

Citation:

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The black substance was washed with carbon disulphide and alcohol and dried in a desiccator in vacuo. Apparently it has absorbed oxygen during this operation for the analysis showed a deficit of about 13 %. We found: 78.5 % P, 1.9 % H and 6.5 % N.

When treated with dilute acids a red substance was again formed which in appearance and properties corresponded exactly with the one already described and contained the same amount of phosphorus [found, average 92 %]. The hydrazine has passed into the acid.

3. From the foregoing it follows that substances quite analogous to those formed by SCHENCK's (impure) red phosphorus and ammonia are generated directly from hydrazine and yellow phosphorus. Evidently, the black compounds which are formed from aqueous and anhydrous hydrazine are of a different nature; their investigation remains however very unsatisfactory, owing to their amorphous conditions and want of tests for purity, in addition to their unstability towards washing-liquids. But it is pretty certain that the orange red product which both yield, when treated with acids, is a weak acid composed of phosphorus, hydrogen (and oxygen?)

Hydrazine is therefore capable of directly giving up hydrogen, not only to sulphur but also to phosphorus.

Organic chem. Lab. University. Amsterdam, April 1903.

Chemistry. — "*The electromotive force of the DANIELL-cells.*" By Mr. J. W. COMMELIN and Prof. ERNST COHEN. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of April 24, 1903).

1. In the present state of our electro-chemical knowledge an exhaustive study of the electromotive force of the DANIELL-cell would have but little importance if it related to the use of this cell as a standard-cell, as we are now in possession of standard-cells which, if properly constructed, satisfy all requirements.

We have, nevertheless undertaken an exhaustive investigation of such a cell because J. CHAUDIER has published in the "Comptes Rendus"¹⁾ certain views which are entirely opposed to our modern theories on the origin of the electromotive force in cells of this kind.

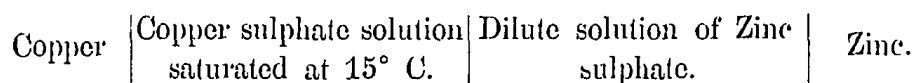
¹⁾ 134, 277 (1902).

2. CHAUDIER gives the following form to the well-known formula of NERNST for the electromotive force:

$$E = KT \left(\log \frac{P}{p} - \log \frac{P_1}{p_1} \right) + T \frac{dE}{dT}.$$

This is evidently a mistake as the second term after the sign of equality does not belong to this formula but forms part of the well-known equation of GIBBS and VON HELMHOLTZ¹⁾.

This mistake we may pass over. The following table contains CHAUDIER's results which have been obtained by means of BOUTY's method for the measurement of electromotive forces. His cells were constructed according to the scheme:



3. The paper contains but few details of the manner in which the experiments were conducted: "l'élément DANIELL est constitué par deux vases en verre, contenant l'un la solution de sulfate de zinc, l'autre la solution de sulfate de cuivre; ces deux vases sont réunis par un siphon formé d'un tube de verre rempli de coton imbibé de la solution de sulfate de zinc dans l'une des branches, de la solution

TABLE I.

ZnSO ₄ . 7H ₂ O in 100 parts of water	Elektromot. force (15° C.)	Coefficient of temperature.
0	1.0590 Volt	-0.0024
1/12	1.1138	-0.0015
1/6	1.1151	-0.0013
1/2	1.1368	+0.0005
1	1.1331	+0.0005
2	1.1263	+0.0003
4	1.1249	+0.0003
6	1.1208	+0.0016
10	1.1188	-0.0003
30	1.1054	-0.0002
60	1.1003	-0.0002
200 (saturated)	1.0902	-.00026

¹⁾ CHAUDIER wrongly calls this equation, the equation of Lord KELVIN.

de sulfate de cuivre dans l'autre. Ce dispositif m'a paru donner des resultats plus constants que les autres."

It seems to us strange that the E. M. F. should be given to $\frac{1}{10}$ millivolt. All authors who up to the present have made a study of the DANIELL-cell have pointed out how difficult it is to obtain constant values with such cells. For instance, the E. M. F. is in a high degree dependent on the nature of the copper or zinc electrode. For particulars in this direction we refer to the researches of ALDER WRIGHT¹⁾.

In connection with the measurements under consideration the following table of FLEMING's will be found interesting:

E. M. F. of a certain DANIELL-cell.

COPPER, perfectly pure, unoxidised	1.072 Volt
" slightly oxidised, brown spots	1.076 "
" more oxidised	1.082 "
" covered with dark brown oxide film	1.089 "
" cleaned, replated with fresh pinkish electro-surface	1.072 "

4. In repeating CHAUDIER's measurements it is of the greatest importance to have the determinations mutually comparable; errors caused by an unlike nature of the electrodes had to be carefully excluded.

As negative electrodes we used pure zinc amalgam (1 part of zinc to 9 parts of mercury) as used in the CLARK standard-cell. The zinc was a very pure specimen from MERCK of Darmstadt in which iron was not even detectable. The mercury was first shaken with nitric acid and then distilled twice in vacuum according to HULETT's²⁾ method. As we know, the potential difference between this amalgam and pure zinc is very small. Previous experiments by one of us³⁾ have shown that this difference is only 0.00048 volt. at 0° and 0.000570 volt. at 25°.

As positive electrode we used at first a thick wire of pure copper.

The copper sulphate solution in the different cells was prepared

¹⁾ Philosophical magazine (5), 13, 265 (1882); FLEMING, *ibid.* (5), 20, 126 (1885).
ST. LINDECK, *Zeitschr. für Instrumentenkunde* 12, 17 (1892). Comp. also CARHART, *Primary Batteries* (Boston 1899). Literature up to 1893 in: WIEDEMANN, *die Lehre von der Elektrizität.* (Braunschweig 1893). pag. 798.

²⁾ *Zeitschr. für phys. Chemie* 33, 611 (1900).

³⁾ COHEN, *Zeitschr. für phys. Chemie* 34, 619 (1900).

by first making a saturated solution at 15°. Pure, MERCK's copper sulphate (free from iron) was dissolved in water and boiled with copper hydroxide to remove traces of free acid. After filtration the liquid was cooled and after introducing a crystal of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ set aside to crystallise. The salt was then shaken for a long time (3 to 5 hours) with water at 15° in a thermostat, use being made of NOYES¹⁾ shaking apparatus. All the thermometers used in this investigation were tested by means of a standard thermometer from the "Physikalisch-technische Reichsanstalt" at Charlottenburg.

To make sure that complete saturation had indeed been attained we took after 3 and 5 hours small samples from the solution in the shaking bottles and analysed these liquid by means of NEUMANN's electrolytic process²⁾.

In this way we found:

(5 hours) 100 parts of water dissolve 19.22 parts of anhydrous CuSO_4 .

(3 hours) 100 parts of water dissolve 19.28 parts of anhydrous CuSO_4 .

The zinc sulphate solutions were prepared from a solution which was saturated at 15° in the same thermostat as the copper sulphate solutions. The different dilutions were done by weighing.

The zinc sulphate gave no reaction with congo-red; moreover the same preparation had served in the construction of CLARK-cells which appeared to be perfectly correct. By way of a check we also determined the quantity of ZnSO_4 which at 15° is present in the saturated solution. A weighed quantity of the solution was evaporated in a platinum dish and the residue ($\text{ZnSO}_4 \cdot 1 \text{H}_2\text{O}$) was weighed³⁾. In 100 grams of water we found 50.94 grams of ZnSO_4 (as anhydride) whereas previous determinations had given 50.88. If we accept the figure 50.94, the saturated solution then contains at 15°, 150.56 grams of $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ to 100 grams of water. We fail to see how CHAUDIER has arrived at the figure 200 (see table 1).

6. Measurements with DANIELL-cells are rather difficult, for if the smallest amount of copper sulphate solution comes in contact with

¹⁾ Zeitschr. für phys. Chemie 9, 603 (1892).

²⁾ NEUMANN, Analytische Elektrolyse der Metalle, (Halle 1897). Pag. 106.

We may casually remark that the figures given in the literature for the solubility of copper sulphate are incorrect. Compare: ERNST COHEN, Vorträge für Aerzte über physikalische Chemie (Leipzig 1901) pag. 70.

³⁾ See CALLENDAR en BARNES, Proc. Royal Society 62, 147 (1897); ERNST COHEN, Zeitschrift für phys. Chemie 34, 181 (1900).

the zinc electrode by diffusion, the E. M. F. of the system is diminished considerably.

FLEMING for instance states, "the smallest deposit of copper upon the zinc, due to diffusion of the coppersalt into the zinc is indicated by a marked depression amounting to 2 or 3 percent", whilst WRIGHT (after prolonged diffusion) noticed depressions up to 6 percent.

After a few preliminary experiments which convinced us of the accuracy of these remarks we constructed for the definitive measurements the little apparatus shown in fig. 1.

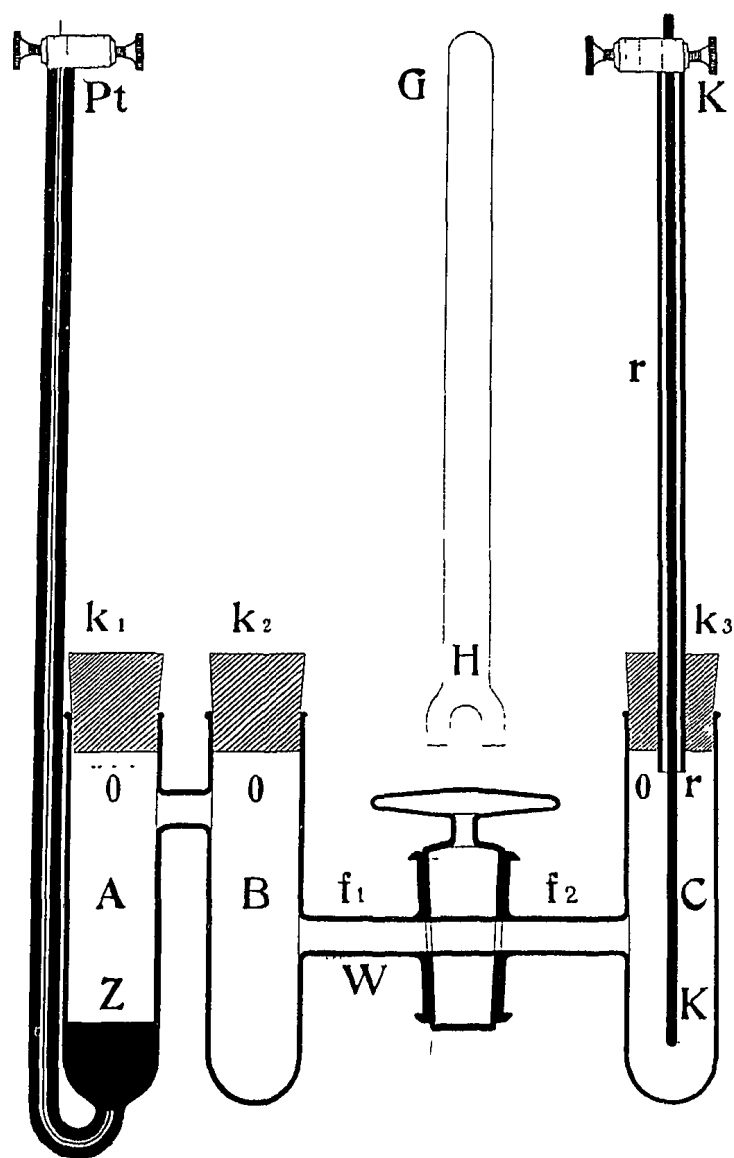


Fig. 1.

It consists of three tubes *A*, *B*, *C*, (8 cm. high, internal diameter 1.8 cm.) which communicate by means of connecting tubes. To the tube f_1, f_2 a glass tap with a very wide bore (5 or 6 m.m.) is attached. The zinc amalgam is introduced into *A* and the platinum wire *Pt* is then fused into it. *A* and *B* also f_1 are now filled with the zinc sulphate solution after the bore of the tap has been plugged with fat-free cottonwool previously sucked in the same zinc sulphate solution. While the tap is still closed, the saturated copper sulphate solution is poured into *C* and also into f_2 . The cell is now closed with the india-rubber corks K_1 , K_2 and K_3 . Through K_3 is introduced a thin glass tube reaching just below the cork. Through this tube the copper electrode *K* may be introduced into the solution when the measurements take place. The whole apparatus is now plunged as deep as possible in a thermostat (15°). If required the tap may be opened or closed by means of the wooden rod *GH*.

By the introduction of the tube *B* the possibility of contact of the zinc electrode with the copper sulphate solution is quite excluded. Even if a trace of copper sulphate has diffused into the lower part of *B* (if the copper solution is lighter than the zinc solution, the former will float in *B* on the latter) we never find a trace of copper in the tube *A*. In the final experiments, the measurements lasted so short a time that as a rule no copper diffused even into *B*.

7. After preliminary experiments had shown that the cells cannot be reproduced when we make use of copper electrodes which have been cleared with nitric acid, we afterwards followed the direction of *WRIGHT* and *FLEMING* who electrolytically cover the copper electrode with a layer of copper immediately before the measurement. For this purpose we used the bath described by *ORTTEL*,¹⁾ for the copper coulometer. After being copperplated the electrode was rinsed with distilled water and dried with cottonwool. It was then at once put through the tube into the cell. We always take care that only the electrolytically copper plated part of the electrode gets into contact with the liquid.

8. The E. M. F. of the cells was determined by the compensation method of *POGGENDORFF*. As working cell we used a storage

¹⁾ *Electrochemische Uebungsaufgaben* (Halle 1897) pag. 5. All copper electrodes were always copperplated during 10 minutes with the same current-strength (0.15 ampère) (or density) and at the same temperature. We have also tried, but unsuccessfully, to work with copper amalgam. As to copper amalgam, compare *PETTENKOFER*, *DINGLER Polytechnisches Journal* **109**, 444 (1848) and v. *GERSHEIM*, *Ibid.* **147**, 462 (1858).

cell (Deutsches Telegraphenelement), as normal cell a WESTON-cell which was always kept in a thermostat at 25°.

In this thermostat was also placed a CLARK normal cell to allow comparison between the normal elements.

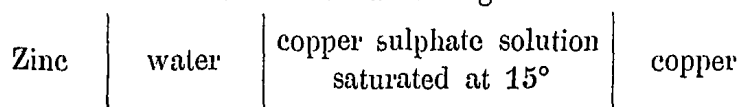
The rheostats used (2 rheostats of 11111.11 ohms each HARTMANN and BRAUN) were carefully compared with a third rheostat standardised by the "Physikalisch-Technische Reichsanstalt."

9. The measurements took place as follows: after a cell had been filled with the required solutions it was (without the copper electrode) placed in the thermostat at 15°. After having reached that temperature the copper electrode was taken from the copperplating bath and after having been treated as directed it was introduced through the tube into the solution. The tap was now opened and the measurement carried out; this lasted 1 or 2 minutes. When the tap had been closed, the cell was taken from the thermostat. The solution in A was then tested for copper, but as already stated not the slightest trace of copper was found in this part of the apparatus.

10. As the measurements of ALDER WRIGHT, FLEMING and LORD RAYLEIGH¹⁾, which were done with fairly concentrated solutions of zinc sulphate had proved that the reproduction of these cells to less than 1 millivolt is almost impossible and as our own experiences had shown us that with more dilute zinc sulphate solutions we get still greater deviations, we only give our measurements in millivolts although the method of measuring employed rendered the determination of tenths of millivolts (and less) quite possible.

As CHAUDIER only gives one series of measurements we can say nothing as to the reproduceableness of his cells. According to our experience no importance need be attached to statements of tenths of millivolts. Whether it would be possible to attain a greater accuracy when working with solutions quite free from air is a matter which we cannot go into any further as our results are quite accurate enough to completely answer the question in dispute²⁾.

11. Before proceeding to communicate our figures we would point out that a cell constructed according to the scheme:



cannot practically be classed among the reversible cells.

¹⁾ Transactions of the Royal Society of London. Vol. 76, 800 (1886).

²⁾ See EBELING, WIED. Annalen, 30, 530 (1887) and G. MEYER, *ibid*, 33, 265 (1888).

We have, therefore, not repeated CHAUDIER's experiment with this cell. When we consider that cells with very dilute solutions show deviations amounting to 6 millivolt, we cannot expect much from measurements with an element of the kind described

12. The subjoined table contains the results of our measurements. Below I and II are placed the values of the E. M. F. which we found for the same cell in independent experiments. From these figures it may at the same time be seen in how far the said cells may be reproduced.

TABLE II.

Grams of Zn SO ₄ . 7 H ₂ O to 100 gram water.	Electromotive force at 15° 0 C. in Volt. (COMMELIN and COHEN).			Electromotive force at 15° 0 in Volt. (CHAUDIER).
	I	II	average.	
1/12	1 143	1 149	1.146	1.1138
1/6	1.141	1 146	1.144	1 1151
1/2	1 135	1.134	1.135	1 1368
1	1 131	1.131	1.131	1 1331
2	1.125	1 124	1 125	1.1263
4	1.119	1.119	1 119	1 1249
6	1.116	1 116	1 116	1 1208
10	1.112	1 112	1 112	1 1188
30	1 104	1 104	1.104	1.1054
150.65 (saturated).	1 081	1 081	1 081	1 0902 (200 saturated?)

15. From this table it will be seen at once that a maximum value of the E. M. F. at about 1/2 gram of ZnSO₄ . 7 H₂O to 100 grams of water, as CHAUDIER claims to have found, does not exist. The progressive change of the values is on the contrary, quite in harmony with the equation given by NERNST, which shows a decrease of the E. M. F. for an increase of the concentration of the zinc sulphate. It would be superfluous to criticise the other conclusions of CHAUDIER as these are based on the figures discussed.

Utrecht, April 1903.