

*Citation:*

E. Cohen, Thermodynamics of Standard-Cells(3rd Part), in:  
KNAW, Proceedings, 3, 1900-1901, Amsterdam, 1901, pp. 208-216

**Chemistry.** — “*Thermodynamics of Standard-Cells*” (3<sup>d</sup> Part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. It is my intention, in this communication, to apply the previously developed theory to the WESTON-cadmiumstandard-cell and to show that it is also here in perfect agreement with experiment. In the first place the mechanism of the reaction will be more closely considered.

The cell is constructed <sup>1)</sup> as follows:

Hg—Hg<sub>2</sub>SO<sub>4</sub>—saturated solution of cadmium sulphate—cadmium amalgam (14.3 pCt. of Cd.)

We must notice here, as I have already said in my second communication, that cadmium amalgam does not behave in the same way as pure cadmium. The measurements of HOCKIN and TAYLOR <sup>2)</sup> and those of JÄGER <sup>3)</sup> have plainly proved this. The following table taken from JÄGER's communication shows this:

T A B L E I.

Composition of the amalgam.		E.M.F. against the 14.3 percent Cd amalgam (Volt)
% Cd.	Cd: Hg.	
1	1 : 100	— 0.021
2	2 : 100	— 0.013
5	5.3 : 100	nearly 0
10	11.1 : 100	0
11.4	12.9 : 100	0
13.0	15.0 : 100	0
14.3	16.7 : 100	0
15.4	18.2 : 100	0 up to + 0.001
20.0	25.0 : 100	+ 0.001 up to + 0.011
Cd. amalga- mated.		0 to about + 0.044
Cd. pure.		+ 0.051

} up to 1/100 millivolt

} gradually rising.

<sup>1)</sup> JÄGER and WACHSMUTH, WIEDEMANN'S Annalen 59, 575 (1896).

<sup>2)</sup> Journal of the Society of Telegraph-Engineers, VIII p. 282 (1879).

<sup>3)</sup> WIEDEMANN'S Annalen, 65, 106 (1893).

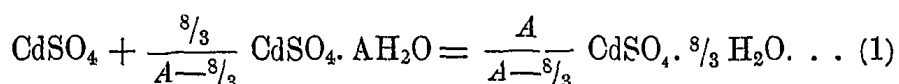
When  $2 \times 96540$  Coulombs pass through the cell, then

a. 1 gram atom of Cd will be withdrawn from the cadmium amalgam (Heat effect  $W_1$ )

b. the liberated Cd will combine with the  $\text{SO}_4$  of the  $\text{Hg}_2\text{SO}_4$  to  $\text{CdSO}_4$  (Heat effect  $W_2$ ),

c. which will then abstract water from the saturated solution of cadmium sulphate and form  $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$  (Heat effect  $W_3$ ). This salt will deposit in the saturated solution.

The said abstraction of water will take place according to the equation:



in which  $A$  represents the number of mols. of water associated with 1 mol. of  $\text{CdSO}_4$  in the saturated solution at the temperature of the cell.

2. The total heat effect in the cell on the passage of  $2 \times 96540$  Coulombs is now:

$$W_1 + W_2 + W_3 \text{ calories.}$$

The heat of formation of  $\text{CdSO}_4$  and  $\text{Hg}_2\text{SO}_4$  are known and amount to respectively 219900 and 175000 calories.

The heat evolved when 1 gram atom of Cd is withdrawn from the amalgam ( $W_1$ ) has been experimentally determined by me (see below) whilst the quantity of heat ( $W_3$ ) evolved by the process represented in equation (1) may be deduced from the thermochemical determinations of THOMSEN, taken together with those of Mr. H. B. HOLSBOER which he has kindly placed at my disposal.

a. *Experimental determination of the Heat evolution ( $W_1$ ) which takes place on the withdrawal of 1 gram atom of cadmium from the 14.3 pCt. Cd amalgam.*

3. I have not determined this heat effect by thermochemical, but by electrochemical means by a method which in a case like this deserves the preference on account of its very great accuracy<sup>1</sup>).

For this purpose I constructed a cell according to the following scheme:

Cd - dilute solution of cadmium sulphate of arbitrary concentration - 14.3pCt. Cd amalgam.

<sup>1</sup>) Compare RICHARDS and LEWIS, Proc. Americ. Acad. of Arts and Sciences. Vol. XXXVI, 87, Dec. 1898. Zeitschr. fur phys. Chemie 23.1 (1899).

When in such a cell the current is closed, Cd will pass from the cadmium electrode to the amalgam.

If we apply to this cell the well-known equation of GIBBS and VON HELMHOLTZ.

$$E = \frac{E_c}{n\varepsilon_0} + T \frac{dE}{dT} \dots \dots \dots (2)$$

we can find  $E_c$  by the determination of the E. M. F. of the cell and its temperature coefficient and this quantity is simply the amount of heat evolved when 1 gram atom of cadmium is added to the amalgam, in other words, the quantity of heat which we wish to determine but with the opposite sign.

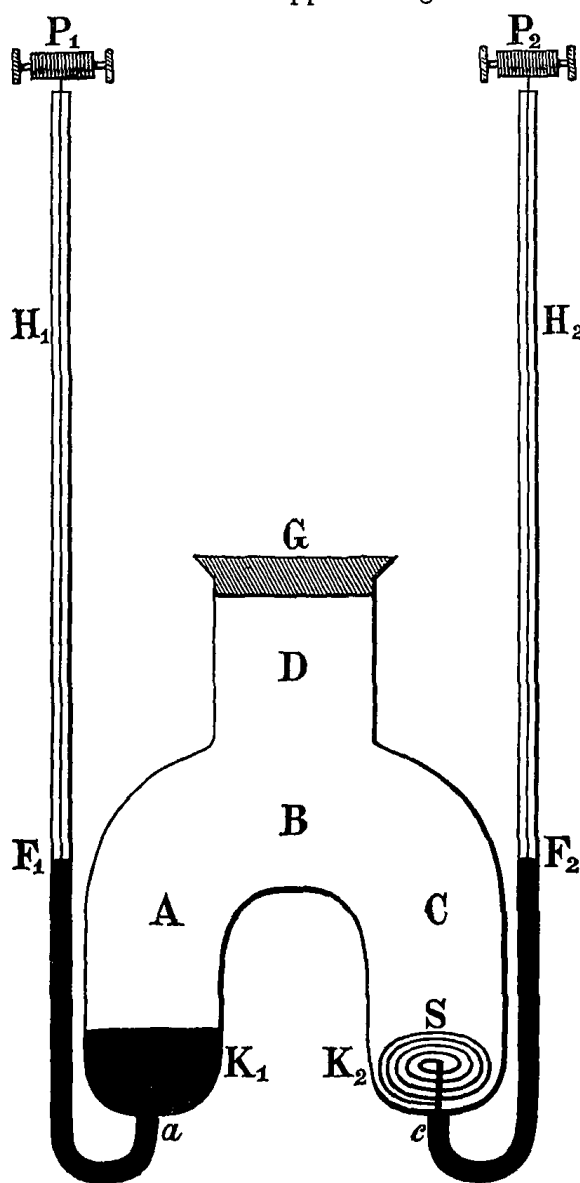


Fig. I.

4. The cell used had the form indicated. The capillaries  $F_1$  and  $F_2$  are sealed to the arms  $A$  and  $C$  of the vessel  $ABC$ . The capillary  $F_1$  communicates with  $A$  but  $F_2$  on the other hand is closed at the spot where it is sealed to  $C$  and admits a platinum wire which in  $C$  is wound up to a spiral  $S$  and projects into  $F_2$  about 1 cm.

Into  $A$  is poured the amalgam (14.3 pCt. of cadmium) which is in direct contact with the platinum wire  $H_1$ , which runs into  $A$ .

Into  $C$  is introduced metallic crystalline cadmium so as to quite surround the platinum spiral  $S$ . Into  $F_2$  mercury is poured which forms the contact between  $S$  and the platinum wire  $H_2$ .

5. The metallic crystalline cadmium was prepared as follows <sup>1)</sup>: 200 grams of crystallized cadmium sulphate were dissolved in warm water precipitated with ammonia and redissolved in a slight excess of the same. After diluting to 600 cc., the liquid was electrolyzed between two platinum electrodes of 55 cm<sup>2</sup>. surface at a tension of 6—8 volts and with a current of 4—5 ampères. Splendid dendritic crystals of Cd are deposited at the negative electrode which are left in the liquid until enough of the metal has separated.

The crystalline metal is first washed a large number of times with very dilute sulphuric acid, then with the same solution of cadmium sulphate which serves afterwards in the cell Cd - CdSO<sub>4</sub> Cd-amalgam. The solution, the concentration of which may be chosen at will, was prepared by dissolving 200 grams of crystallized cadmium sulphate in 500 cc. of water <sup>2)</sup>.

The metallic cadmium after being well washed (reaction with congo-red) was kept in this solution; the electrodes thus prepared are electrically well-defined and different preparations only showed a mutual potential difference of 0.00001 volt.

6. The cadmium amalgam of 14.3 pCt. was prepared by weighing the respective quantities of the components. In the metallic cadmium from MERCK no impurities could be detected by analytical means and the test recommended by MYLIUS and FUNK <sup>3)</sup> which shows 0.01 pCt. of zinc with certainty also gave a negative result.

The mercury was purified with mercurous nitrate and then distilled twice in vacuo.

7. After the electrodes in the cell fig. 1 were put in their place, the above mentioned solution of cadmium sulphate (which was far from saturation even at 0°) was poured in and the cell closed by means of an india-rubber stopper, *g*.

The length of the capillaries renders it possible to completely immerse the whole cell in a thermostat.

The E.M.F. of this cell of which I first constructed 2 specimens for control (I and III) was determined at 0°.0 C. and 25°.0 C.

The cells were kept at zero in a thermostat consisting of a copper cylinder isolated with cotton-wool and containing a mixture of finely

---

<sup>1)</sup> Compare RICHARDS and LEWIS, Proc. Amer. Acad. Arts and Sc., Vol. XXXIV, p. 87, Dec. 1898. Zeitschr. phys. Chem. 28, 1 (1899).

<sup>2)</sup> The water was the same as used for determinations of the electrical conductivity and consequently very pure.

<sup>3)</sup> Zeitschr. anorg. Chem. 13, 157 (1897).

crushed ice and water. Only by vigorously stirring with three screw propellers fixed at different heights in the cylinder and kept in rotation by a HEINRICI hot-air motor, was it found possible to maintain in every part of the thermostat an equal temperature <sup>1)</sup> of 0°.

The thermometer used was divided in  $\frac{1}{10}^{\circ}$  and compared with a standard instrument from the Physikalisch-Technische Reichsanstalt at Charlottenburg.

At 25°,0 C. the temperature was regulated with a toluene-regulator within 0°,03 C.

The E.M.F.'s were measured, by means of POGGENDORFF's compensation method. A THOMSON's mirror galvanometer was used as the zero instrument, a small accumulator as the working cell and a WESTON-cell and two CLARK-cells as standards.

The WESTON and the CLARK-cells stood in the thermostat at 25°,0 C. (also in the experiments at 0°) <sup>2)</sup>. After each measurement the accumulator was tested by means of the WESTON-cell.

8. In the first place, I determined the relation between the E.M.F. of the WESTON-cell and of both the CLARKS *A* and *B*.

$$\frac{2}{6}^{00} \quad \frac{\text{CLARK } A_{25^{\circ}}}{\text{WESTON } 25^{\circ}} = 1.3942 \quad \frac{\text{CLARK } B_{25^{\circ}}}{\text{WESTON } 25^{\circ}} = 1.3942.$$

If we take as the E.M.F. of the CLARK-cell at 25°,0 1.4202 Volt then that of the WESTON-cell at 25°,0 = 1.0185 Volt whilst in the Reichsanstalt 1.0184 Volt has been found at this temperature.

9. The E.M.F.'s of the cells I and III were then determined at 25°,0 C. and 0°,0 C.

T A B L E II.

Electromotive force at 25°.0 C. of the cell]					
Cd—CdSO <sub>4</sub> solution — Cd-amalgam 14.3 % Cd. in Volts.					
Date	No. I.	Date	No. III.		
$\frac{2}{6}^{00}$ 4.00 p.m.	0.04998	$\frac{5}{6}^{00}$ 3.45 p.m.	0.04989		
4.30	0.04995				
5.10	0.04999				
$\frac{4}{6}^{00}$ 12.25 p.m.	0.04995				
average 0.04997			average 0.04989		

<sup>1)</sup> The method so frequently used for the testing of thermometers of placing these instruments in a funnel with crushed ice, seemed to me to be untrustworthy as differences in temperature up to 0°.3 C. were observed.

<sup>2)</sup> Proc. Nov. 25, 1899, p. 290.

At 0°,0 C. the following was found :

T A B L E III.

Electromotive force at 0°0 C. of the cell  
Cd—CdSO<sub>4</sub> solution — Cd. amalgam 14.3 % Cd. in Volts.

Date	No. I.	Date	No. III.
$\frac{2}{8}^{\circ}$ 1h.50 p.m.	0.05571	$\frac{5}{6}^{\circ}$ 4h 50 p m.	0.05571
2h.25	0.05571	5h 24	0.05581
2h.50	0.05571		
$\frac{4}{6}^{\circ}$ 11h.15 a m.	0.05591		
11h.50	0.05591		
average 0.05579		average 0.05576	

We, therefore, find as the mean of the observations with both the cells :

$$\text{E.M.F. at } 25^{\circ}\text{0, C.} = 0,04993 \text{ Volt.}$$

$$\text{E.M.F. at } 0^{\circ}\text{0, C.} = 0,05577 \text{ „}$$

The temperature coefficient of the E.M.F. is therefore on the average

$$\frac{0,04993 - 0,05577}{25} = - 0,000233 \text{ Volt.}$$

10. On this result I had a check <sup>1)</sup>, which was very welcome to me. JÄGER <sup>2)</sup> has determined the E.M.F. of a similar cell and has found 0,051 volt, but he has not given the temperature at which his determination was made. I have now calculated from my determinations the temperature at which  $E$  would be 0,051 volt according to my observations. I find from

$$E_t = E_{25} + (25-t) 0,000233$$

$$t = 20^{\circ}\text{C.}$$

In reply to my inquiry, Prof. JÄGER was kind enough to state that he had indeed made his observations at about 20° C.

<sup>1)</sup> Subsequent experiments proved to me the correctness of the supposition that the temperature coefficient between 0° and 25° does not alter with the temperature.

<sup>2)</sup> WIEDEMANN'S Annalen, 65, 106 (1893).

11. If we now introduce the values of  $E$  and  $\frac{dE}{dT}$  found, into the equation 2 on page 210 and calculate  $E_c$  for 18° C., we find:

$$(E_{291} = 0,0515; \frac{dE}{dT} = - 0,000233; T = 291)$$

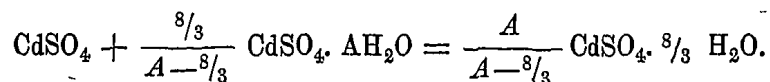
$$E_c = 2(0,0515 + 291 \times 0,000233) \times 22782 \text{ calories} = + 5436 \text{ calories.}$$

The heat effect of the withdrawal of 1 gram atom of  $Cd$  from the 14.3 pCt.  $Cd$  amalgam is therefore,

$$W_1 = - 5436 \text{ calories}^1).$$

*β. Determination of the Heat effect  $W_3$ .*

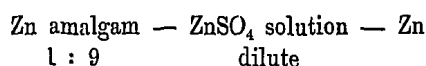
12. We have still to determine the heat effect which accompanies the change:



The factor  $A$  (see page 209) may be taken from the solubility determinations of MYLIUS and FUNK<sup>2)</sup> and KOHNSTAMM and COHEN<sup>3)</sup>, who have found quite identical figures.

<sup>1)</sup> In my second communication on the thermodynamics of the standard-cells (these Proceedings 26 May 1900 pag. 36) it was concluded from older and newer statements in the literature that the abstraction of 1 gram atom of zinc from the zinc-amalgam of the CLARK-cells took place without any heat effect. That such is really the case is taught by the following experiment:

I constructed a cell according to the scheme:



just in the same manner as described above for the  $Cd$ -cells. Of this cell the E.M.F. was determined at 0°,0 C. and 25°,0 C. There was found at:

$$\begin{array}{ll} 0^\circ,0 \text{ C.} & 0,000488 \text{ Volt.} \\ 25^\circ,0 \text{ C.} & 0,000570 \text{ " } \\ \text{therefore } \frac{dE}{dT} & = + 0,00000328 \text{ Volt.} \end{array}$$

$$\begin{array}{l} \text{From this follows: } E_c = 2(0,00048 - 273 \times 0,00000328) 22782 \text{ calories} \\ E_c = - 9 \text{ calories.} \end{array}$$

The quantity of heat required, is therefore + 9 calories or practically nil.

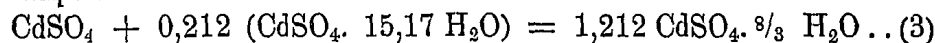
<sup>2)</sup> B. B. 30, 824 (1897).

<sup>3)</sup> WIEDEMANN'S Annalen 65, 344 (1898).



At 18°C.,  $A = 15,17$ .

The equation representing the change therefore becomes at this temperature:



If the systems to the left and the right of the sign of the equality are dissolved in so much water, that both have the concentration  $\text{CdSO}_4 - 400 \text{H}_2\text{O}$ , we can find the quantity of heat  $W_3$  (p. 209) from the heat effects so obtained.

I now reproduce the following from the data put at my disposal by Mr. HOLSBOER:

Heat of dilution	$\text{CdSO}_4 \cdot 13,6 \text{H}_2\text{O}$	to	$\text{CdSO}_4 \cdot 30 \text{H}_2\text{O}$	=	+ 1034	calories.
"	$\text{CdSO}_4 \cdot 15,6 \text{H}_2\text{O}$	"	$\text{CdSO}_4 \cdot 20,6 \text{H}_2\text{O}$	=	+ 405	"
"	$\text{CdSO}_4 \cdot 20,6 \text{H}_2\text{O}$	"	$\text{CdSO}_4 \cdot 30,6 \text{H}_2\text{O}$	=	+ 285	"
"	$\text{CdSO}_4 \cdot 30,6 \text{H}_2\text{O}$	"	$\text{CdSO}_4 \cdot 50,8 \text{H}_2\text{O}$	=	+ 231	"
"	$\text{CdSO}_4 \cdot 50 \text{H}_2\text{O}$	"	$\text{CdSO}_4 \cdot 100 \text{H}_2\text{O}$	=	+ 220	"
"	$\text{CdSO}_4 \cdot 100 \text{H}_2\text{O}$	"	$\text{CdSO}_4 \cdot 200 \text{H}_2\text{O}$	=	+ 171	"
"	$\text{CdSO}_4 \cdot 200 \text{H}_2\text{O}$	"	$\text{CdSO}_4 \cdot 400 \text{H}_2\text{O}$	=	+ 103	"

From this I calculate:

H. o. d.	$\text{CdSO}_4 \cdot 15,17 \text{H}_2\text{O} - \text{CdSO}_4 \cdot 20,6 \text{H}_2\text{O}$	=	$\frac{405}{5} \cdot 0,43 + 405$	=	+ 440	calories.
"	$\text{CdSO}_4 \cdot 20,6 \text{H}_2\text{O} - \text{CdSO}_4 \cdot 30,6 \text{H}_2\text{O}$	=		=	+ 285	"
"	$\text{CdSO}_4 \cdot 30,6 \text{H}_2\text{O} - \text{CdSO}_4 \cdot 50 \text{H}_2\text{O}$	=		=	+ 222	"
"	$\text{CdSO}_4 \cdot 50 \text{H}_2\text{O} - \text{CdSO}_4 \cdot 400 \text{H}_2\text{O}$	=		=	+ 499	"
Heat of dilution	$\text{CdSO}_4 \cdot 15,17 \text{H}_2\text{O} - \text{CdSO}_4 \cdot 400 \text{H}_2\text{O}$	=		=	+ 1446	"

The heat of solution of  $\text{CdSO}_4 - \text{CdSO}_4 \cdot 400 \text{H}_2\text{O} = + 10740$  calories (THOMSEN, Thermochem. Untersuchungen III, S. 201), and the the heat of solution of  $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O} - \text{CdSO}_4 \cdot 400 \text{H}_2\text{O} = + 2660$  calories.

The heat effect ( $W_3$ ) which accompanies the change represented in equation (3) is therefore:

$$W_3 = 10740 + 0,212 \times 1446 - 1,212 \times 2660 = + 7822 \text{ calories.}$$

13. The heat evolved at 18° C. in the WESTON-cell at a passage of  $2 \times 96540$  Coulombs may now be calculated:

$$E_c = W_1 + W_2 + W_3 = - 5436 + (219900 - 175000) + \\ + 7822 = + 47286 \text{ calories.}$$

14. This quantity must now be compared with that obtained

from the direct observations of the E.M.F. of the WESTON-cell by JÄGER and WACHSMUTH <sup>1)</sup>:

From their measurements it follows that the E.M.F. at  $\bar{t}^0$  is represented by the equation:

$$E_t = 1,0186 - 0,000038(t-20) - 0,00000065(t-20)^2 \text{ Volt.}$$

therefore:

$$E_{18^0} = 1.0186 \text{ Volt.}$$

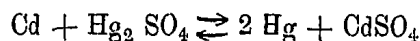
$$\left(\frac{dE}{dT}\right)_{18^0 \text{ C.}} = -0,0000354 \text{ Volt.}$$

$$\text{or } E_c = + 47880 \text{ calories}$$

whilst the thermodynamic calculation gave  $E_c = + 47286$  calories.

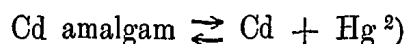
The agreement between theory and experiment is, therefore, very satisfactory.

15. I will not neglect to point out that the idea hitherto prevailing on the mechanism of the change and which was represented by the equation:

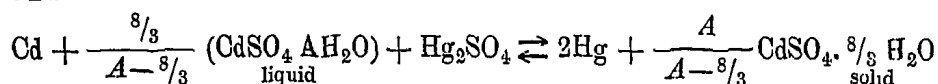


would here also lead to quite wrong results.

From the above it appears that we may represent the mechanism of the change which occurs in the WESTON-cell by



and



Amsterdam, University Chem. Lab.

June 1900.

<sup>1)</sup> WIEDEMANN'S Annalen 59. 575 (1896).

<sup>2)</sup> This provisional equation only represents the change of the amalgam *qualitatively*. The exact *quantitative* equation can only be given when the behaviour of the cadmium amalgam has been more exactly studied. (See my next paper on the metastability of the WESTON-cell).