Chemistry. — "*The metastability of the Weston-Cadmiumcell and its insuitability as Standard of electromotive force*". By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. As is well known the CLARK-cell is inconvenient for accurate measurements on account of its great temperature coefficient (1 millivolt degree). For a number of years JÄGER and WACHSMUTH of the Physikalisch-Technische Reichsanstalt have been engaged with the study of a cell which does not suffer from this drawback. As is known, the result of their investigations has been [1]) that in 1896 they proposed to employ the cadmium cell of WESTON in a somewhat modified form as a standard.

This cell, constructed according to the scheme:

Cadmium amalgam (14.3 pCt. of Cd) — saturated solution of cadmium sulphate — Hg_2SO_4—Hg

possesses, according to their communications, all the good qualities of the CLARK-cell as regards constancy and ease of construction, but its temperature coefficient is 25 times smaller than that of the CLARK-cell.

The change of the E.M.F. amounts to only $^4/_{1000}$ pCt. per degree centigrade whilst that of the CLARK-cell is $^1/_{10}$ pCt.

Thermostats become superfluous even when very accurate measurements are required, which is a fact of some importance when it is considered that standard cells are much used for industrial purposes.

2. The connection between the E.M.F. and the temperature was determined by JÄGER and WACHSMUTH. They found (between 0° and 26°).

$$E_t = E_{20} - 3.8 \times 10^{-5}(t-20) - 0.065 \times 10^{-5}(t-20)^2,$$

but they observed at the same time that some cells did not follow this curve but showed certain irregularities at low temperatures; these cells had a much greater E.M.F. (about 1 millivolt) than the others.

In view of these deviations, Mr. KOHNSTAMM and I, in 1898, made a closer study of the behaviour of cadmium sulphate and found [2]) that the temperature coefficient of the solubility of $CdSO_4 \cdot {}^8/_3 H_2O$ undergoes a sudden change at 15°.

Solubility determinations which were executed with many precautions gave the following result.

---

[1]) WIEDEMANN's Annalen, 59. 575 (1896).
[2]) WIEDEMANN's Annalen, 65, 344 1898).

TABLE I.

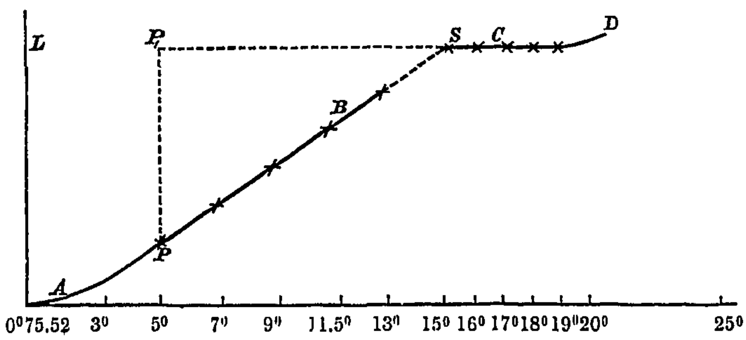
Temperature.	Grams of $CdSO_4$ dissolved in 100 grams of water. I.	II.	III.	Average.
0°0	75.52	—	—	75.52
5°0	75.69	75.61	—	75.65
7°0	75.73	—	—	75.73
9°0	75 84	75.87	—	75 85
11°5	75.98	75.90	—	75 94
13°0	76.00	76 07	—	76.04
15°0	76°11	76.14	76.09	76.11
16°0	76.16	—	—	76.16
17°0	76.14	76.12	—	76 13
18°0	76.13	76.15	—	76.14
19°0	76 18	76.18	—	76.18
25°0	76 82	76.78	76.84	76.79

The accuracy could be controlled by determinations which Mylius and Funk had made in the Reichsanstalt at the same time. The following table contains a comparison of the results.

TABLE II.

Temperature.	In 100 grams of water dissolve grams of $CdSO_4$. Mylius and Funk.	Kohnstamm and Cohen.
0°	75.47	75 52
10°	76.00	75 90
15°	76 06	76.11

Figure I represents the progressive change of the solubility.



At about 15° C. the $Cd SO_4 . {}^8/_3 H_2O$ must, therefore, undergo a change. This change has been already proved by means of the dilatometer [1]).

The deviations found by JÄGER en WACHSMUTH in the E.M.F. were explained by assuming that $CdSO_4 . {}^8/_3 H_2O$, the solubility of which is represented by the curve *SCD* remains, as a rule, somewhat obstinately in the metastable condition. A smaller E.M.F. of the WESTON-cells then corresponds to the greater solubility of the metastable phase (curve P_1S). If the salt passes into the stable modification (curve *APBS*), the solubility is lowered and the E.M.F. of the cells in which that modification exists is raised.

No objections to this view have been raised since the appearance of our paper; on the contrary in his publication on deviations noticed by himself in the behaviour of cadmium-cells, BARNES [2]) accepts our view. I will however, not neglect to point out that it always astonished me that such a small difference in solubility as represented by the points P and P_1 should lead to such an important difference in E M.F.

At the end of our paper we concluded that the WESTON-cell in the form used at the Reichsanstalt, i.e. containing the solid salt $Cd SO_4 . {}^8/_3 H_2O$, should not be used below 15°, if the risk of having a cell which considerably deviates from the temperature formula given by JÄGER and WACHSMUTH is to be avoided.

3. My investigations on the thermodynamics of the standard cells made me return to the WESTON-cell which was now extensively studied in another direction.

In the following lines, I wish to give a summary of this investigation.

4. In order to find the heat-effect caused by the withdrawal of 1 gram-atom of Cd from the 14.3 pCt. cadmium amalgam used in the WESTON-cells, I constructed (see previous paper pg. 208) a number of cells of the type: Cd—dilute solution of cadmium sulphate — Cd-amalgam 14.3 pCt. The solution of cadmium sulphate was not saturated at 0°,0 C., so that no crystals could be deposited at that temperature. The details of the construction of the cells together with the precautions taken in view of impurities contained in the

---

[1]) l. c.
[2]) Journ. of physical Chemistry, May 1900.

materials have been fully described by me in my third communication on the thermodynamics of the standard cells (see communication (p. 208).

The E.M.F.'s of cells I, II and III at 0°,0 C. and 25°,0 C. were determined by POGGENDORFF's method as described in the paper already referred to.

The WESTON-cell and the CLARK cells which served as standards were always kept in a thermostat at 25°,0 C. In this way I found:

TABLE III.

At 25°.0 C.

No. I.		No. II.		No. III	
Date	E.M.F in Volt.	Date	E.M.F. in Volt.	Date	E.M.F. in Volt.
$^2/_6{}^{00}$ 4h p.m.	0.04998	$^2/_6{}^{00}$ 4h 0 p m.	0.04999	$^5/_6{}^{00}$ 3h 45 p.m.	0.04989
4 30	0.04995	4 30	0.04992		
5 10	0.04999	5 10	0.04992		
$^4/_6{}^{00}$ 12 25 p.m.	0.04995	$^4/_6{}^{00}$ 12 25	0.04995		
average	0.04997 Volt	average	0.04992 Volt.	average	0.04989 Volt.

At 0°.0 C

No. I.		No. II.		No. III.	
Date	E.M.F. in Volt	Date	E.M.F. in Volt.	Date	E.M.F. in Volt.
$^2/_6{}^{00}$ 1h.50 p.m.	0.05571	$^2/_6{}^{00}$ 1h 50 p.m	0.05520	$^5/_6{}^{00}$ 4h 50 p.m.	0 05571
2 25	0.05571	2 25	0.05408	5 24	0.05581
2 50	0.05571	2 50	0.05347		
$^4/_6{}^{00}$11 15 p.m.	0.05591	$^4/_6{}^{00}$11 15 p m.	0 05082		
11 50	0.05591	11 50 p.m.	0.05092		
average	0.05579 Volt.			average	0.05576 Volt.

As regards this table it must be observed that the cells I and II were kept in ice from $^2/_6{}^{00}$ to $^4/_6{}^{00}$. They were then measured at $^4/_6{}^{00}$, first at 0°,0 and then at 25°,0 C.

The result of these measurements is therefore, that whilst I, II and III have exactly the same E.M.F. at 25°,0 C. namely

I. = 0,04997 Volt.

II. = 0,04992 Volt.

III. = 0,04989 Volt.

an important difference exists at 0°,0 C. between I and III on the one hand and II on the other.

I. = 0,05579 Volt.

II. = 0,05092 Volt.

III. = 0,05576 Volt.

It is moreover of importance to point out that I and III after they were cooled from 25°,0 C. to 0°,0 C. very soon reached their end-value whilst with II this was only the case after a few days.

5. The observations described immediately gave rise to the suspicion that the Cd-amalgam used in the cell is a metastable substance [1]). This, it is true, appeared to be in contradiction with the investigation of JÄGER [2]) who states that amalgams with 5—15 pCt. of Cd are unchangeable to $^1/_{100}$ millivolt but there were so many indications which appeared to contradict this, that I continued the investigation in the original direction. In what follows it will be seen that JÄGER's view is incorrect; the reason why he was unable to prove the instability of the 14.3 pCt. cadmium amalgam used will also appear.

6. I tried in the first place to find the temperature at which the difference between the cells I (and III) and II first appears.

For this purpose the E.M.F. of I and II was determined at different temperatures between 0°,0 C. and 25°,0 C.

The temperatures 5°, 10°, 15° and 20° were kept constant for a long time by allowing ice-water to flow from an elevated reservoir into a bath provided with stirring apparatus and toluene regulator, the supply being regulated by means of a tap. The heat given off by the flame is compensated for by the refrigeration caused by the iced water and in this manner the temperature may be kept constant all day long within 0°,03 C.

---

[1]) It might be thought that metallic cadmium, which formed the negative electrode of the cells, might be metastable like tin. A special investigation, however, gave indications that such is *not* the case and I, therefore, occupied myself in the first place with the cadmium amalgam.

[2]) WIEDEMANN, Annalen 65, 107 (1898).

TABLE IV.

Cell I.			Cell II.		
Temperature	Time	E.M.F. in Volt.	Temperature	Time.	E.M.F. in Volt.
0°0	9h	0.0559 [1]	0°0	9h 10	0.0509
	10 30	0.0559		10 40	0.0509
5°0	11 7	0.0549	5°0	11 12	0.0515
	11 30	0.0549		11 35	0.0515
10°0	12 0	0.0536	10°0	12 10	0.0517
	12 17	0.0536		12 22	0.0517
15°0	12 47	0.0524	15°0	12 52	0.0517
	2 20	0.0524		2 30	0.0517
20°0	3 10	0.0513	20°0	3 15	0.0510
	3 45	0.0513		3 50	0.0510
25°0	5 15	0.0501 [1]	25°0	5 20	0.0501 [1]
	5 50	0.0501		6 0	0.0501

If with these data we construct a curve which has the temperatures as abscissae and the electromotive forces as ordinates fig. 2 is obtained.

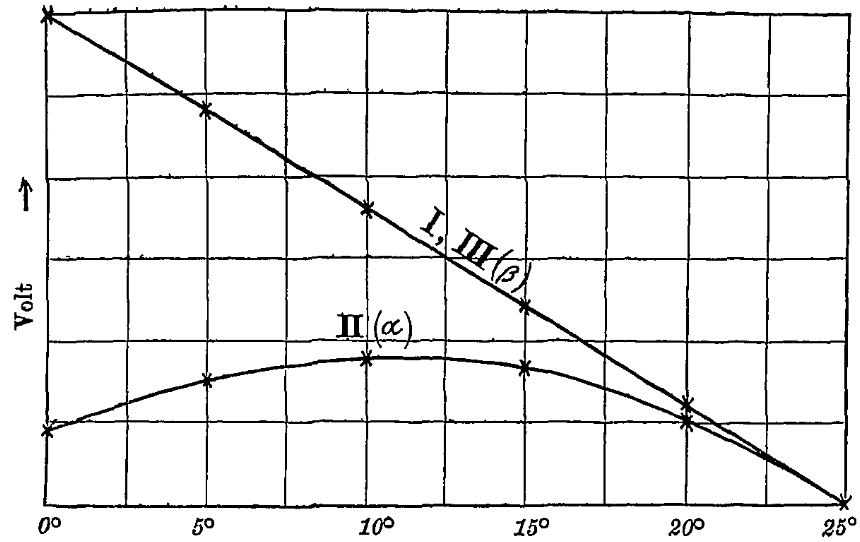


Fig. 2

The two curves intersect at about 23°.

From this it is seen that the cadmium amalgam (14.3 pCt. of Cd.) *contained in cell I and III is metastable below* 23°.

---

[1]) These measurements took place 6 days after the cell had been constructed. It will be seen that in that time the E M F has been raised about 0,0002 Volts. This corresponds with the observations of Richard and Lewis, Zeitschr fur phys. Chemie 28, 1. (1899) on Cd-electrodes of this kind.

7. As these observations as we will see later on, are of great importance when judging of the suitability or otherwise of the WESTON-cells as standards, I have convinced myself of the correctness of these conclusions by the dilatometric process.

For this purpose the cadmium-amalgam which had served for the construction of the electrodes was introduced into a dilatometer filled with petroleum as measuring liquid.

That the amalgam is not in equilibrium at 0° is seen from the following observations:

TABLE V.

Time in hours.	Height of the level in the dilatometer
0	107
2½	99
4	96
4¾	94
5¾	92
6⅔	91
24	71
48	55
72	40

8. It now becomes more plain from the electric measurements (fig. 2) why JÄGER [1]), who according to his communication, made his measurements at about 20°, did not notice the metastability, for that temperature is so close to 23° that under these circumstances any change in the amalgam could only be observed after the lapse of an exceedingly long time.

9. Apparently the amalgam electrodes of the cells I (and III) and II had been treated in the same manner and yet that of II had changed into the stable modification whilst I and III continually remained metastable. That the change may often occur is

[1]) See my previous communication p. 213.

shown by the fact that of the three cells which I had made, one contained stable cadmiumamalgam [1]).

Provisionally we will call the amalgam contained in the cells I and III (the metastable modification below 23°) the β-amalgam whilst that in cell II will be given the name of α-amalgam.

From table IV we see that cells with the β-amalgam have at 0° an E. M. F. which is not less than 5 millivolt larger than those of the cells in which the α-amalgam forms the positive electrode.

10. The question now at once arises: Do the observations made by JÄGER and WACHSMUTH with the WESTON-cell relate to cells in which stable amalgam is present, or have they been made with cells which have the metastable body as negative electrode?

The fact that with some cells at 0° they found a higher E. M. F. than with others would indicate that they have mostly worked with the metastable modification This cannot, however, be stated with certainty, because it follows from the results of our investigation on the behaviour of cadmium sulphate that the presence of the stable form of this salt may have increased the E.M.F. at 0°.

I, therefore, have studied this point more closely. For this purpose the cells I, II and III were transformed into WESTON cells (cells I^a, II^a and III^a) except that they were filled with a *clear* solution of $Cd\,SO_4 \cdot {}^8/_3\,H_2O$ (stable modification) at 0° *without* any crystals at the bottom.

The dilute solution of $Cd\,SO_4$ was poured out of *ABC* (previous communication fig. 1), the arm *A* provided with a layer of cottonwool, and the metallic Cd removed from *C* and replaced by mercurous sulphate.

The solution of $Cd\,SO_4 \cdot {}^8/_3\,H_2O$ (stable modification) saturated at 0° was prepared by mixing the anhydrous salt with water at 0°, care being taken to cool the liquid so as to prevent the temperature from rising over 15°.

The bottles containing the salt and the water were shaken for 4 hours at 0°.0 C. and the solution was filtered. The saturated solution thus obtained was introduced into I, II and III and the cells which previously had been rinsed with this solution were closed and brought, in the thermostat, to 0° C. The E.M.F. of the cells (I^a, II^a, III^a) was then determined.

In this way the following values were found:

1) Compare BARNES l. c.

TABLE VI.

		Temperature 0°.0 C
WESTON-Cell	Ia	1.0198 Volt.
WESTON-Cell	IIa	1.0231 Volt [1])
WESTON-Cell	IIIa	1.0197 Volt.

We, therefore, see that all the measurements of JÄGER and WACHSMUTH have been made with WESTON cells which are *metastable* [2]).

11. The formula given by the Reichsanstalt for the connection between the E.M.F. of WESTON-cells and the temperature and which should be used between 5° and 26° C., therefore loses its value on account of these facts and, considering the metastability of the cadmium amalgam, is only true for temperatures between 23° C. and 26° C., whilst the metastability of cadmium sulphate as we have previously demonstrated is a second reason of its insuitability.

12. Since 1892, a standard-cell has been sold by WESTON at Newark (obtainable in Europe from the "European WESTON Electrical Instrument Co.", Berlin) which is constructed in accordance with the scheme:

Cd-amalgam 14.3 pCt. — solution of cadmium sulphate — Hg_2SO_4—Hg.
(Saturated at + 4° C.) without solid phase.

It was thought, even after our investigation on the change which $CdSO_4 . {}^8/_3 H_2O$ undergoes at 15° C., that this cell constituted a perfectly trustworthy standard, since above 4° C., no solid phase is present.

But since it has been proved that cadmium amalgam below 23° C. may occur in two modifications, it follows that even this standard may show a different E.M.F. below that temperature according to which of the two modifications of the amalgam is present.

13. Owing to the fact that both in the WESTON-cell of the Reichsanstalt and in that of the WESTON Co. there exists cadmium amal-

---

[1]) It will be noticed that whilst at 0°.0 C. the difference in E.M.F. of the cells I (or III) and II amounted to 5 millivolt, the WESTON-cells showed a difference of 3,4 millivolt at that temperature. I will afterwards return to this matter.

[2]) Between 0° C. and 23° C.

gam which readily remains in the metastable form (it must be remembered that all the measurements of the R. A. have been made with metastable cells) and that this amalgam may spontaneously pass into its stable form which change is accompanied by a change in the E.M.F. (up to 5 millivolt at 0°)] we must come to the conclusion *that both forms*[1]) *are unsuitable as standards of electromotoric force.*

A cell which at the time of its construction is compared with another standard and found to possess the E.M.F. indicated by the Reichsanstalt at the given temperature, may subsequently come to have some totally different E.M.F.

What is required of a standard cell is that, when constructed in a definite way, its E.M.F. shall be positively defined at a stated temperature; it will be seen from the foregoing that the WESTON-cells do not by any means conform to this specification.

14. Above 23° C. all the WESTON-cells, as seen from the foregoing, possess a sharply defined E.M.F. which follows the temperature formula given by the Reichsanstalt (to 26°). Only by making use of a thermostat in which the cell is placed when in use (and for some times beforehand in order to convert any metastable amalgam into the stable form) can these drawbacks be avoided. But then the great advantages which this standard seemed to possess compared with others with a larger temperature coefficient are lost. Moreover, working with thermostats is far too tedious for technical purposes.

15. After reading the above, the question naturally arises; do such complications arise with the CLARK-cell?

The amalgam which is used there as negative electrode has the composition Zn : Hg = 1 : 9.

Although my investigations in this direction are not yet quite finished, I think that it is very probable that we shall meet with similar phenomena. I mention, therefore, briefly the investigations of WILLOWS[2]) on the changes in the electrical conductivity of different amalgams at a constant temperature, when those amalgams have been exposed to changes in temperature.

For the sake of brevity I will here bring forward only one case

---

[1]) The first named is moreover often metastable owing to the presence of the solid salt $CdSO_4 . {}^8/_3 H_2O$.

[2]) Philos. Magazine, November 1899, 433.

from the large number studied by WILLOWS and choose as an example, the zinc amalgam containing 9,5 pCt. of zinc and having therefore, about the same composition as the amalgam used in the CLARK-cells.

In fig. 3 the resistance of the amalgam as a function of the

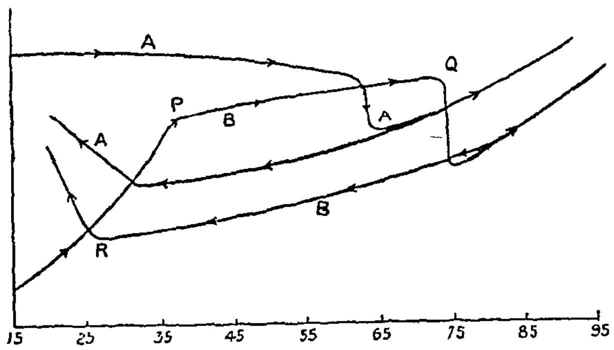


Fig. 3.

temperature is shown. The arrows indicate whether the temperature was rising or falling. The curve *A* was obtained immediately after the amalgam had been heated several times, whilst *B* represents the results which were found after the amalgam had been kept for some weeks at the temperature of the room.

It is plainly visible from this figure that the amalgam can have very different resistances at the same temperature, a good proof that even after a long time a condition of equilibrium in the amalgam is not reached.

WILLOWS has found similar curves for cadmium amalgam, but the amalgam which interests us here most (1 : 6) has not been investigated by him.

The former observations on cadmium sulphate and also those which have been communicated in this paper on cadmium amalgam may be summarised as follows:

Results of the Investigation.

1. Cadmium sulphate ($Cd SO_4 . {}^8/_3 H_2O$) can exist below 15° C. in two modifications.

2. Cadmium amalgam (14.3 pCt. of Cd) can appear in two modifications [1]) below 23° C.

[1]) The word "modifications" is here only preliminary. A further investigation will have to show what changes take place in the amalgam.

3. At 0° C. a potential difference of 5 millivolt exists between those modifications of the cadmium amalgam.

4. *The* WESTON-*Cadmium-cells, both the form studied and recommended by the Physikalisch-technische Reichsanstalt, and that sold by the European Weston Electrical Instrument Co. are metastable systems* (below 23°) *which may pass quite spontaneously into the stable condition. As this change is coupled with a great change in the E.M.F. these cells are unsuitable for standard of electromotive force.*

5. The researches at the Reichsanstalt are made with *metastable* WESTON-cells and the temperature-formula given by JÄGER and WACHSMUTH therefore relates to *metastable* cells.

When a better insight into the behaviour of cadmium amalgams has been obtained a proposal may, perhaps, be made for the construction of a standard-cell which possesses all the advantages and none of the drawbacks of the WESTON-cell.

Mr. H. C. BIJL has already made a beginning with the investigation of these amalgams in this laboratory.

Amsterdam, University Chem. Lab., June 1900.

(August 28, 1900.)