

Citation:

E. Cohen, Thermodynamics of standard-cells. (2nd part), in:
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in the "American Chemical Journal" April 1900 by H. N. Mc. Coy. The resemblance is striking, the only difference is that the tube *a* through which the vapour passes into the solution has been placed by Mc. Coy inside the vessel *A*, whilst in my apparatus it is situated outside it. Mc. Coy, has not however taken the precaution to prevent the vapour coming into contact with the thermometer and this, as we have seen, is very essential, if great accuracy is to be attained, as only then the boiling temperature is independent of the degree of heating of the flask *B*.

Amsterdam, University Chem. Lab. May 1900.

Chemistry. — "*Thermodynamics of Standard Cells*" (2nd part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read May 26, 1900).

1. In the first paper on this subject¹⁾ I have shown that the ideas prevailing on the reactions which take place in the standard cells are incorrect and ought to be replaced by others.

With the CLARK-normal cell, a very satisfactory agreement was found between the theory and the measurements.

Before subjecting the existing data of the WESTON-normal cell to calculation in an analogous way, a calculation which as will appear later on, is more complicated than for the CLARK-cell, I would like to further explain a few points about the latter.

2. In the theory and in the calculation in the previous paper it was assumed that the cell was built up as follows:

Hg—Hg₂SO₄ — saturated solution of zincsulphate — Zn

whilst for the calculation measurements made with cells of the following construction were used;

Hg — Hg₂ SO₄ — saturated solution of zinc sulphate — zinc amalgam,

about which it may be observed that the amalgam was composed of 1 part of zinc to 9 parts of mercury²⁾).

We may now inquire whether such cells may be theoretically treated as if the negative pole consisted of pure zinc. It has already

¹⁾ Proc. Roy. Acad. Amsterdam. 1900, pag. 719.

²⁾ Compare KAHL, WILDEMANN'S Annalen, 51 205 (1894).

been shown by LINDECK ³⁾ in 1888 that zinc and zinc amalgam show, towards solution of zinc sulphate, the same potential difference when a certain minimum of about 2 per cent of zinc in the amalgam is exceeded.

The zinc amalgam used in the CLARK-cells, therefore, behaves like pure zinc. That the presence of mercury exercises no influence is shown, moreover:

a. from the observations of KAHLE who showed that cells constructed with an amalgamated zinc rod instead of a 10 per cent amalgam showed an E.M.F. which differed by less than 0.2 millivolt from that of the amalgam cells; it may be observed that in these cases the amalgamation had taken place but very superficially.

b. From the communications of CALLENDAR and BARNES ¹⁾, who have always worked with an amalgamated zinc rod instead of the amalgam and have still obtained results perfectly identical with those of KAHLE.

3. In the amalgam-cells, a new link enters into the mechanism, because on the passing of 2×96540 coulombs, the zinc must be first abstracted from the amalgam before it can unite with SO_4 to ZnSO_4 which then undergoes the hydration which has been discussed in the previous paper.

That the evolution of heat involved in the abstraction of zinc from the amalgam is of no importance, is shown from the fact that the E.M.F. and the temperature coefficient are exactly the same for the amalgam cells and for those where a superficially amalgamated zinc rod is employed

4. It appeared to me of importance to lay stress on the foregoing, as in contrast to the zinc amalgams, the cadmium amalgams behave quite differently and this becomes important in the application of my theory on the WESTON-standard cells in which the negative electrode happens to be formed by cadmium amalgam.

I hope to make more extensive communications on the theory of these standards as soon as I have experimentally determined the required data.

Amsterdam, University Chem. Lab. May 1900.

³⁾ WIED. Ann. 35, 311 (1888).

¹⁾ About the diluted amalgams, compare LINDECK, l. c. 324. Also RICHARDS and LEWIS, Proc. American Acad. of Arts and Sciences. Vol. XXXIV 87 (Dec. 1898). Zeitschrift für phys. Chemie 28. 1 (1899).

¹⁾ Compare my first paper.

²⁾ Compare WIED. Annalen 65, (1898) 926. CROVA, Ann. de chim. et de physique (3) 69, 458 (1863) had already found that if in a DANIELL-cell the zinc is replaced by zinc amalgam, the properties of the cell thereby undergo no change.