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III. Finally my attention was given to the nerve of the subcutaneous muscle. Nährich 1) testifies that by irritation of this nerve, in addition to contraction of the cutaneous muscle, also pain-symptoms are brought forth, whilst after the sectioning of this nerve, the sensibility of the skin had diminished. I have not been able to verify this latter fact. It is not to be doubted moreover that e.q. an isolated root-area, if either the isolated root or the peripherical branches have been cut through, becomes entirely and completely insensible, whilst the nerve of the cutaneous muscle remains intact. It is therefore probable that this nerve does not contribute to the sensibility of the skin. Nevertheless I can confirm the statement of Nährich, that after its having been cut through, irritation of the central end proves painful. It may be that the muscular sensibility plays a part in producing these symptoms of pain.

Chemistry. — "The Allotropy of Cadmium." IV. By Prof. Ernst Cohen and W. D. Helderman.

(Communicated in the meeting of September 26, 1914).

The electromotive behaviour of Cadmium. II.

- 1. Up to the present we have only directed attention to the electromotive behaviour of  $\alpha$  and  $\gamma$ -cadmium; the  $\beta$ -modification has not been mentioned hitherto. It will be treated in the following lines.
- 2. It may be remembered that a number of cells constructed according to the scheme:

had an E.M.F. of 0.050 Volt at 25°.0, whilst the E.M.F. of others was only 0.047 Volt at the same temperature. (The cells were reproducible within 0.5 millivolt).

3. Now we were struck by the fact that when constructing a large number of these cells we often got cells which had an E.M.F. of 0.048 Volt at 25°.0.

The E.M.F. of cells which originally had an E.M.F. of 0.050 Volt at 25°.0, spontaneously *decreased* till the value 0,048 Volt was reached. After this their E.M.F. remained constant.

4. The conclusion was plain that the cells giving 0.048 Volt might

<sup>1)</sup> L. c. p. 95-96,

contain  $\beta$ -cadmium, those giving 0.047 Volt  $\alpha$ -cadmium, whilst those giving 0.050 Volt have  $\gamma$ -cadmium as a negative electrode.

- 5. If this were really the case, it would be possible to construct a transition cell by combining a cell with  $\alpha$ -cadmium with one containing  $\beta$ -cadmium; the E.M.F. of this combination would be zero at the transition temperature of the change  $\alpha$ -cadmium  $\geq \beta$ -cadmium.
- 6. However it is impossible to carry out an exact determination of the transition point in this way, as the E.M.F. of the combination is (at  $25^{\circ}.0$ ) only (0.048-0.047) = 0.001 Volt and the reproducibility of each of the cells is only 0.5 millivolt.
- 7. In order to ascertain if the E.M.F. of the  $\beta$ -cells has a real significance, experiments may be carried out on the following lines:

At temperatures above the transition point of the change  $\alpha$ -cadmium  $\gtrsim \beta$ -cadmium (which we found in the neighbourhood of  $60^{\circ}$  by dilatometric measurements) the E.M.F. of  $\alpha$ -cells must be higher than that of  $\beta$ -cells. After cooling the cells below the transition point mentioned, the contrary will occur.

8. Our experiments in this direction were carried out in the following way:

We constructed a large number of Hulett cells '); one of these, the E.M.F. of which had been originally 0.050 Volt at 25°.0, had an E.M.F. of 0.047 Volt (at 25°.0) after having been kept for 4 weeks at 47°.5. After this time it remained constant.

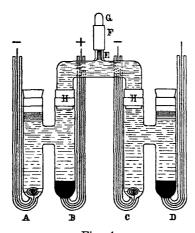


Fig. 1.

will at 25°.0 or 64°.5.

We combined this cell (N°. 7) with another one (N°. 22) the E.M.F. of which was 0.048 Volt at 25°.0. The two cells AB (N°. 7) and CD (N°. 22) were connected by a siphon H, which contained the same solution of cadmium sulphate as was present in the cells. (Fig. 1).

The lateral tube E of the siphon was closed by a rubber tube F, in which was put a glass rod G. The little apparatus was brought into a thermostat which could be kept at

9. We measured the E.M.F. between the cadmium which had been electrolytically deposited on the platinum spirals A and C

<sup>1)</sup> Proceedings 17, 122 (1914).

against the common amalgam electrode B. (12.5 %) by weight). It is absolutely necessary to use a common electrode as the cadmium amalgam of 12.5 percent by weight does not form a heterogeneous system at 64°.5; its E.M.F. is then a function of its composition. The use of the two amalgam electrodes B and D might give rise to serious mistakes, if there were only small differences in their composition.

The absolute E.M.F. of our amalgam electrode against cadmium in A and C does not play any role in our measurements.

10. The determinations of E.M.F. were carried out by the Poggendorff compensation method. The resistances used, had been checked by the Physikalisch-Technische Reichsanstalt at Charlottenburg—Berlin. The same was the case with the thermometers used. Our two standard elements (Weston) were put into a thermostat which was kept at 25°.0. We used as a zero instrument a Deprez-d'Arsonval galvanometer, which was mounted on a vibration-free suspension (Julius). The readings were made by means of a telescope and scale; 0.02 millivolt could easily be measured.

The determinations were continued during several days, until the E.M.F. of the cells had become constant.

Our table I shows the results.

## TABLE I.

Temperature 25°.0.

E.M.F.

Cell 7 0.04741 Volt

Cell 22 0.04815 ,,

Temperature 64°.5

Cell 7 0.04029 Volt.

Cell 22 0.03979 ...

After having brought the cells to 25°.0, we found:

Cell 7 0.04741 Volt.

Cell 22 0.04806 ,,

The table shows that at 64°.5 there has taken place an inversion of the poles and that the cells regain their original E.M.F. at 25°.0.

A second experiment with two cells (nº. 4 and 8) newly constructed, gave the following results:

TABLE II.

Temperature 25°.0,

E.K.

Cell 8 0.04757 Volt

Cell 4 0.04839 ,,

Temperature 64°.5.

Cell 8 0.04737 Volt

Cell 4 0.04633 ,,

After having brought the cells to 25°.0, we found:

Cell 8 0.04776 Volt

Cell 4 0.04789 ,, .

- 11. From table II it may be seen that we are here at the limit of measurement obtainable in working with cells of so small an E.M.F. the reproducibility of which is 0.5 Millivolt.
- 12. From the inversion of poles which has been observed, we may conclude that the value 0.048 Volt at 25°.0 really has significance and is to be attributed to the presence of  $\beta$ -cadmium.
- 13. As to the bearing of the existence of different modifications of cadmium on the E. M. F. of the standard cell of Weston, we refer to our paper "On the Thermodynamics of standard cells" (sixth communication), published some months ago 1).

Utrecht, September 1914.

VAN 'T HOFF-Laboratory.

Chemistry. — "The Allotropy of Zinc." III. By Prof. Ernst Cohen and W. D. Helderman.

(Communicated in the meeting of September 26, 1914).

1. In our first communication on the allotropy of zinc<sup>2</sup>), we summarized the earlier literature on this subject as follows: as long as half a century ago various investigators tried to solve the problem whether zinc might be capable of existing in different allotropic modifications. As late as 1890 Le Chatelier proved that this metal does really show a transition point in the neighbourhood of 350°. Mönkemeyer found this point at 321°, Benedicks at 330° (melting point of pure zinc 419.°4) whilst the measurements of Max Werner

<sup>1)</sup> Chemisch Weekblad 11, 740 (1914). This paper will be published before long in the Zeitschr. f. physik. Chemie.

<sup>2)</sup> Proceedings 16, 565 (1913).