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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 β-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 [2]), 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

[1]) Chemisch Weekblad **11**, 740 (1914). This paper will be published before long in the Zeitschr. f. physik. Chemie.

[2]) Proceedings **16**, 565 (1913).

(who found 300°), published some weeks ago, agree sufficiently with those of LE CHATELIER. We shall discuss in a subsequent paper the differences which exist amongst the results of the investigators mentioned above. Whilst BENEDICKS mentions a second transition point (at 170°), MAX WERNER was unable to find this point. The question as to whether it really exists or not, may be left open for the moment.

2. Since writing the above we became acquainted with the paper of LE VERRIER [1]), which has been summarized by one of us [2]). LE VERRIER found that the specific heat of zinc varies greatly between 100 and 140° and that there occurs an absorption of heat within this interval of temperature of 0—8 calories. This result indicates that there exists here a transition point. Mr. G. DE BRUIN is carrying out a systematic investigation in this direction.

3. BENEDICKS and RAGNAR ARPI have recently published [3]) a new investigation of this subject. In his first paper BENEDICKS pointed out that "bezüglich der Frage, ob die für das Zinc. puriss. MERCK (garantiert frei von Eisen und Arsen in Stäben) gefundenen Angaben auch für das absolut reine Metall gelten, bedarf es ebenfalls weiterer Versuche".

That there was no reason to suppose that this sample contained impurities may be concluded from the authors' words: "Jedoch ist es im Hinblick auf die Wichtigkeit der Reinheit dieses Produktes für seine Verwendung für analytische Zwecke sehr wahrscheinlich, dass die Menge von Fremdkörpern zu vernachlässigen ist".

4. However BENEDICKS writes in his most recent paper: "Es ist deshalb hier eine Revision der einschlägigen Verhältnisse vorgenomen worden, die zu ziemlich unerwarteten Ergebnissen geführt hat. Nämlich, dass überhaupt keine Allotropiebeweise für Zink z. Z. vorliegen". He adds: " Abgesehen wird dabei zunächst von derjenigen Andeutung von Allotropie, die neuerdings von E. COHEN und W. D. HELDERMAN durch spez. Gewichtsbestimmungen gefunden wurde". We shall revert to this point later.

5. The method followed by BENEDICKS and ARPI to discover possible transition points was the same as used formerly by BENEDICKS, viz. the determination of the electrical conductivity of the metal at different temperatures.

Whilst he found in his first determinations (working with zinc. puriss. MERCK) transition points at 170° and 330° respectively, he was not able to find them when he used "Zinc KAHLBAUM" which

[1]) C. R. **114**, 907 (1892).
[2]) ERNST COHEN, Proceedings **17**, 200 (1914).
[3]) Zeitschr. f. anorg. Chemie **88**, 237 (1914).

only contained 0,0047% of Cd., 0,0033% of Pb., 0,00045% Fe,Cu).

But working with the same material to which 0.52 per cent by weight of Cd, resp. 0,5 per cent of Pb. or 0,5 per cent of Cd+0,5 per cent of Pb had been added, he found several transition points which grosso modo agreed with those found formerly by BENEDICKS a.o. On account of these results BENEDICKS and ARPI conclude that the transition points found by BENEDICKS in his first investigation are to be attributed to impurities in the metal used and that zinc which is pure does *not* show transition points.

6. In the first place it may be pointed out that the curves which form the basis of the authors' conclusions, are so roughly defined, that it is almost impossible to conclude anything from them. For example, from a consideration of the curve 2 in Fig. 2 (which refers to pure zinc), one might arrive at the conclusion that a break [1]) exists at 150°.

7. However, a more serious objection to the method followed, may be pointed out. Our recent investigations on the allotropy of metals have shown that the changes in these substances take place very slowly even at high temperatures. These retardations can only be removed by special means (inoculating in contact with an electrolyte, repeated changes of temperature etc.). We may call to mind the fact that we were able to heat cadmium 95 degrees above one of its transition points without any changes occurring. It will be necessary to give special attention in future to these phenomena, which play also a role in "thermal analysis" and which may falsify its results.

BENEDICKS and ARPI did not make any provision to eliminate these phenomena. On account of what we know now about these hysteresis phenomena it was to be expected that any transition point, if it really existed, would only be found under favourable circumstances, or by a systematic elimination of the retardations mentioned above.

8. Moreover it may be pointed out that BENEDICKS and ARPI *made the supposition* "dass die betreffenden Metalle nicht genügend rein waren" (viz. the zinc. puriss. MERCK, used by BENEDICKS in his first investigations and by LE CHATELIER among others). We think that the opinion put forward by BENEDICKS in his first paper (see above § 3) "dass die Menge von Fremdkörpern zu vernachlassigen ist", is the just one. As we were told by Messrs. MERCK at Darmstadt their "Zinc. puriss. MERCK (garantiert frei von Eisen und Arsen in Stäben)" contains only small traces of cadmium. We carried out an analysis of this material

[1]) Whether this point really exists or not may be left open for the moment.

following the method described by MYLIUS [1]). In 100 gr. of this metal we could only detect small traces of cadmium (lead and iron). We think that the explanation of B. and A. which is based on the presence of large amounts of impurities falls to the ground.

9. That it is not the presence of foreign substances which give rise to the strongly marked change of the mechanical properties of zinc at higher temperatures (which fact has been the starting point of BENEDICKS' investigations) is evident from the fact, that this change may also be observed in the purest zinc (Zink "Kahlbaum", comp. § 5). We have been able to confirm this result repeatedly ourselves.

10. Finally some remarks, made in a note by BENEDICKS and ARPI may be considered here.

In the first place they believe, on account of an investigation concerning the quenching velocities of metals, carried out by BENEDICKS [2]), that "eine besonders grosse Abkühlungsgeschwindigkeit nicht zu erzielen ist" when the method is followed which we used. (1 kilo of zinc was chilled in a mixture of solid carbid dioxide and alcohol). It may be pointed out that the velocity we used has been greatly exaggerated; we got the same results by using water or air of room temperature. We also carried out some experiments with carbon dioxide and alcohol in order to vary the external conditions of our experiments as much as possible. In our researches on the allotropy of copper and cadmium we also used water or air as a cooling medium.

11. Secondly BENEDICKS and ARPI raise the question as to whether there has not taken place an "Auflockerung der Oberfläche" of our preparations when we washed them with dilute hydrochloric acid. By this operation a change of density might have occurred.

They have however overlooked two facts: in the first place the recent investigations of JOHNSTON and ADAMS [3]), which prove that the density of any substance is *independent* of its state of division. Moreover they have not taken into account the results of our investigations on cadmium [4]), where the same difficulties would have occurred. The reproducibility and reversibility of the phenomena prove that the disturbances, mentioned by BENEDICKS and ARPI really do not occur.

We hope to report shortly on the real transition points of zinc.

Utrecht, September 1914. VAN 'T HOFF-*Laboratory*.

[1]) Zeitschr. f. anorg. Chemie **9**, 144 (1895); MYLIUS, ibid. **74**, 407 (1912).

[2]) Journ. of the Iron and Steel Institute **77**, 153 (1908).

[3]) Journ. Americ. Chem. Soc. **34**, 563 (1912).

[4]) Proceedings **16**, 485 (1913).