 = 1 \cdot 434 = E.$	

The electromotive force of a Clark element is therefore 1.434 volts, the exact value given by Lord Rayleigh* instead of the formerly accepted value of 1.457 volts.

The mean of all the values of the electromotive force in the last column of the table is 1.122, which is the value obtained by Sir William Thomson by the electrostatic method, if the velocity expressing the ratio between the electrostatic and electromagnetic units be taken as 3×10^{10} .

In figure 2 the results of the investigation are set forth graphically; the ordinates represent the excess of the quantities in column seven of the table above 74, the value obtained with distilled water; while the corresponding abscissæ denote percentages of zinc sulphate. It will be observed that little variation in the value of the electromotive force occurs after reaching ten per cent. of zinc sulphate, and that the maximum value appears to be at about five per cent. I have some reasons for doubting the accuracy of the larger of the two values found with the five per cent. solution. If the smaller value alone is employed the points laid off may be connected by nearly a plane curve.

It thus appears that the variation in the concentration of the zinc sulphate solution is sufficient to account for the larger part of the discrepancy between the results obtained by different experimenters in measuring the electromotive force of a Daniell cell. It would therefore seem desirable that a

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standard Daniell element should be so constructed as to admit of employing a zinc sulphate solution of known concentration. The form proposed by Professor G. F. Barker,† in which the solutions are saturated appears to meet the requirements in this respect.

Northwestern University, Evanston, Ill., August, 1884.

* Nature, March 20, 1884, p. 495. In his Montreal Presidential address Lord Rayleigh gave the value 1.435 volts.

† Proc. Amer. Philos. Soc., Jan. 19, 1883, p. 654.